POLYMERS 2024, COMPOSITES 2024 AND 3BS MATERIALS 2024

INTERNATIONAL JOINT CONFERENCE

06 - 08 MARCH 2024 | SEVILLE, SPAIN

Book of Abstracts

Organizer

SETCOR
Conferences & Exhibitions

Polymers / Composites / 3Bs Materials 2024
Joint International Conferences Program
06-08 March 2024, Seville - Spain

Wed. 06 March 2024		
08:00 - 12:00	**Conference Registration / Welcome Coffee Break / Posters Installation**	
Polymers / Composites / 3Bs Materials 2024 Session I. A		
Santa Cruz Conference Room		
Session's Chairs: **Prof. Robert J Young, University of Manchester, UK** **Prof. De-Yi Wang, IMDEA Materials Institute, Spain**		
10:00 - 10:30	Nanofibrillar Multifunctional Thermoplastic Materials Prepared by Solution Blow Spinning. **J. González-Benito**	**Prof. Javier Gonzalez-Benito**, University Carlos III de Madrid, **Spain**
10:30 - 11:00	Carbon Fibers from Lignin Limitations & Opportunities. **D.S Argyropoulos**	**Prof. Dimitris Argyropoulos**, North Carolina State Univ., **USA**
11:00 - 11:30	Incidence of the Mechanisms of Damage in the Performance of Composites. **F. P. Carballo**	**Prof. Federico Paris Carballo**, University of Seville, **Spain**
11:30 - 12:00	Experiments and Analysis of Delamination in Composite Materials. **J. Botsis**	**Prof. John Botsis**, EPFL, **Switzerland**
12:00 - 12:30	Biomimetic Spirocyclizations for the Synthesis of Indole Alkaloids. **R.V.A. Orru**	**Prof. Romano V.A. Orru,** Maastricht University, **The Netherlands**
12:00 - 14:00	**Lunch Break**	
Polymers 2024 Session I. B: Synthesis, Processing and Characterization		
Session's Chairs: **Prof. Javier Gonzalez-Benito, University Carlos III de Madrid, Spain** **Prof Joana Vaz Pinto, FCT NOVA University Lisbon, Portugal**		
14:00 - 14:15	Synthesis of metal-free semiconducting polymers via organocatalysis: sustainable materials for renewable energies. **L. Caponecchi**, P.Y. Toullec, C. Brochon	**Mr. Luca Caponecchia**, University of Bordeaux, **France**
14:15 - 14:30	Fibrous Nanocomposites based on Polylactic acid filled with Fe3O4 Nanoparticles Produced by Solution Blow Spinning. **N. Nikolić**, D. Olmos and J. González-Benito	**Ms. Natasa Nikolic,** University Carlos III of Madrid, **Spain**
14:30 - 14:45	Exploring the Properties of Solution Blow Spun PLA/Sargassum Fibrillar Nanocomposite Materials as a Novel Approach for Sustainable Bioplastics. N. Nikolić, M. González-Hurtado, A. Martínez-García, J. González-Benito and **D. Olmos**	**Dr. Dania Olmos**, University Carlos III of Madrid, **Spain**
14:45 - 15:00	Achieving high impact strengths for polyamide 6 by adjusting the grafting degree of ethylene/1-octene copolymers. **A.K. Deeb**, O. Neuß and S. Rathgeber	**Mr. Abdul Kadir Deeb**, University Koblenz, **Germany**
15:00 - 15:15	Analyzing the Influence of Color Masterbatch in the Injection Molding of Post-Industrial Plastic Waste. **M. Pöttinger**, C. Marschik, K. Straka, K. Fellner and G. Steinbichler	**Ms. Magdalena Poettinger**, Competence Center CHASE GmbH, **Austria**
15:15 - 15:30	Advancing Free Radical Photopolymerization (FRP) and 3D Printing: Exploiting the Potential of Novel Ni(II) Complexes bearing NHC lig-ands as photocatalysts. **N. M. Pesqueira**, C. Bignardi, V. P. Carvalho-Jr, B. Eleutério Goi and J. Lalevée	**Ms. Naralyne Pesqueira**, São Paulo State University (UNESP), **Brazil**/ University of Haute-Alsace, **France**

15:30 - 15:45	Photocatalytic degradation of methylene blue dye using a visible active photocatalyst immobilized on polypropylene films. **O. Sacco**, R. Rescigno, S. Pragliola, V. Vaiano and V. Venditto	**Dr. Olga Sacco**, University of Salerno, **Italy**
15:45 - 16:00	Photoreactive polymer composites based on visible-light active photo-catalysts for selective benzene hydroxylation to phenol. **A. Mancuso**, O. Sacco, V. Venditto and V. Vaiano	**Dr. Antonietta Mancuso**, University of Salerno, **Italy**
16:00 - 16:30	**Afternoon Coffee Break / Posters Session**	
16:30 - 16:45	Core-skin morphology analysis of calendered isotactic polypropylene (iPP) foils. **M. Mihelčič**, M. Huskić and L. Slemenik Perše	**Dr. Mohor Mihelčič**, University of Ljubljana, **Slovenia**
16:45 - 17:00	Ammonia triggered self-healing of an ozone cracked high strength ionomeric elastomer. **S. Billa** and S. K Rath	**Mr. Srikanth B. Billa**, Naval Materials Research Laboratory, **India**
17:00 - 17:15	Numerical Simulation of Thermal Frontal Polymerization in Polymer Composites: The Role of Nanoparticle Fillers. **M.Lang**, C.Schmidleitner, P.Fuchs and E.Rossegger	**Dr. Margit C. Lang**, Polymer Competence Center Leoben GmbH, **Austria**
17:15 - 17:30	Challenges and solutions to assess the real true stress – true strain response of pure and recycled polymers under large strains **P. Hao**, C. Siebers, K. Ragaert and F. A. Gilabert	**Dr. Pei Hao**, Ghent University, **Belgium**

Wed. 06 March 2024		
Composites Session I. C: Synthesis, Processing and Characterization		
Nervion Conference Room		
Session's Chairs: **Prof. John Botsis, EPFL, Switzerland** **Prof. Dimitris Argyropoulos, North Carolina State University, USA**		
14:00 - 14:30	Electrofluids: liquid composites as soft electrical components. **L. González-García**	**Prof. Lola Gonzalez- Garcia,** INM - Leibniz Institute for New Materials, **Germany**
14:30 - 14:45	Integration of electro-fluids for sensor applications using 3D printing. **N. Hautz**, D.S. Schmidt, S; Arora, S. Lago-Garrido and L. González-García	**Mr. Niclas Hautz**, Leibniz Institute for New Materials, **Germany**
14:45 - 15:00	Cross-linking reaction of bio-based epoxy systems: a study on cure kinetics. **P. Di Matteoa**, A. Iadarolab, V. Brunellaa, R. Ciardiellob, D.S. Paolinob, F. Gazzac and V.G. Lambertinic	**Dr. Pietro Di Matteo**, University of Turin, **Italy**
15:00 - 15:15	Pt/WO3 Nanoparticle-Dispersed Polydimethylsiloxane Membranes for Transparent and Flexible Hydrogen Gas Leakage Sensors. **R. Ishihara**, Y. Makino, Y. Yamaguchi and K. Nishio	**Dr. Ryo Ishihara**, Tokyo University of Science, **Japan**
15:15 - 15:30	Network metrics of percolating silver-PDMS composites and their correlation with electrical conductivity. **D. Perius**, A. Taranovskyy, L. González-García and T. Kraus	**Mr. Dominik Perius,** Leibniz Institute for New Materials, **Germany**
15:30 - 15:45	Structure and photoluminescence properties of NiW1-xMoxO4 (x = 0, 25, 50, and 75%) solid solutions: A Comprehensive Experimental and Theoretical Exploration. **A.F. Gouveia**, M. Assis, E.O. Gomes, M.T. Daldin and J. Andrés	**Dr. Amanda Gouveia**, University Jaume I, **Spain**
15:45 - 16:00	Evaluation of Radiation Shielding Properties for Innovative Concrete with Oil Shale and Basalt-Boron Fiber Additives. **A. Slavickas**, M. Vaišnoras, E. Babilas	**Mr. Andrius Slavickas**, Lithuanian Energy Institute, **Lithuania**
16:00 - 16:30	**Afternoon Coffee Break / Posters Session**	
Session's Chairs: **Prof. John Botsis, EPFL, Switzerland** **Prof. Dimitris Argyropoulos, North Carolina State University, USA** **Prof. Lola Gonzalez- Garcia, INM–Leibniz Institute for New Materials, Germany**		
16:30 - 16:45	Advanced Characterization of Short Fibre Reinforced Concrete in Dynamic Regime through Hopkinson bar and X-ray inspection. N. Krčmářová, J. Šleichrt, J. Falta and T. Fíla	**Mrs. Nela Krčmářová**, Czech Technical University in Prague, **Czech Rep.**
16:45 - 17:00	Empowering Environmental Sustainability Functionalized SBA-15 as a Cutting-Edge Solution for Effective Metal Uptake. **M. Dulski**, A. Strach, M. Wojtyniak, B. Chrzaszcz, M. Laskowska, P. Duda, J. Karczewski, J. Goscianska, A. Jankowska and Ł. Laskowski	**Dr. Mateusz Dulski**, University of Silesia, **Poland**
17:00 - 17:15	An experimental investigation of spreading behavior of carbon fiber rovings. **S. Kohl**, C. Marschik, T. Kranzl, M. Schnaitter and G. R. Berger-Weber	**Mr. Stefan Kohl,** Competence Center CHASE GmbH, **Austria**
17:15 - 17:30	A new optical method for surface quality analyses of thermoplastic composite parts. **J. Birtha**, E. Kobler, C. Marschik, K. Straka and G. Steinbichler	**Mr. Janos Birtha**, Competence Center CHASE GmbH, **Austria**
17:30 - 17:45	Inline Quality Assurance of Glass-Fiber-Reinforced Unidirectional Thermoplastic Tapes using Optical Coherence Tomography. **M. Wenninger**, C. Marschik and G. Berger-Weber	**Dr. Michael Wenninger**, Competence Center CHASE GmbH, **Austria**

17:45 - 18:00	Stress wave attenuation in bi-material 3D printed metallic structures. **R. Kolman**, R. Dvořák, M. Mračko, A. Berezovski, M. Kylar and V. Kotek	**Prof. Radek Kolman**, Institute of Thermomechanics of the CAS, **Czech Rep.**
18:00 - 18:15	Erosion Characteristics of SCR Material Under Diverse Temperature Conditions: An Experimental and Computational Inquiry. **S. Rajath** and N D Shivakumar	**Mr. Rajath S**, Indian Institute of Science, Bangalore, **India**
18:15 - 18:30	Method of localized Lagrange multipliers for coupling of 1D and 3D finite elements. **R. Dvořák**, J.A. Gonzalez, R. Kolman and O. Jiroušek	**Mr. Radim Dvorak,** Czech Technical University in Prague, **Czech Rep.**
18:30 - 18:45	Multiscale modelling of composite pressure vessels. **L. Bouhala**, A. Laachachi, A. Karatrantos	**Dr. Lyazid Bouhala**, Luxembourg Institute of Science and Technology, **Luxembourg**

Wed. 06 March 2024		
3Bs Materials Session I. D: Synthesis, Processing and Characterization		
Arenal Conference Room		
Session's Chairs: **Prof. Romano V.A. Orru, Maastricht University, The Netherlands** **Prof. Mariana Ionita, University of Science and Technology Polytechnic of Bucharest, Romania**		
14:00 - 14:15	Combinatorial Synthesis of polymeric non-viral nanovectors for gene delivery: use of Box Behnken design and Response Surface Methodology. **S. Schirinzi**, G. Gigli, I. E. Palamà and G. Maiorano	**Mr. Simone Schirinzi,** University of Salento, **Italy**
14:15 - 14:30	Improving Comfort and Performance of Contact Lenses Through Hydrophilic Polyphenolic Coatings. P. Demian, D. Nagaya, K. Lee, G. A. Lee, K. Iwai, D. Hasegawa, M. Baba, P. B. Messer-smith, R. Refaei and **M. Lamrani**	**Dr. Mouad Lamrani**, Menicon Co., Ltd, **Switzerland**
14:30 - 14:45	Gallic Acid Loaded-Poly (Lactic Acid) Electrospun Fibers for Bone Tissue Engineering. **N. Sribungngaw**, P. Naruphontjirakul, P. Namchaiw and K. Ngamkham	**Mr. Nuttawut Sribungngaw**, King Mongut's University of Technology Thonburi, **Thailand**
14:45 - 15:00	Engineered anisotropic interlocking strategy for interface toughening in 3D printed bi-material thermoplastic polymers **L. Farràs-Tasias**, J. Topard, S. Panier, F. A. Gilabert and F. H. Marchesini	**Ms. Laia Farràs Tasias**, Ghent University, **Belgium**
15:00 - 15:15	Mesoporous bioactive glass nanoparticles doped with cobalt and boron for theragnostic applications. **M. Vitázková**, F. Kurtuldu, N.Mutlu, E.Vidomanová, Z.Vargas and M. Michálek	**Mrs. Martina Vitázková**, FunGlass, Alexander Dubček University of Trenčín, **Slovakia**
15:15 - 15:30	Spray dried drug loaded zein microparticles for active wound healing. **C. Gnoccchi**, M. Lenzuni, F. Fiorentini, D. Merino, M. Summa, R. Bertorelli, G. Suarato and A. Athanassiou	**Ms. Chiara Gnocchi**, University of Genoa, **Italy**
15:30 - 15:45	Complex composites based on collagen scaffold as wound dressings. **M. Deaconu**, A.-M. Brezoiu , A.-M. Prelipcean, R. Mitran, C. Matei and D. Berger	**Dr. Mihaela Deaconu**, Politehnica University of Bucharest, **Romania**
15:45 - 16:00	Functional characterization of Hermetia illucens-derived chitosans for wound healing applications. **M. Giani**, B, Vigani, G. Sandri, A. Guarnieri, P. Falabella and S. Rossi	**Dr. Micaela Giani Alonso**, University of Pavia, **Italy**
16:00 - 16:30	**Afternoon Coffee Break / Posters Session**	
16:30 - 16:45	Nanostructured Multi-Responsive Coatings for Tuning Surface Properties. **S. Giasson** and A. Guerron	**Prof. Suzanne Giasson**, University of Montreal, **Canada**
16:45 - 17:00	Novel antibacterial coating: functionalization with bovine serum albumin and silver. **C.Reggio**, S. Spriano, A. C. Scalia and A. Cochis	**Dr. Camilla Reggio**, Politecnico di Torino, **Italy**
17:00 - 17:15	Mechanical Characterization of Electrospun Tubular Scaffolds with Randomly Distributed PLA/PCL Bicomponent Fibers. J. Oztemur, S. Ozdemir, H. Sezgin and I. Yalcin-Enis	**Mrs. Janset Oztemur**, Istanbul Technical University, **Turkey**
17:15 - 17:30	Fibroblast Growth Factor 21 Adsorption on Polyelectrolyte Layers: Modelling and Experimental Studies. **A. Michna**, P. Batys, M. Dąbkowska, B. Kowalski, A. Pomorska, M. Wasilewska and Z. Adamczyk	**Dr. Aneta Michna**, Jerzy Haber Institute of Catalysis and Surface Chemistry, **Poland**
17:30 - 17:45	Glass Fiber-reinforced Bio-derived Polybenzoxazine Composites for Medical Application. **C. Jubsilp**, P. Mora and S. Rimdusit	**Dr. Chanchira Jubsilp**, Srinakharinwirot University, **Thailand**
17:45 - 18:00	Synthesis and evaluation of poly(propylene fumarate)-grafted graphene oxide as nanofiller for porous scaffolds. **A.M. Pandele**	**Dr. Andreea Madalina Pandele**, National Polytechnic University of

		Science and Technology Bucharest, **Romania**
Thu. 07 March 2024		
Polymers / Composites / 3Bs Materials 2024 Session II. A		
Santa Cruz Conference Room		
Session's Chairs: **Prof. De-Yi Wang, IMDEA Materials Institute, Spain** **Prof. Federico Paris Carballo, University of Seville, Spain**		
09:00 - 09:30	Polymers and Green Chemistry: Materials for a Circular Economy. **J.H. Clark**	**Prof. James Clark**, University of York, **UK**
09:30 - 10:00	Stimulating Biomaterial Innovation: Why the Hip Implant Has Not Changed Since 1967. **T.J. Webster**	**Prof. Thomas J. Webster**, Hebei University of Technology, **China**
10:00 - 10:30	The Role of Nanofiller Geometry in the Reinforcement of Polymer-based Nanocomposites. **R.J. Young**, Z. Li and M. Liu	**Prof. Robert J Young**, University of Manchester, **UK**
10:30 - 11:00	**Morning Coffee Break / Posters Session**	
11:00 - 11:30	Molecular raincoats are better that coatings: enabling water-resistant biocomposites. J. Andrew, P. Ramadoss and **G.R. Stephenson**	**Prof. G. Richard Stephenson**, Cellexcel Ltd, **UK**
11:30 - 12:00	Microbial polymers: novel biomaterials with improved properties. **F. Freitas**	**Dr. Filomena Freitas**, NOVA Lisbon, **Portugal**
12:00 - 14:00	**Lunch Break**	
Group Photo at 13:45		
Polymers / Composites 2024 Session II. B		
Santa Cruz Conference Room		
Session's Chairs: **Prof. Robert J Young, University of Manchester, UK**		
14:00 - 14:30	Fire-safe Strategies on Fiber Reinforced Polymer Composites: Progress and Challenge. **D-Y. Wang**	**Prof. De-Yi Wang**, IMDEA Materials Institute, **Spain**
14:30 - 14:45	BIO-IGNITION Project: Development of Innovative Fire-Retardant Additives from Renewable Resources Compatible with Various Polymers in Construction, Automotive and Railway Sectors. **A. González-Jiménez**, J.V. Izquierdo and B. Galindo	**Dr. Antonio Gonzalez-Jimenez**, AIMPLAS, **Spain**
14:45 - 15:00	Smart ethylene-octene copolymer nanocomposites with hybrid MWCNT- Fe3O4 fillers: development, properties and applications. J. Zicans, **R. Merijs-Meri**, I. Reinholds and T. Ivanova	**Prof. Remo Merijs-Meri**, Riga Technical University, **Latvia**
15:00 - 15:15	Surface and mechanical properties of polymer nanocomposite PVDF-HFP/PVP/SiO2 with anti-fouling properties **U. Gradišar Centa**, M. Sterniša and L. Slemenik Perše	**Dr. Urška Gradišar Centa**, University of Ljubljana, **Slovenia**
15:15 - 15:30	Effect of a Nanocellulose on the Optical and Mechanical Properties of Flax Pulp. **J. Bárta**, K. Hájková and A. Sikora	**Mr. Josef Bárta**, Czech University of Life Sciences Prague, **Czech Rep.**
15:30 - 15:45	Effect of Solvent Additives on Polyelectrolyte Physicochemical Properties and Complexation. **P. Batys**, M. Morga, M. Khavani, T. Kastinen, I. Leszczyńska, S. M. Lalwani, C. I. Eneh, J. L. Lutkenhaus and M. Sammalkorpi	**Dr. Piotr Batys**, Jerzy Haber Institute of Catalysis and Surface Chemistry, **Poland**
15:45 - 16:00	Influence of external factors on the structure of poly-L-lysine (PLL) and poly-L-glutamic acid (PGA) and formation of PLL/PGA complexes. **M. Morga**, A. Harmat, T. Kastinen, P. Bonarek, D. Lupa, D. Kosior, Z. Adamczyk, J. L. Lutkenhaus , M. Sammalkorpi and P. Batys	**Dr. Maria Morga**, Jerzy Haber Institute of Catalysis and Surface Chemistry, **Poland**

16:00 - 16:30	Afternoon Coffee Break / Posters Session	
16:30 - 16:45	The effect of copper flakes surface modification on physical properties of conductive polymer composites. M. Mihelčič, A. Oseli and **L. Slemenik Perše**	**Dr. Lidija Slemenik Perse**, University of Ljubljana, **Slovenia**
16:45 -17:00	Chemically degradable thermoset matrix for recycling structural polymer composites. **J.W. Yi**, S.W. Kim, J.W. Lee, J.S. Kim, and M.K. Um	**Dr. Jinwoo Yi**, Korea Institute of Materials Science-Changwon, **Rep. of Korea**
17:00 - 17:15	Polymer-infiltrated zirconia ceramic networks with biodegradable and bioactive biocomposites produced by additive manufacturing. **G. Fargas**, E.J. Pujol, B. Begines, Y. Torres, L. Llanes and A. Alcudia	**Ms. Gemma Fargas Ribas**, Polytechnic University of Catalonia, **Spain**
17:15 - 17:30	Application of treatment methods for recycled concrete aggregates to improve their properties **A. Al-Yaqout**	**Dr. Anwar Al-Yaqout**, Kuwait University, **Kuwait**

Conference Dinner at 19:30, Mosaico Restaurant – Level 1

Thu. 07 March 2024		
3Bs Materials Session II. C: Biomaterials Synthesis, Processing and Characterization Biobased and Biomimetic Materials / Bio interfaces / Biomaterials applications		
Nervion Conference Room		
Session's Chairs: Prof. Thomas J. Webster, Hebei University of Technology, China Prof. Ivan Chodak, Polymer Institute SAS, Slovakia		
14:00 - 14:30	Anti-infection Strategies Applied to Design Coating Materials for Stable and Biodegradable Biomedical Implants. **J.V. Rau**	**Prof. Julietta V. Rau**, Institute of Structure of Matter, CNR, **Italy**
14:30 - 15:00	CaCO3 Ceramics - A Bioresorbable Bone Grafting Material. **S. Umemoto**, H. Unuma, T. Furusawa, T. Goto and T. Sekino	**Prof. Hidero Unuma**, Yamagata University, **Japan**
15:00 - 15:15	Bio-based flexural structures based on epoxidized plant oils. **A. Solt-Rindler**, J. Janesch, L. Dumschat, O. Vay and C. Hansmann	**Dr. Axel Solt-Rindler**, Wood Material Technologies, **Austria**
15:15 - 15:30	Design of stimuli responsive antimicrobial materials based on the reversible surface grafting of trans-2-hexenal on chitosan films through imine linking. **P. Esteve-Redondo**, R. Heras-Mozos, C. López de Dicastillo, R. Gavara and P. Hernández-Muñoz	**Mrs. Patricia Esteve Redondo**, IATA-CSIC, **Spain**
15:30 - 15:45	Holistic approach to understand how teleost fish scales fulfil their biological function - from nano to macro structure organization. **A. Petitpas**, J. Veillon, L. Rubatat, P. Moonen, V. Pellerin and S.C.M. Fernandes	**Mr. Arnaud Petitpas**, University of Pau et des Pays de l'Adour, **France**
15:45 - 16:00	Moisture Sensor Inspired by Natural Cellulosic Networks. S. D. Almeida, P. L. Almeida, M. H. Godinho and **A P. C. Almeida**	**Dr. Ana Almeida**, NOVA School of Science and Technology, **Portugal**
16:00 - 16:30	**Afternoon Coffee Break / Posters Session**	
Session's Chairs: Prof. Julietta V. Rau, Institute of Structure of Matter, CNR, Italy Prof. Hidero Unuma, Yamagata University, Japan		
16:30 - 17:00	Modification of thermoplastic starch to achieve a broad range of properties in mixtures with biopolymers. **I. Chodak** and H. Peidayesh	**Prof. Ivan Chodak,** Polymer Institute SAS, **Slovakia**
17:00 - 17:15	Bio-inspired multilayered nanocellulose-based assemblies with anisotropic properties. **L. Garnier**, O. Felix and B. Jean	**Ms. Leila Garnier**, Institut Charles Sadron, **France**
17:15 - 17:30	Bioinspired Two Photon Polymerized Micro-Pillar Antibacterial Surfaces. **G.E. Marsh**, T. Ning, K. Jodeiri Iran, R.D. Wildman and M.SL. Yee	**Dr. Georgina Marsh**, Swansea University, **UK**
17:30 - 17:45	Evolution and characterization of Drosophila glue, a model for biomimicry. **M. Monier**, J-N. Lorenzi, F. Borne, V. Contremoulins, L. Mevel, R. Petit, F. Graner and V. Courtier	**Ms. Manon Monier**, Institut Jacques Monod, **France**
17:45 - 18:00	Guiding Cellular Behaviour via Contact with Nature Inspired, ECM- mimetic Hierarchical Topographic Cues. **A. Gope**, A. Mukhopadhyay and R. Mukherjee	**Mr. Ayan Gope**, Indian Institute of Technology Kharagpur, **India**

Conference Dinner at 19:30, Mosaico Restaurant – Level 1

Thu. 07 March 2024		
Polymers / Composites/ 3Bs Materials Session II. D: Biobased Materials/ Biopolymers/ Biocomposites		
Arenal Conference Room		
Session's Chairs: **Prof. John Botsis, EPFL, Switzerland** **Prof. James Clark, University of York, UK** **Dr. Filomena Freitas, NOVA Lisbon, Portugal**		
14:00 - 14:15	Bio-based hybrid composite epoxy/NIPU foams for constructive Applications. **L. Gryshchuk**	**Dr. Liudmyla Gryshchuk**, Leibniz-Institut für Verbundwerkstoffe GmbH, **Germany**
14:15- 14:30	Shape Memory Composites based on Bio-Benzoxazine/Bio-Urethane Copolymers Reinforced with Graphene with NIR Actuation Ability. **S. Rimdusit**, W. Jamnongpak, K. Charoensuk and C. Jubsilp	**Prof. Sarawut Rimdusit**, Chulalongkorn University-Bangkok, **Thailand**
14:30 - 14:45	Impact and flexural properties of woven flax-carbon thermoplastic hybrid bio-composites. **M. Bahrami**, M. Mehdikhani, Y. Swolfs, J. Abenojar and M.A. Martinez	**Mr. Mohsen Bahrami**, Universidad Carlos III de Madrid, **Spain**
14:45 - 15:00	Degradation behavior of poly(lactic acid) biocomposites filled with natural materials. **M. Musiol**, S. Jurczyk, W. Sikorska, H. Janeczek, J. Rydz and K. Molnar	**Mrs. Marta Musioł**, Centre of Polymer and Carbon Materials, **Poland**
15:00 - 15:15	Green composites reinforced with sisal fabric: a preliminary investigation on mechanical response. C. Santulli, **S. Boria**, G. Del Bianco, V. Giammaria, M. Capretti, and V. Castorani	**Dr. Simonetta Boria**, University of Camerino, **Italy**
15:15 - 15:30	Development of sustainable corn derivates-based composites. **A. Cunha**, P. Teixeira, S. Gomes, A. Monteiro, N. Senhorães, R. Malta, C. M. Brito, L.F.S. Silva, N.M. Pereira, I. Oliveira, J.Viegas.	**Mr. Américo Cunha**, CeNTI - Centre of Nanotechnology and Smart Materials, **Portugal**
15:30 - 15:45	Supercritical CO2 impregnation of PHB-HV in submerged and non-submerged mango leaves extract. **L. León**, D. Valor, I. García-Casas, A. Montes, C. Pereyra and E.J. Martínez de la Ossa	**Ms. Ludisbel León Marcos**, University of Cadiz, **Spain**
15:45 - 16:00	Scaling-up of supercritical solvent impregnation of olive leaf extract into polypropylene films. Á. Pineda, C. Cejudo, L. Verano, **N. Machado**, C. Mantell, L. Casas	**Dr. Noelia Machado**, University of Cadiz, **Spain**
16:00 - 16:30	**Afternoon Coffee Break / Posters Session**	
16:30 - 16:45	Inclusion of natural antioxidants from olive pruning waste in porous biomaterials using supercritical technology. **I. García-Casas**, D. Valor, H. Elayoubi, L.León, C. Pereyra and A. Montes.	**Dr. Ignacio Garcia Casas**, University of Cadiz, **Spain**
16:45 - 17:00	Hydrothermal treatment to optimize supercritical CO2 polycaprolactone foaming processes for tissue engineering scaffolds. **B. García-Jarana**, D. Valor López, J. M. Abelleira, J. Sánchez-Oneto, J. R. Portela and E. J. Martínez de la Ossa	**Dr. Belen Garcia-Jarana**, University of Cadiz, **Spain**
17:00 - 17:15	Antiviral activity of silk fabric functionalized with SnO2 nanoparticles **A. Baranowska-Korczyc**, D. Kowalczyk, K. Sobczak, M. Krzyżowska and M. Cieślak	**Dr Anna Baranowska-Korczyc**, Lodz Institute of Technology, **Poland**
17:15 - 17:30	Assumptions for obtaining thermoactive wood-based composites for furniture and interior design **A. Jeżo**, G. Maksymiuk, M. Wronka and G. Kowaluk	**Ms. Aleksandra Jeżo**, Warsaw University of Life Sciences, **Poland**

17:30 - 17:45	Selected Challenges when Preparing and Characterizing Thermoactive Wood-based Composites for Furniture and Interior Equipment **A. Wronka**, A. Jeżo and G. Kowaluk	**Ms. Anita Wronka**, Warsaw University of Life Sciences, **Poland**

Conference Dinner at 19:30, Mosaico Restaurant – Level 1

Fri. 08 March 2024		
Polymers / Composites 2024 Session III. A: Energy and Environmental Applications		
Arenal Conference Room		
Session's Chairs: **Prof. Federico Paris Carballo, University of Seville, Spain** **Prof Joana Vaz Pinto, FCT NOVA University Lisbon, Portugal**		
09:00 - 09:15	3D printed Schwarz primitive lattice based interpenetrating phase composites for improved energy absorption. **W. Feng Lu** and X. Guo	**Prof. Wen Feng Lu**, National University of Singapore, **Singapore**
09:15 - 09:30	Solvent Delamination of Multilayer Composite Waste –Challenges and Experiences. **G. Denafas**, I. Pitak, V. Makarevičius, A. Baltušnikas, R. Kriukienė, A. R. Zubas, A. Šleiniūtė and T. Mumladze	**Prof. Gintaras Denafas**, Kaunas University of Technology, **Lithuania**
09:30 - 09:45	Metal Foam in Lightweight Heat-Exchangers: Innovation and Recycling Imperatives. **J.E. Grimmenstein**	**Mr. Julius Grimmenstein**, TU Bergakademie Freiberg, **Germany**
09:45 - 10:00	Electromagnetic properties of polymer composites based on 2000HH/2000HM-ferites and ferroelectric matrices. **V.G. Kostishin**, R.I. Shakirzyanov, I.M. Isaev, A.Yu. Mironovich, B.M. Skibo and M. Jaloliddinzoda	**Prof. Vladimir Kostishin,** National Research Technological University "MISiS", **Russia**
10:00 - 10:30	**Morning Coffee Break**	
10:30 - 10:45	Tailoring the Dielectric Properties of Binder-ST Composites: RTF Experiments vs. OOF2 Modeling. **N. Kuzmić**, D. Fabijan, S. Davor Škapin, M. Nelo, H.Jantunen and M. Spreitzer	**Mrs. Nina Kuzmić,** Jožef Stefan Institute, **Slovenia**
10:45 - 11:00	Na-ion battery using a composite electrolyte. Y. Wang, X. Xu and **L. Lu**	**Prof. Li Lu**, National University of Singapore, **Singapore**
11:00 - 11:15	Radio absorption properties of magnetic polymer composites based on Li-Mn-Zn-spinel ferrites in the range of 0.1 – 7.0 GHz. **V.G. Kostishin**, R.I. Shakirzyanov, I.M. Isaev, A.Yu. Mironovich, B.M. Skibo and M. Jaloliddinzoda	**Prof Vladimir Kostishin,** National Research Technological University "MISiS", **Russia**
11:15 - 11:30	Multifuctional Parylene C membranes for microelectronic devices integration. **J.V. Pinto**, B.J. Coelho, D. Carvalho, J. Coelho. J.P. Neto, J. Martins, A. Roviso, R. Martins, L.N. Boane, M. Cortinhal, H. Águas, M. Mendes, R.Igreja and P. Barquinha	**Prof Joana Vaz Pinto**, FCT NOVA University Lisbon, **Portugal**
11:30 - 11:45	Structural simulation and alternative fabrication of a rear suspension fork link using composite materials for electrical vehicle applications. M. Lasheras-Zubiate, J:L Fernández , E. Teiletxea, G. Argandoña, I. Landa, **R. Herrero** and R. Mazquiarán	**Dr. Rakel Herrero**, NAITEC, **Spain**
11:45 - 12:00	Addressing fire risk in electric vehicles battery boxes using inorganic polymer-based fiber-reinforced composites. **A. Natali Murri**, E. Papa, E. Landi, C. Mingazzini and V. Medri	**Dr. Annalisa Natali Murri**, CNR-ISSMC, **Italy**
12:00 - 12:15	Strong and tough double-network hydrogels with excellent adsorption performance for diclofenac: behaviors and mechanisms. **L. Wang**, G-J. Euverink and F. Picchioni	**Mrs. Lin Wang**, University of Groningen, **The Netherlands**

Fri. 08 March 2024		
3Bs Materials 2024 Session III. B: Biomaterials / Biomimetics Materials / Biobased Materials applications		
Nervion Conference Room		
Session's Chairs: **Prof. Magdalena Ziąbka, AGH - University of Krakow, Poland** **Dr. Georgina Marsh, Swansea University, UK** **Dr. Corine Tourne-Peteilh, Univ Montpellier, France**		
09:00 - 09:15	3D-printed poly(lactic acid) structures coated in hydroxyapatite and loaded with a drug delivery system for the reconstruction of cranial defects. **A. D'Andrea**, R. Donate, M. Monzón and I. Cacciotti	**Ms. Alessia D'Andrea**, University of Rome Niccolò Cusano, **Italy**
09:15 - 09:30	Encapsulation of ectoine in lipid nanoparticles for the treatment of in-flammatory bowel disease. M. Abajo and **V. Saez-Martinez**	**Dr. Virginia Saez**, i+Med S. Coop, **Spain**
09:30 - 09:45	Lymphatic Network Engineering and Regeneration in Vitro and in Vivo for the Lymphedema Treatment. **Q. Zhang**, Y. Wu, M. Fowler, E. Chang, M. Schaverien and P. Yu	**Dr. Qixu Luke Zhang**, UT MD Anderson Cancer Center, **USA.**
09:45 – 10:00	Delivering Parasite-Derived Immunotherapeutics from Hyaluronic Acid Hydrogels Acting as Soft Tissue Supports. **V. Ward**, J. O'Dwyer, R. Lalor, J. P. Dalton and G.P. Duffy	**Ms. Victoria Ward**, Univ. of Galway, **Ireland**
10:00 - 10:30	**Morning Coffee Break**	
10:30 - 10:45	A novel approach in bone regeneration and detection of ALP and RUNX2 osteogenic biomarkers. **M. Ionita**	**Prof. Mariana Ionita**, University of Science and Technology Politechnic of Bucharest, **Romania**
10:45 - 11:00	Hybrid silylated hydrogels for biomecules encapsulation: design, stability, and controlled release. **C. Tourne-Peteilh**, G. Subra and A. Mehdi	**Dr. Corine Tourne-Peteilh**, Univ Montpellier, **France**
11:00 - 11:15	Core-shell hydrogels as in vitro tumor models. **I. Parodi**, M.M. Fato and S. Scaglione	**Dr. Ilara Parodi,** University of Genoa, **Italy**
11:15 - 11:30	Cell desiccation: a cheaper and more efficient alternative for storage and transport. **L.V. Barrios Silva**, N.S. Sharifulden, N. Mandakhbayar, S.J. Shin, J.H. Park, D.J. Player, H.W. Kim, D. Vllasaliu and D.Y.S. Chau	**Ms. Lady Barrios Silva**, University College London, **UK**
11:30 - 11:45	Elevating Wound Healing: Unveiling the Impact of Wireless Electrical Stimulation on Cell Differentiation and Observed Improved Cell Attachment and Expansion. **L. Gazvoda**, M. Zabčić, M. Spreitzer and M. Vukomanović	**Mrs. Lea Gazvoda**, Jožef Stefan Institute, **Slovenia**

Polymers / Composites / 3Bs Materials 2024 Posters

06 and 07 March 2024 Sessions

N.	Poster Title	Author, Affiliation, Country
1.	Development of Models to Predict the Properties of Materials Produced of Polymeric Yarns. T. Rolich, I. Salopek Čubrić and **G. Čubrić**	**Prof. Goran Čubrić**, University of Zagreb Faculty of Textile Technology, **Croatia**
2.	On The Measurement of the With of the Distribution of Retardation Times in Polypropylene **J. André** and J. Cruz Pinto	**Prof. José André,** Guarda Polytechnic Institute, **Portugal**
3.	Synchrotron radiation-based FTIR Microspectroscopy and TEM investigations on the Core-Shell structure PEGylated polymeric particles. **D.Makharadze**, LJ.del Valle, T. Kantaria, T.Kantaria, R. Katsarava AND J.Puiggali	**Mr. Davit Makharadze,** Polytechnic University of Catalonia, **Spain**
4.	Photocatalytic carbon dioxide reduction using titanium dioxide modi-fied with metal salts. **I. Pełech**, K. Sobczuk, K. Ćmielewska, P. Staciwa, D. Sibera, E. Kusiak-Nejman , A.W. Morawski and U. Narkiewicz	**Prof. Iwona Pełech**, West Pomeranian University of Technology in Szczecin, **Poland**
5.	Synthesis of Graphene/Polymer Nanocomposites based for additive manufacturing technologies. **S. Mikaberidze**, M. Maisuradze and N. Jalagonia	**Mrs. Sopo Mikaberidze**, Tbilisi Technical University, **Gerogia**
6.	Polyhydroxybutyrate-co-hydroxyvaleriate composites with rapeseed microfibers throughout its life cycle. M. Žiganova, A. Ābele, I. Bochkov, T. Ivanova, R. Merijs-Meri and **J. Zicāns**	**Dr. Janis Zicans**, Riga Technical University, **Latvia**
7.	Pectic polysaccharides extracted from melissa and lavender solid by-products of essential oil industry. **A. Slavov** and G. Marovska	**Dr. Anton Slavov**, University of Food Technologies Plovdiv, **Bulgaria**
8.	Supercritical Solvent Impregnation of poly-lactic acid food films with olive leaf extract for fresh fish preservation. M. Tirado, **C. Cejudo**, F. Sánchez, A. M. Roldán, L. Casas and C. Mantell	**Ms. Cristina Cejudo Bastante,** University of Cadiz, **Spain**
9.	Sustainable Gum Arabic Adhesives intended for Corn Seed Coating **S. Fuster-Esteso**, R. Torres-Vera, J. Martínez-Ruiz and J.M. Martín-Martínez	**Ms. Sara Fuster Esteso**, University of Alicante, **Spain**
10.	Phosphorus-Nitrogen synergic bio-based flame retardant from chitosan and phytic acid for plastic matrices applications. **M. Expósito** and L. Agostinis	**Ms. María Expósito**, AIMPLAS, **Spain**
11.	Removal of Emerging Contaminants in waters by filtration with biochars. **T. Undabeytia**, J.M. De la Rosa, Á. Sánchez-Martín, S Nir, M. Arenas-Arévalo, F. Behrendt and A. Diéguez-Alonso	**Dr. Tomas Undabeytia**, Instituto de Recursos Naturales y Agrobiología (IRNAS-CSIC), **Spain.**
12.	The bio-based cellulose produced by acetic acid bacteria as a potential material for sustainable packaging. **C. M. Kuo**, S. Q. Huang, B. C. Shi, Y. R. Chang and Y. T. Chen	**Dr. Chiu-Mei Kuo**, Chung Yuan Christian University, **Taiwan**
13.	Polymeric films conjugated with silver and copper nanoparticles to enhance the antimicrobial activity. **E. Hernández-Martín**, B. Merás-Saiz and M. Iriarte-Cela	**Mrs. Esther Hernández Martín**, Nanotechnology Department, Technological and Research Centre, **Spain**
14.	Development of novel drug delivery systems based on polymeric nanofibers for the treatment of glioblastoma. **P.V. Badía Hernandez**, J. Moll-Carrió, M. Fuentes-Baile, R. Díaz-Puertas, M. Saceda, M.P. García-Morales and R. Mallavia	**Mr. Pedro V.B. Hernández**, Miguel Hernández de Elche University, **Spain**
15.	Assessing Smoke Emission Characteristics of Innovative Cork-Based Composites Incorporating Recycled Plastic Materials. **T. Barboni**, S. Petlitckaia and P-A. Santoni	**Mr. Toussaint Barboni**, University of Corsica, **France**
16.	Multiferroic ceramic composites obtained by three sintering methods. **P. Niemiec**, D. Bochenek, G. Dercz, A. Chrobak and G. Ziółkowski	**Dr. Przemysław Niemiec**, University of Silesia in Katowice, **Poland**

17.	Multiferroic composites based on BaTiO3 and nickel-zinc ferrite material. **D. Bochenek**, P. Niemiec, G. Dercz, A. Chrobak and G. Ziółkowski	**Prof. Dariusz Bochenek**, University of Silesia in Katowice, **Poland**
18.	Optimization of parameters for producing piezoelectric BT/PVDF nanocomposites using additive manufacturing. **L. Santiago-Andrades**, M. J. Sayagués, F. J. Gotor and R. Moriche	**Ms. Lucía Santiago Andrades,** University of Seville, **Spain**
19.	Influence of the addition of BT nanoparticles on the piezoelectrical, mechanical and tribological properties of BT/PVDF nanocomposites. A. Otero, M.J. Sayagués, F. J. Gotor, R. Donate, M. Monzón, R. Paz, **F. Gutiérrez-Mora** and R. Moriche	**Dr. Felipe Gutiérrez Mora**, University of Seville, **Spain**
20.	High-temperature mechanical and electrical characterization of zirconia composites with 2D nanomaterials. **F.J. Coto-Ruiz** A. de la Cruz-Blanco, R. Moriche, Á. Gallardo-López, F. Gutiérrez-Mora, A. Morales-Rodríguez and R. Poyato	**Mr. Francisco Javier Coto Ruiz,** University of Seville, **Spain**
21.	Photoreduction of carbon dioxide over TiO2/Ru composites. **D. Sibera**, I. Pełech, P. Staciwa, K. Ćmielewska, K. Sobczuk, E. Ekiert, E. Kusiak-Nejman, A. W. Morawski and U. Narkiewicz	**Dr. Daniel Sibera**, West Pomeranian University of Technology, **Poland**
22.	Dynamics of a thin-walled composite structure with a piezoelectric sensor deformation. **L.Zárybnická**, M. Marek and R.Kolman	**Dr. Lucie Zárybnická**, College of Polytechnics Jihlava, **Czech Rep.**
23.	Laboratory Evaluation of the Use of Seashell and Bio-based Epoxy Asphalt in Porous Asphalt Mixtures. **M. Alharthai**	**Dr. Mohammad Alharthai**, Najran University, **Saudi Arabia**
24.	Recovering and Transforming fishing waste for a sustainable future. **S. Miranda**, M. Fernandes, R. Reis, T. Simões, J. Redol, P. Manuel, C. Serralheiro and P. Ramalhete	**Ms. Sónia Miranda**, Innovation in Polymer Engineering (PIEP), **Portugal**
25.	Development of feather-based materials. **K. Wrześniewska-Tosik**, T. Mik, E. Wesołowska, T. Kowalewski, M. Pałczyńska and **J. Wietecha**	**Mrs. Justyna Wietecha**, Lodz Institute of Technology, Lodz, **Poland**
26.	Alimentary Protein Isolate and Chitosan Derivatives Complexes as Novel Biomaterials for Skin Repair. **D. Ianev**, B. Vigani, M. Mori, C. Valentino, M. Ruggeri, G. Sandri, and S. Rossi	**Dr. Daiana Ianev**, University of Pavia, **Italy**
27.	Cellulosic responsive membranes for dynamic water collection. **S. D. Almeida**, P. L. Almeida, M. H. Godinho and A P. C. Almeida	**Mr. Sérgio Almeida**, NOVA School of Science and Technology, **Portugal**
28.	Development of 3D graphite scaffolds due to carbonization of biomaterial spongin at temperatures up to 2200 ℃. **M. Kotula**, A. Kubiak, B. Leśniewski, M. Pajewska-Szmyt and H. Ehrlich	**Ms. Martyna Kotula**, Adam Mickiewicz University, **Poland**
29.	Marine Spongin-containing Scaffolds for Creation of functional Iron-Based 3D Composite Materials. **A. Kubiak**, M. Pajewska-Szmyt, M. Kotula, B. Leśniewski and H. Ehrlich	**Ms. Anita Kubiak**, Adam Mickiewicz University, **Poland**
30.	Slow crack growth resistance of zirconia-hydroxyapatite composites. **A.Wojteczko** and M. Ziąbka	**Dr. Agnieszka Wojteczko,** AGH - University of Krakow, Faculty of Materials Science and Ceramics, **Poland**
31.	Optimizing Advanced Implant Surfaces: Employing Composite Coatings of Bioglasses and Antimicrobial Substances for Improved Bone Repair and Enhanced Antimicrobial Protection. **I. Ungureanu Negut**, C. Ristoscu, V. Grumezescu and C. Hapenciuc	**Dr. Irina Ungureanu Negut**, National Institute for Lasers, Plasma and Radiation Physics, **Romania**
32.	Characterization & Degradation of Polymers using Various Scaffold Designs for Use in Critical Size Bone Defects. **S. Meyr**, E. Mirdamadi , R. Smith and M.O. Wang	**Ms. Samantha Meyr**, University of Maryland, **USA**
33.	Antibacterial activity and biological response of zirconia based ceramic composites. **M. Ziąbka** and A.Wojteczko	**Prof. Magdalena Ziąbka**, AGH - University of Krakow, Faculty of Materials Science and Ceramics, **Poland**

34.	Stimuli responsive imine bonds for the green synthesis of antimicrobial-chitosan conjugates. **E. Simó-Ramírez**, R. Heras-Mozos, C. López de Dicastillo, R. Gavara and P. Hernández-Muñoz	**Mr. Ernest Simó Ramírez**, IATA-CSIC, **Spain.**
35.	Novel functionalized gold nanoparticles with improved contact-based antimicrobial properties. **M. Žabčić**, L. Gazvoda, M. Spreitzer and M. Vukomanović	**Ms. Martina Žabčić**, Jožef Stefan Institute, **Slovenia**
36.	Poly(alkylene citrate) (PAC) and PAC-based materials as novel promising candidates for vascular graft production. **L. Svobodová**, F. Koper, A. Flis, M. Trávníčková, E. Pamuła, L. Bačáková and W. Kasprzyk	**Dr. Lucie Svobodová**, Institute of Physiology of Czech Academy of Sciences, **Czech Rep.**
37.	The Role of Manganese in the Evolution of Calcium Phosphate Bioceramics. **B. Tyliszczak**, D. Słota, K. Niziołek, J. Sadlik, A. Tomala and A. Sobczak-Kupiec	**Prof. Bożena Tyliszczak**, Cracow University of Technology, **Poland**
38.	Polymer - Ceramic Composites Enriched in Silk Fibroin for Osteochondral Applications. **A. Sobczak-Kupiec**, D. Słota, K. Niziołek, D. Trager and B. Tyliszczak	**Prof. Agnieszka Sobczak-Kupiec**, Cracow University of Technology, **Poland**
39.	Tissue-Engineered Tri-leaflet Valved Stents on Biodegradable Poly-ε-Caprolactone Scaffolds. **M. Saeid Nia**, J. A. Seiler and G. Lutter	**Dr. Monireh Saeid Nia**, University Hospital Schleswig-Holstein, **Germany**
40.	Silver nanoparticle as therapeutic options to fight the resistome, mobilome and virulome of multidrug resistant Acinetobacter baumannii circulating clones in South Romania. **I. Gheorghe-Barbu**, I. Czobor Barbu, V.M. Corbu, A-Ș. Dumbravă, D-M Găboreanu, G.-A Grigore, C.O. Vrâncianu, M. Surleac, S. Paraschiv, D. Oțelea, D. Ficai, A. Ficai and M.C. Chifiriuc	**Mrs. Irina Gheorghe-Barbu,** University of Bucharest, **Romania**
41.	Inorganic nanoparticle-based multifunctional coatings for the preservation of Romanian cultural heritage objects. **A.Ş. Dumbravă**, I. Gheorghe-Barbu, V.M. Corbu, D.M. Găboreanu, I.C. Marinaș, I. Pecete, D. Ficai, A. Ficai, M.C. Chifiriuc and T.E. Șesan	**Ms. Andreea Stefania Dumbrava,** University of Bucharest, **Romania**
42.	Biomechanical and Morphological Evaluation of Cryopreserved Porcine Tissues. **M. Casarin**, M. Todesco, C.G. Fontanella, A. Morlacco, F. Dal Moro, L. Astolfi and A.Bagno	**Mrs. Martina Casarin**, University of Padua, **Italy**
43.	Understanding cell-matrix interactions between primary neurons and breast tumor cells in a brain-like 3D microenvironment. **E. Türker**, J. Faber, M.S. Andrade Mier, N. Murenu, P. Stahlhut, G. Lang, S. Budday, N. Schaefer, P.Strissel R.Strick and C.Villmann	**Ms. Esra Türker**, University of Würzburg, **Germany**
44.	Using Biosurfactant Molecules for hydrocarbon desorption from solid surfaces: A Molecular Dynamics Study **A. B. Salazar-Arriaga** and H. Dominguez	**Ms. Ana Beatriz Salazar-Arriaga**, National Autonomous University of Mexico, **México.**
45.	Polyvinyl caprolactam polyvinyl acetate-polyethylene glycol grafted copolymer as an excellent solubility enhancer of apigenin and its neuroprotective potential **A. Stasiłowicz-Krzemień**, N. Rosiak and J. Cielecka-Piontek	**Mrs Anna Stasiłowicz-Krzemień**, Poznan University of Medical Sciences, **Poland**

SETCOR
Conferences & Exhibitions

Oral Presentations Abstracts

Polymers / Composites / 3Bs Materials 2024 Session I. A

Nanofibrillar Multifunctional Thermoplastic Materials Prepared by Solution Blow Spinning

Javier González-Benito
Department of Materials Scienc & Engineering & Chemical Engineering, University Carlos III of Madrid, Leganés (Madrid), Spain

Abstract:
For applications such as filters and membranes, wound dressings, scaffolds for tissue engineering, materials require mechanical consistency, biocompatibility, biodegradability and, a particular microstructure or morphology since it can highly influence on other properties such as mechanical properties, wettability and even on adhesion, differentiation and development of cells.

One particularly interesting morphology is that one constituted by fibers. Their high aspect ratio, size, concentration and preferential orientation can highly affect the properties and performance of materials.

On the other hand, in order to improve or even to find new properties, materials can also be combined in the form of composites looking for synergy. Special cases are those for which at least one of the constituents has nanoscopic dimensions (nanocomposites) since the nanoscopic condition itself can also improve properties or lead to the appearance of new ones. However, to have better control of tuned properties from the composition, the achievement of uniform dispersions of nanoparticles in matrices is usually one of the requisites. Although many methods have been tried to achieve uniform dispersion of nanoparticles in polymer matrices when, at the same time, fibrillar morphology constituted by submicrometric fibers is required only electrospinning (ES) and solution blow spinning (SBS) seem feasible techniques. ES is probably the most used technique to obtain polymer-based materials constituted by submicrometric fibers. A polymer solution is stretched by the action of a relatively high electric field generating on the air fibers that are deposited on a collector. With ES is possible to obtain quite homogeneous morphologies. However, since the driving force is the proper interaction between the electric field and the polymer solution some systems are difficult to work with. Besides, the necessity of relatively high electric fields makes difficult its use to prepare materials in-situ.

On the other hand, SBS is a more recent processing method based on the use of a concentric nozzle where through the inner channel is made to flow a polymer solution while through the outer channel flows a pressurized gas. At the exit of the nozzle the solution is ejected by the action of the gas, being drawn to finally form fibers while the solvent is evaporated.[1] Although with SBS is really difficult to have high control on the morphology obtained, it is simple, cheap and high productions rates can be achieved. Besides, it can be adapted to prepare materials in specific sites. For these reasons, SBS is considered very promising in some fields of application.

This work reviews some achievements of the Group of Polymer Composite Materials and Interphahes of the University Carlos III of Madrid on the preparation of thermoplastic nanofibrous materials and nanocomposites by the use of SBS:

1. Materials with antibacterial behavior.
2. Materials with especial dielectric behavior.
3. Superhydrophobic materials with high ability of oil absorption.
4. Fibrous morphology and mechanical properties.

Keywords: Solution Blow Spinning, Nanocomposites, Thermoplastics, Multifunctional materials.

Acknowledgments: This work was financially supported by AEI (Ministerio de Ciencia e Innovación of Spain, PID2020-112713RB-C21 and -C22), the Universidad Carlos III de Madrid, Fondos de Investigación of Fco. Javier González-Benito [2012/00130/004] and the strategic Action in Multifunctional Nanocomposite Materials [Code: 2011/00287/003].

References:

1. E.S. Medeiros, G.M. Glenn, A.P. Klamczynski, W.J. Orts, L.H.C. Mattoso, (2009), Solution blow spinning: A new method to produce micro- and nanofibers from polymer solutions. *J. Appl. Sci.* 113, 2322.

Limitations in Creating Lignin-Derived Carbon Fibers

Dimitris S Argyropoulos
Departments of Chemistry and Forest Bomaterials, North Carolina State University, Raleigh , NC, USA

Abstract:
Single component lignin-derived carbon fibers have been under development for many years, but strength properties are still inferior to those of commercial carbon fibers. The extent of graphitization is an overlooked limitation to lignin-derived carbon fiber development, particularly for high-modulus fibers treated at high temperatures. The tensile moduli of commercial carbon fibers increase with temperature during graphitization, however, lignin-derived carbon fiber moduli stay the same or decrease. This review exposes the inability of lignin-derived carbon fibers to graphitize in a manner similar to commercial carbon fibers, thereby providing rationale for the aforementioned discrepancy in tensile moduli-temperature trends and offering possible tangible future areas of research and development.

Incidence of the Mechanisms of Damage in the Performance of Composites

F.París
School of Engineering, University of Seville, Spain

Abstract:
The main feature when dealing for first time with composites is the non-isotropic behaviour based on the presence of oriented fibres. This is correct when dealing with aspects associated with the stiffnes of a component made of composites. However, when dealing with the strength or toughness of composite structures, the main feature of these materails is their non-homogeneosus character, as it conditions the mechanisms of failure of composites, which is obviously linked with the reperesentativity of failure criteria of composites used to design composite structures, París [1]. Many phenomena associated with composites as the scale-effect, Parvizzi et al [2], has been not completely understood till the existance of a physically based explanation, connected to the damage mechanisms of composites, París et al [3]. Thus, Figure 1 presents a clear explanation of the scale effect based on the damage observed in a cross-ply laminate as a function of the thickness of the 90 degrees lamina. The typical statement that the damage in the 90 degrees ply is a function of its thickenss has to be redefined. The correct statement is that damage starts at the same level of deformation independently of the thickness of the 90 degrees lamina. However, the severity of the damage is completely different depending on the thickness of the 90 degrees ply. In presence of an ultra thin ply, see Figure 1, the damage can be isolated debonds, a damage that do not affect the integrity neither of the 90 degrees ply nor of the laminatewhere the lamina is. On the contrary, in presence of a thick ply the first damage can have catastrophic effects, with the presence, see Figure1, of a total transverse crack in the 90 degrees ply as well as the presence of delaminations between 0 and 90 degrees plies, a fact that can have very detrimental effects for the laminate under loading like bending or torsion, for instance.
The knowledge about the actual mechanisms of damage of composites has the inmediate effect on an optimum design of a laminate, as the thickness of the weakest lamina of the laminate may be designed to generate a damage not affecting the behaviour of a laminate till the appearance of a failure of the fibres in the 0 degrees ply.
Also, the identificaction of the mechanisms of damage may help in the most appropriate definition of tests to estimate the properties of composites. Thus, in this way, tests of cross-ply laminates can be designed with the correct thicknesses of the laminas of the laminate to generate exactly the damage configuration controlled by the fracture toughness more involved in the generation of damage: fracture toughness of the 90 degrees ply and fracture toughness associated with a delamination damage between 0 and 90 degrees plies.

Keywords: Composite mechanisms of damage, scale effect, ultra thin plies, optimum design of composite structures.

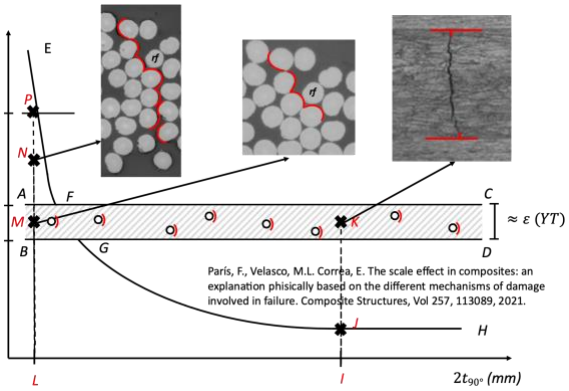


Figure 1: Evolution of the damage with the thickness of the 90 degrees ply in a cross-ply laminate.

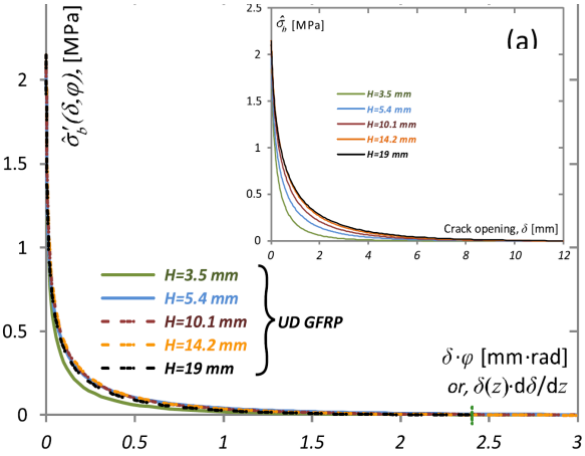
References:

1. F. París, A study of failure criteria of fibrous composites materials. NASA/CR-2001-210661, 2001
2. A. Parvizi, K. V. Garret, J. E. Bailey, Constrained cracking in glass fibre-reinforced epoxy cross-ply laminates. J. Mat. Sci. 13, 195–201, 1978.
3. F. París, M.L. Velasco, E. Correa, The scale effect in composites: An explanation physically based on the different mechanisms of damage involved in failure. Comp Struct; 257:113089, 2021.

Experiments and Analysis of Delamination in Composite Materials

J. Botsis[1]
[1] School of Engineering, École Polytechinque Fédérale de Lausanne (EPFL), Lausanne, Switzerland

Abstract:
It is well known that large scale bridging in delamination of layered composites is one of the most important toughening mechanisms. The increased resistance to fracture, however, is dependent on specimen geometry and microstructure rendering its modeling challenging. In this presentation, experimental results and modeling of fracture in layered composite specimens are discussed. The experimental work consists of monotonic and load-controlled fatigue tests of DCB specimens made of UD laminates. Selected specimens are equipped with wavelength multiplexed fiber Bragg grating (FBG) sensors to monitor crack propagation and strains over several millimeters in the wake of delamination. Modeling involves an iterative scheme to calculate traction-separation relations, due to bridging, using the strains from FBG sensors, parametric finite elements and optimization. The results demonstrate an important effect of specimen thickness in fracture response under monotonic and fatigue loads and allow deducing scaling relationships due to large scale bridging. The thickness dependent traction-separation relations are employed in cohesive zone simulations to predict very well the corresponding load-displacement and fracture resistance for several thicknesses. Large scale bridging in fatigue is also characterized using the same methodology and crack propagation is found independent of specimen thickness if bridging tractions are properly accounted for in terms of specimen thickness. To elucidate further the phenomenological response, computational micromechanics models are developed to predict specimen thickness effects on large scale bridging and delamination. Analysis shows that when traction-separation relation is enriched with the local crack opening angle, the obtained single traction-separation and angle relation is independent of geometry and predicts very well both load and fracture responses. Furthermore, micromechanics models demonstrate that matrix material and fiber distribution within the composite plies play the important roles in the extent of bridging.



Keywords: composites, delamination, large scale bridging, traction-separation, scale effects, crack opeing displacement, crack opening angle.

Figure 1: Traction-separation relation in delamination for five specimen thicknesses (insert) from the inverse identification technique based on strain data from FBG sensors and parametric FE. When the traction data are plotted against the product of opening δ and local angle φ, the curves collapse to one traction-separation and angle relation (the thinnest specimen deviates slightly due to geometrical non-linearity) [5].

References:

1. Manshadi B., Farmand-Ashtiani, E., Botsis, J., Vassilopoulos A. (2014), An iterative analytical/experimental study of bridging in delamination of the double cantilever beam specimen, *Composites Part A*, 61, 43-50.
2. Canal, L. P., Pappas, G. A., Botsis J. (2016), Large scale fiber bridging in mode I intralaminar fracture. An embedded cell approach, *Compos. Sci. Technol.*, 136, 52-59.
3. Farmand-Ashtiani, E., Cugnoni, J., Botsis J. (2016), Effects of large scale bridging in load controlled fatigue delamination of unidirectional carbon-epoxy specimens, *Compos. Sci. Technol.*, 137, 52-59.
4. Naya, F., Pappas, G. A., Botsis, J. (2019),Micromechanical study on the origin of fiber bridging under interlaminar and intralaminar mode I failure, *Compos. Struct.*, 210, 877-891.

5. Pappas, G. A., Botsis, J. (2020), Towards a geometry independent traction-separation and angle relation due to large scale bridging in DCB configuration, *Compos. Sci. Technol.*, 197, Article 108172.

Polymers 2024 Session I. B: Synthesis, Processing and Characterization

Synthesis of metal-free semiconducting polymers via organocatalysis: sustainable materials for renewable energies

L. Caponecchia [a,b,*], P.Y. Toullec[b], C. Brochon[a]
[a] LCPO, Université de Bordeaux, Bordeaux, France
[b] ISM, Université de Bordeaux, Bordeaux, France

Abstract:
Semi-conducting π-conjugated polymers are key organic materials for the development of green and low-cost optoelectronic devices [1] and for renewable energy production. Nowadays, such polymers are obtained through metal-based catalyzed cross-coupling routes and usually rely on complex protocols by resorting to costly and hardly removable catalysts. In addition, residual metal traces can affect performances, hence numerous and often tedious purification steps are required [2]. It is thus highly desirable to develop versatile, alternative synthetic approaches to semi-conducting polymers.
The aim of this work is to develop new synthetic methodologies for π-conjugated polymers in a "green" way using "metal-free" organocatalysis. Original polymers with aryl-vinylidene repeating units are targeted with the possibility to tune their optoelectronic properties, by playing on the planarity of the chain, the nature of the substituents, the stereo- and enantio-selection to use them as active materials in OPV cells. We focused on the synthesis of regio-/stereo-regular PPV-like polymers (Figure 1) obtained via hydroarylation reaction [3]. One of the key aspect of this project is to obtain these materials using a metal-free reaction; in fact, because of the presence of metals (that are at the most widely used polymerization reactions), their properties can be affected by the presence of metal residues that can act as recombination centers for both positive and negative charges. So, the use of a metal-free polymerization technique and the possibility of use bio-based monomers open to the possibility of getting 'greener' and purer materials for OPV devices.

Keywords: Conjugated polymers, semi-conducting polymers, energy production, optoelectronic devices, hydroarylation, metal-free polymerization, organocatalysis, renewable energies.

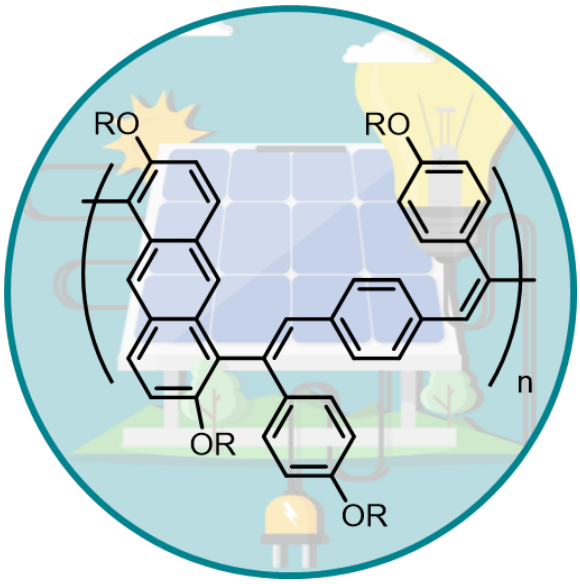


Figure 1: Figure illustrating the structure of one of the PPV-like polymers obtained via Brønsted acid organocatalysis.

References:

1. Facchetti A.; π-Conjugated Polymers for Organic Electronics and Photovoltaic Cell Applications; Chem. Mater. 2011, 23, 733–758 733
2. Ö. Usluer, M. Abbas, G. Wantz, L. Vignau, L. Hirsch, E. Grana, C. Brochon, E. Cloutet, and G. Hadziioannou; Metal Residues in Semiconducting Polymers: Impact on the Performance of Organic Electronic Devices; *ACS Macro Lett.* 2014, 3, 1134−1138.
3. Gicquiaud, J., Dhara, K., Karnat, A., Berlande, M., Hermange, P., Sotiropoulos, J. M., Toullec, P. Y.; Brønsted Acid-Catalyzed Enantioselective Cycloisomerization of Arylalkynes; *Chem. Eur. J.* 2020, 26, 16266–16271.

Fibrous Nanocomposites based on Polylactic acid filled with Fe_3O_4 Nanoparticles Produced by Solution Blow Spinning

N. Nikolić, D. Olmos and J. González-Benito
Department of Materials Science and Engineering and Chemical Engineering, Technological Institute of Chemistry and Materials, University Carlos III of Madrid (UC3M), Leganés, Spain

Abstract:
Some unique properties of nanocomposites usually arise from the nanoscopic character of at least one of their constituents. Perhaps those nanocomposites constituted by a polymer matrix and inorganic nanoparticles are receiving more attention nowadays. Among the nanoparticles, magnetic ones are a very interesting choice because they can provide active performance to the nanocomposites under the action of external magnetic fields. When preparing nanocomposites, one of the main challenges is achieving uniform nanoparticle dispersion within the matrix. During the last eight years, the Group of Polymer Composite Materials and Interphases of the UC3M have been working on the preparation of nanocomposites by solution blow spinning and it was demonstrated that to obtain relatively uniform dispersion of nanoparticles is possible.[1-3]

Solution blow spinning is based on the use of a concentric nozzle where a polymer solution or suspension is made to pass through the inner channel while pressurized air flows along the outer channel. At the exit of the nozzle, the gas exerts a force that causes a solution stretching while the solvent is evaporated. If processing conditions are adequate, thin fibers can finally be deposited on a collector. Figure 1 shows a representative image of the SBS device.

In the present work nanocomposites based on polylactic acid modified with magnetic nanoparticles (Fe_3O_4) were prepared by solution blow spinning. Concentration of nanoparticles (0.0, 0.5, 1.0, 2.0, 3.0, and 5.0 weight percent) in the final nanocomposite was chosen as the variable to prepare different materials. Morphological and structural characterization was carried out as preliminary studies to finally understand the performance of materials.

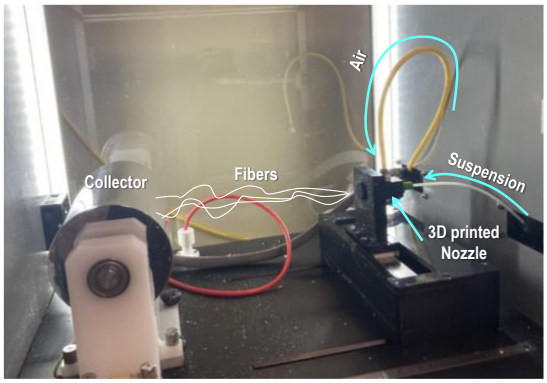


Figure 1. Representative image of the solution blow spinning device used to prepare fibrous nanocomposites.

Keywords: Solution Blow Spinning; Polylactic acid; magnetic nanoparticles; Fe_3O_4; Nanocomposites; nanofibers.

References:

1. Teno, J., Gorrasi, G., Sorrentino, A., González-Benito, J., (2019), Fibrous Nanocomposites Based on EVA40 Filled with Cu Nanoparticles and their Potential Antibacterial action, *Materials Today Communications*, 20, 100581.
2. González-Benito, J., Torres, D., Ballesteros, C., Ruiz, V.M., Teno, J., (2019), PVDF Based Nanocomposites Produced by Solution Blow Spinning, Structure and Morphology Induced by the Presence of MWCNT and their Consequences on Some Properties, *Colloid Polym. Sci.*, 297, 1105-1118.
3. J. González-Benito, J. Teno, G. González-Gaitano, S. Xu, M. Chiang, (2017), PVDF/TiO_2 Nanocomposites Prepared by Solution Blow Spinning: Surface Properties and their Relation with S. mutans Adhesion, *Polym. Test.*, 58, 21-30.

Exploring the Properties of Solution Blow Spun PLA/*Sargassum* Fibrillar Nanocomposite Materials as a Novel Approach for Sustainable Bioplastics

[1] N. Nikolić, [2]M. González-Hurtado, [2]A. Martínez-García, [1]J. González-Benito, [1] D. Olmos*
[1] Department of Materials Science and Engineering and Chemical Engineering, Technological Institute of Chemistry and Materials, University Carlos III of Madrid (UC3M), Leganés, Spain
[2] Instituto de Ciencia y Tecnología de los Materiales. IMRE. Universidad de la Habana, Cuba

Abstract:
In recent years, bioplastics have gained significant attention as an environmentally friendly alternative to traditional plastics. Among all the biodegradable polymers, polylactic acid (PLA) is a promising alternative. In response to the growing demand for eco-friendly products, researchers are currently exploring new possibilities to develop sustainable and innovative bioplastics. One approach to satisfy these needs is the development of polymer nanocomposite materials. Modification of bioplastics with natural materials such as those coming from algae is of interest in the field of sustainable materials. One example could be the incorporation of *Sargassum* in the form of nanofibers or nanoparticles within well-known bioplastics such as PLA to create composite materials with improved properties. Some potential benefits of using *Sargassum* or other natural materials in composites include reduced environmental impact, biodegradability, and the utilization of renewable resources. This study focuses on the preparation fibrillar materials based on commercial PLA filled with seaweed particles *(Sargassum)*. To produce the PLA/*Sargassum* fibrillar nanocomposites solution blow spinning was used. Over the past eight years, the Group of Polymer Composite Materials and Interphases of the UC3M has been investigating on the production of fibrillar polymers and polymer nanocomposite materials using Solution Blow Spinning (SBS).[1-3] The solution blow spinning technique employs a concentric nozzle, wherein a polymer solution or suspension is propelled through the inner channel while pressurized air is directed through the outer channel. At the exit of the nozzle, the pressurized air causes the solution to stretch and the solvent to evaporate. Under the correct processing conditions, this can lead to the formation of fine fibers that usually are collected on a cylindrical or plane substrate. In the present work nanocomposites based on polylactic acid (PLA) modified with sargassum algae particles were prepared by solution blow spinning. The concentration of sargassum particles was kept constant in the PLA and maintained to 10 % (wt/wt) in the final nanocomposite. The polymer concentration used in the solution was chosen as the variable to prepare different materials for which changes in the morphology are expected. Morphological and structural characterization was carried out as preliminary studies to finally understand the performance of materials in terms of active components realeasing. In Figure 1, an example of PLA/*Sargassum* the fibrillar materials is shown.

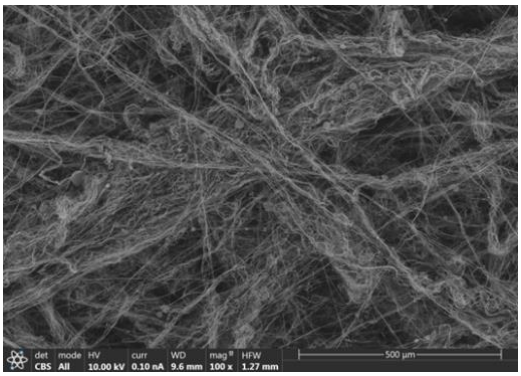


Figure 1. SEM image of the PLA/*Sargassum* fibrous nanocomposites.

Keywords: Polylactic Acid (PLA); *Sargassum*; Solution Blow Spinning; Nanocomposites; Nanofibers.

References:

1. Teno, J.; González-Gaitano, G.; González-Benito, J. Poly (ethylene-co-vinyl acetate) films prepared by solution blow spinning: Surface characterization and its relation with E. Coli adhesion (2017). *Polym. Test*. 60, 140–148.
2. González-Benito, J; Olmos, D., Teno, J., González-Gaitano, G. Nanomorphology and nanomechanical characteristics of solution-blow-spun PVDF-based fibers filled with carbon nanotubes. (2019). *J. Appl. Polym. Sci*. 136, 47115.
3. Ruiz V.M., Olmos, D., González-Benito, J. PVDF/MWCNT nanocomposites with complex configurations prepared by solution blow spinning and their flexoelectric responses. (2023). Polymer, 267, 125669.

Achieving high impact strengths for polyamide 6 by adjusting the grafting degree of ethylene/1-octene copolymers

A.K. Deeb [1,2,*], O. Neuß [2], S. Rathgeber [1]
[1] Physics Dept., Institute for Integrated Natural Sciences, University Koblenz, Koblenz, Germany
[2] AKRO-PLASTIC GmbH, Niederzissen, Germany

Abstract:
Owing to its high stiffness and strength, polyamide 6 (PA6) is commonly used in technical applications, such as in the automotive sector. However, its notch sensitivity restricts its usability. Melt blending of PA6 with ethylene/1-octene (EO) copolymers, reduces its notch sensitivity. To achieve adhesion between PA6 and EO and proper dispersion of the modifier particles in the matrix, maleic anhydride (MAH) is often grafted onto the copolymer's backbone using peroxide as initiator. The grafting degree (GD) increases with increasing amount of peroxide added, but at the same time the extent of side reactions, such as cross-linking and ß-scission also increases, consequently changing the molecular weight (MW) distribution of the modifier. ß-scission predominantly occurs at tertiary carbon atoms and thus dominates at high comonomer contents. Previous studies on various modifier-matrix systems showed that modifications of low modulus resulted in higher impact strengths and lower brittle-to-ductile transition temperatures (BDTT) of the compound compared to their high modulus counterparts. This was attributed to a lower glass transition temperature (T_g), thus higher deformability and consequently higher energy dissipation at low temperatures. Higher deformability and lower MW are furthermore believed to be beneficial for cavitation of the dispersed modifiers inducing shear yielding of the matrix. Instead of changing the comonomer content (CC) the modifier type was changed in these studies. No further attention was paid to the impact of modifier's MW on the impact strength of the compound. In addition, many studies suffer from the fact that by changing the modifier's properties also the compound's microstructure changed. However, it is known that the microstructure is crucial to induce shear yielding of the matrix, necessary to achieve high impact strength.
The current study therefore aims to systematically investigate the impact of the modifier's GD, MW and CC on the notched impact strength of the compound without changing the microstructure. Three EO with CC of 13, 15 and 16 mol.-% with comparable initial MW (low and high) were chosen and grafted with 0.5 and 1.0 % MAH, respectively. Their thermal and thermal-mechanical behaviour as well as their MW distribution were examined and correlated with the compound's notched impact strength. Higher CC lead to higher impact strengths in the brittle region, which is caused by the higher deformability, due to their lower T_g and onset of EO melting just above T_g. In the CC range investigated here the changes in T_g do not lead to a shift in BDTT at same MW. However, with increasing temperature the modifier's stability (strength) becomes more important. Thus, the impact strength of the compound is higher when a high-MW instead of low-MW EO is used. Furthermore, a lowered BDTT is achieved using high-MW EO. Due to ß-scission high GD and high CC are detrimental to achieving high impact strength at higher temperatures. By lowering the GD from 1.0 wt.-% to 0.5 wt.-%, MW reduction was decreased, while maintaining sufficient adhesion between PA6 and EO, leading to an improved impact strength over a wide temperature range (see Figure 1). In addition, reducing GD leads to a reduction in compound viscosity of about 10%, which is beneficial for the compound processability as well as energy- and cost-efficient manufacturing.
Finally, we utilized these results for the development of a binary EO/MAH-EO modifier system with effective reduced GD which was optimized in terms of core deformability and high shell strength leading to further improved impact strength of the compounds.

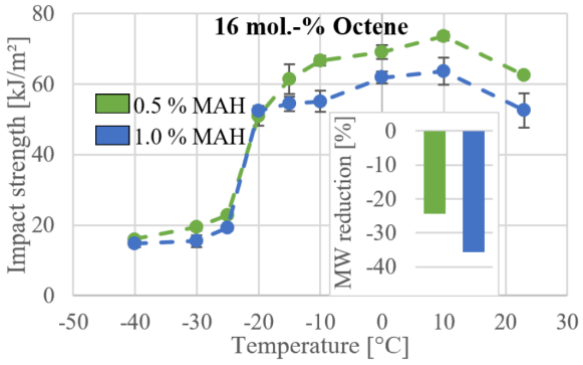


Figure 1: MW reduction and impact strength.

Keywords: Impact modification, polyamide, maleic anhydride grafted copolymers, ethylene/1-octene, molecular weight, comonomer content, grafting degree, automotive.

Analyzing the Influence of Color Masterbatch in the Injection Molding of Post-Industrial Plastic Waste

M. Pöttinger [1,*], C. Marschik [1], K. Straka[2], K. Fellner[3] and G. Steinbichler[2]
[1] Competence Center CHASE GmbH, Hafenstraße 47-51, 4020 Linz, Austria
[2] Institute of Polymer Injection Moulding and Process Automation, JKU - Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz, Austria
[3]ENGEL AUSTRIA GmbH, Ludwig-Engel-Straße 1, 4311 Schwertberg, Austria

Abstract:
In injection molding, achieving a uniform color is essential for ensuring product quality. While reaching this goal is already a challenge when using virgin polymers, it becomes even more complex when processing recycled plastic waste. These materials typically show different levels of contamination and can thus affect the optical properties of the injection molded part. One approach to maintaining a constant product color despite inhomogeneous input materials is to add color masterbatch.
In this work, we experimentally investigate the influence of masterbatch on the product color of injection molded parts. To this end, discs were produced using mixtures of color masterbatch, virgin and recycled materials. The latter was obtained by shredding inhouse production waste of lower and higher color concentration including startup waste, scrap, and runners. Using the single-stage injection molding process in Figure 1, plastic flakes were directly processed without the intermediate step of regranulation. The process involved a robot arm removing the part from the mold and transferring it to a photobox equipped with two inline sensors for color and temperature measurements. The photobox, which was positioned directly over a conveyor belt, helped to shield ambient light, thereby guarantying constant light conditions during color measurements. By systematically varying the masterbatch concentration in the input material, the goal was to determine the minimal content required for achieving a defined reference color derived from discs made from virgin material and 2 wt% of masterbatch.
Our experiments demonstrate the potential for masterbatch savings through using recycled material. Using an inline color sensor further allowed us to adjust the masterbatch content in the process, as the color of each injection molded part is measured inline in real time. The data generated provides the basis for an automated masterbatch control system.

Keywords: injection molding, plastic recycling, inline measurement, process analysis, automation, optical properties, color.

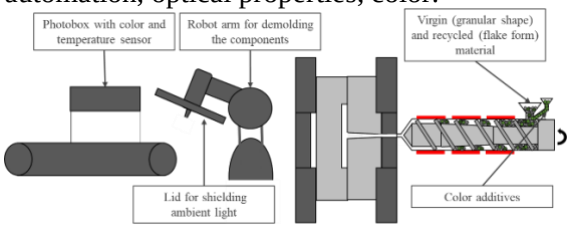


Figure 1: Schematic representation of the inline color measurement of the injection molded part consisting of virgin and recycled plastic material.

References:

1. Agate, S., Williams, A., Dougherty, J., Velev, O.D., Pal, L. (2023) Polymer Color Intelligence: Effect of Materials, Instruments, and Measurement Techniques − A Review, *Int. J. ACS Omega*, 8, 23257-23270.
2. Eriksen, M.K., Christiansen, J.D., Daugaard, A.E., Astrup, T.F. (2019), Closing the loop for PET, PE and PP waste from households: Influence of material properties and product design for plastic recycling, *Int. J. Waste Management*, 96, 75-85.
3. Botos, J., Murail, N., Heidemeyer, P. (2014), Color measurement of plastics – From compounding via pelletizing, up to injection molding and extrusion, *AIP Conf. Proc.*, 1593, 16–19

Advancing Free Radical Photopolymerization (FRP) and 3D Printing: Exploiting the Potential of Novel Ni(II) Complexes bearing NHC ligands as photocatalysts

N. Martins Pesqueira [1*], C. Bignardi [1], V. P. Carvalho-Jr [1], B. Eleutério Goi [1], J. Lalevée [2,3]
[1]Department of Chemistry and Biochemistry, São Paulo State University (UNESP), Presidente Prudente, Brazil
[2]Université de Haute-Alsace, CNRS, IS2M UMR 7361, Mulhouse, France
[3]Université de Strasbourg, Strasbourg

Abstract:
Recently, the utilization of organometallic compounds as photocatalysts (PC) in photoredox catalysis processes has introduced significant possibilities for exploring radical and cationic polymerization. A PC is required to possess at least one photosensitive function, such as a chromophore, to absorb light (photons). This absorption facilitates the generation of active species, including radicals and cations, capable of initiating the photopolymerization reaction.[1] Different chemical mechanisms can be involved in this reaction, both oxidation and reduction reactions can be possible and light is used to generate PC excited states (PC*) which allow more favorable electron transfer processes with additives than their ground states. Moreover, light plays a crucial role in exciting the PCs, enabling electron transfer processes with additives like iodonium salt (Iod) and amine (EDB), for instance (Figure 1). The free radical photopolymerizations (FRP) of ethoxylated trimethylolpropane triacrylate (TMPETA) were conducted using laminates incorporating Ni(II) complexes as photocatalysts, Ni^{II}/Iod/EDB (Figure 1), and a LED emitting at 405 nm. The novel developed nickel complexes ([NiC(NHC-py)$_2$] or [NiC(NHC-ph)$_2$]) were dissolved in the monomer along with Iod and EDB to prepare the formulations. Their weight content ratios in the monomer were as follows: 0.1%/1%/1% w/w/w, 0.2%/2%/2% w/w/w, and 0.2%/1%/1% w/w/w, respectively. The obtained formulations were deposited under air (using pallet) and in laminate (between two polypropylene films to reduce the O_2 inhibition). Throughout the photopolymerization process, the evolution of the C=C peak was monitored in real time by FTIR around 6180 cm^{-1}. To demonstrate the effectiveness of the three-component systems, two-component photoinitiator systems (PIS) with a ratio of Iod:EDB = 1%:1% and 2%:2% (w/w) were employed as references. In the case of Ni(II) complexes, achieving final acrylate function conversions in the range of 70% to 97% was possible in thin films under LED irradiation at 405 nm. However, the best system was in the presence of 0.2%/2%/2%, Ni/Iod/EDB, respectively, obtaining conversions > 97 % in laminate. These conversions were notably higher compared to those obtained with the reference EDB/Iod two-component system (around 65%). Furthermore, it was observed that [NiC(NHC-ph)$_2$] exhibited higher monomer conversions in less than 300 seconds of irradiation. In the context of free radical photopolymerization (FRP) under LED irradiation at 405 nm, [NiC(NHC-ph)$_2$] was better than the [NiC(NHC-py)$_2$] in all conditions due to higher light absorption property, specifically higher extinction coefficients at 405 nm. Interestly, other ratios of photocatalyst/Iod/EDB have been performed to evaluate the photopolymerization using the most efficient photoinitiator systems in the photocontrol of homopolymerization and applied in 3D printing and direct laser write (DLW) experiments.

Keywords: organometallic, nickel, NHC ligand, photopolymerization, photocatalyst, 3D printing.

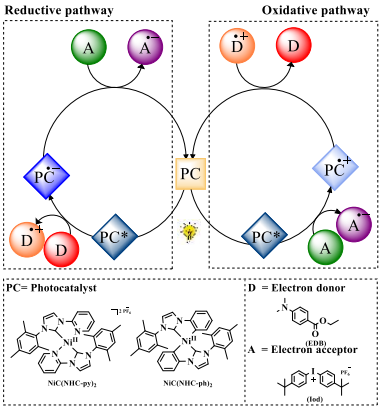


Figure 1: Reductive and oxidative photoredox catalytic cycles, photocatalysts of Ni(II) and additives.

References:

1. Lalevée J, Telitel S, Xiao P, Lepeltier M, Dumur F, Morlet-Savary F, et al. Metal and metal-free photocatalysts: Mechanistic approach and application as photoinitiators of photopolymerization. Beilstein Journal of Organic Chemistry. 2014 Apr 15;10:863–76.

Photocatalytic degradation of methylene blue dye using a visible active photocatalyst immobilized on polypropylene films

Olga Sacco[1*], Raffaella Rescigno[1], Stefania Pragliola [1], Vincenzo Vaiano[2] and Vincenzo Venditto[1]
[1] Department of Chemistry and Biology "A. Zambelli" and INSTM Research Unit, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy *osacco@unisa.it
[2] Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy

Abstract:
Heterogeneous photocatalysis using TiO_2 semiconductor can be applied in various fields, such as air purification, self-cleaning devices, water disinfection, and wastewater treatment[1]. Unfortunately, TiO_2 can be activated only by UV light.
To overcome this disadvantage and enhance the TiO_2 visible light absorption properties, different strategies including doping with metal and/or non-metal elements were adopted. Indeed, the doping procedure is able to generate defects in the semiconductor lattice and decrease the band-gap energy, increasing the photocatalytic efficiency[2]. However, most visible-light active photocatalysts for water and wastewater treatment were used in powder form in slurry photoreactors. This aspect still prevents the development of photocatalytic systems on an industrial scale as it is necessary the separation of photocatalysts in powder from the treated water[3].
Various substrates were used to support TiO_2-based photocatalysts, among which polypropylene is very interesting, because it is chemically inert, cheap and easily available[4].
In this work, P-doped TiO_2 (P-TiO_2) photocatalyst was prepared by a modified sol-gel method at room temperature and then coated on polypropylene films (P-TiO_2/PP).
The physical-chemical properties of the obtained films were investigated with different techniques (XRD, SEM and SSA) and the photocatalytic activity under visible light was assessed in the degradation of methylene blue (MB). The photocatalytic tests were carried out in a batch photoreactor irradiated by a visible lamp (nominal power of 8 W and wavelength emission higher than 400 nm).
The XRD analysis of P-TiO_2/PP evidenced the presence of P-TiO_2 in anatase phase. Moreover SEM-EDX analyses further confirmed the presence of P-TiO_2 particles anchored on the PP surface.
Photocatalytic activity results under visible light evidenced that MB discoloration was 63 % after 240 min of irradiation time. In contrast a PP film functionalized with commercial TiO_2 (Degussa P25) did not shown any photocatalytic activity under visible light.

Keywords: visible light, photocatalysis, P-doped TiO_2, polymeric films, polypropylene, dye, degradation.

References:

1. Pelaez M., Nolan N.T., Pillai S. C., Seery M. K., Falaras P., Kontos A.G., Dunlop P.S.M., et al. (2012), «A Review on the Visible Light Active Titanium Dioxide Photocatalysts for Environmental Applications». Applied Catalysis B: Environmental 125,331–49.
2. Sacco O., Sannino D., Matarangolo M., Vaiano V. (2019), «Room Temperature Synthesis of V-Doped TiO_2 and Its Photocatalytic Activity in the Removal of Caffeine under UV Irradiation», Materials, 12 (6), 911.
3. Krýsa J., Waldner G., Měšťánková H., Jirkovský J., Grabner G., (2006), «Photocatalytic Degradation of Model Organic Pollutants on an Immobilized Particulate TiO_2 Layer», Applied Catalysis B: Environmental 64 (3–4), 290–301.
4. Sacco O., Venditto V., Fittipaldi R., Vaiano V., Daniel C. (2021), «Composite Polymeric Films with Photocatalytic Properties». Chemical Engineering Transactions 86, 571–76.

Photoreactive polymer composites based on visible-light active photocatalysts for selective benzene hydroxylation to phenol

Antonietta Mancuso[1*], Olga Sacco[2], Vincenzo Venditto[2], Vincenzo Vaiano[1]
[1]University of Salerno, Departmentof Industrial Engineering, Via Giovanni Paolo II, 132, 84084 Fisciano (SA)
[2]University of Salerno, Department of Chemistry and Biology "A. Zambelli", Via Giovanni Paolo II, 132, 84084 Fisciano (SA)
*anmancuso@unisa.it

Abstract:
Phenol is widely employed as a precursor for the production of resin plastics and drugs and a main reagent in various chemical syntheses[1]. Currently, the phenol industrial production provides a multi-step cumene process, which is energy consuming due to high temperature and high pressure with generation of the highly explosive cumene hydroperoxide[2,3]. To overcome these disadvantages, it would be essential to find efficient and environmentally benign alternatives for the synthesis of phenol. Heterogeneous photocatalysis represents a promising technology for the phenol production based on semiconducting material activated by a suitable light source at room temperature and pressure [4]. In this work, photoreactive polymer composites based on visible-light active photocatalysts (N-TiO_2 and Fe-N-TiO_2) embedded into the monolithic syndiotactic polystyrene aerogels (N-TiO_2/sPS and Fe-N-TiO_2/sPS) are used to test the photocatalytic hydroxylation of benzene to phenol in presence of H_2O_2 as oxidant. The photocatalytic reactions are performed in aqueous solution containing benzene and acetonitrile (as a co-solvent) with 0.1 g/L of photocatalyst in powder form or 3 g/L of composite aerogel under continuous stirring. Solution aliquots are withdrawn from the reactor at different times and then analyzed by a gas cromatograph to evaluate the benzene and phenol concentration and also by HPLC to determine quantitatively by-products. The visible-driven experimental tests evidence that with N-TiO_2 powder and N-TiO_2/sPS aerogel, benzene conversion was about 62 and 72%, respectively, while phenol is not produced using N-TiO_2 and a phenol yield of only 6.5% is obtained using N-TiO_2/sPS. Similar result was observed in presence of Fe-N-TiO_2 photocatalyst and Fe-N-TiO_2/sPS aerogel. Notably, no phenol formation with Fe-N-TiO_2 was observed while it is promoted with Fe-N-TiO_2/sPS (phenol yield of 14%). In particular, the benzene conversion with Fe-N-TiO_2 powder and Fe-N-TiO_2/sPS aerogel increases from 30 to 80 %. This result can be explained on the basis of the different affinity of benzene (a non-polar compound) and phenol (a polar compound) with sPS aerogel (a non-polar polymer). Indeed, the benzene solubility in the sPS polymer is six times more than the phenol one. Therefore, the phenol obtained by hydroxylation of benzene with N-TiO_2 and Fe-N-TiO_2 photocatalyst dispersed in the sPS matrix, is easily desorbed from the polymer, preventing the over-oxidation reactions and thus ensuring a higher phenol yield.

Keywords: photocatalysis, visible light, syndiotactic polystirene, monolythic composite aerogel, N-TiO_2/sPS, Fe-N-TiO_2/sPS, benzene hydroxylation, phenol yield .

References:

1. T. Takeichi, N. Furukawa, (2012) Epoxy resins and phenol-formaldehyde resins, Polymer Science: A Comprehensive Reference 5, 723-751.
2. V. Zakoshansky, (2007) The cumene process for phenol-acetone production, Petroleum Chemistry, 47, 273-284.
3. G.D. Yadav, N.S. Asthana, (2003) Selective decomposition of cumene hydroperoxide into phenol and acetone by a novel cesium substituted heteropolyacid on clay, Applied Catalysis A: General, 244, 341-357.
4. L. Xiong, J. Tang, (2021) Strategies and challenges on selectivity of photocatalytic oxidation of organic substances, Advanced Energy Materials, 11, 2003216

Core-skin morphology analysis of calendered isotactic polypropylene (iPP) foils

M. Mihelčič [1], Miroslav Huskić [2] and Lidija Slemenik Perše [1*]
[1] Faculty of Mechanical Engineering, University of Ljubljana, Aškerčeva Ulica 6, 1000 Ljubljana, Slovenia
[2] Faculty of Polymer Technology, Ozare 19, 2380 Slovenj Gradec, Slovenia

Abstract:
For the packaging industry, isotactic polypropylene (iPP) is one of the most widely used polymers, which is gaining importance due to the favourable combination of cost and performance and the possibility of extending its range of properties by modification. Many technologically relevant properties of iPP, such as optical transparency, stiffness, stability, shrinkage, hardness, and elasticity, apart from its composition, are related to its crystalline microstructure which is closely related to the processing methods and manufacturing conditions [1].
The calendering process is mainly used in the production of foils in the packaging industry, where the polymer melt is extruded onto rotating rollers that form a foil. It is known that iPP is extremely sensitive to the conditions during its processing and can therefore form different morphologies. The skin-core structure of the foil is formed by rapid cooling of a thin upper part of the skin as opposed to the core, where more relaxed conditions and a longer cooling rate enable the polymer chains to relax and growth of spherulites is possible. The transition region between the thin skin and the core includes an oriented and crystalline structure, which is different from the large and isotropic spherulitic structure of the core. Due to the shear flow, the crystallisation kinetics in the skin is enhanced and leads to the transition from the spherulitic to the shish-kebab morphology [2].
The skin-core microstructure inevitably affects the mechanical and optical properties of the polymers, which emphasises the relevance of studying skin-core structures in terms of the corresponding degrees of crystallinity. Due to the anisotropy of the iPP polymer, the focus of the presented research is on understanding how processing parameters affect the formation of skin-core morphology in calendered iPP films, where processing conditions are much milder than in (micro)injection moulding.
Our objective was to demonstrate the correlation between the surface and core crystallinity of calendered iPP foils produced on an industrial calendering machine. The processing factors, such as processing temperature, roller speed, roller temperature, and the addition of various additives or recycled PP [3] have a significant effect on the processing quality of calendered iPP foils. Therefore, the physical and morphological properties on the macro and micro/nano scales were investigated.
The skin-core microstructure of iPP polymer foils was investigated using polarised optical microscopy (POM), as this allows the skin-core morphology to be determined quickly and efficiently (Fig. 1). The degree of crystallinity was determined by differential scanning calorimetry (DSC) and flash DSC, while the mechanical properties were determined by nanoindentation.

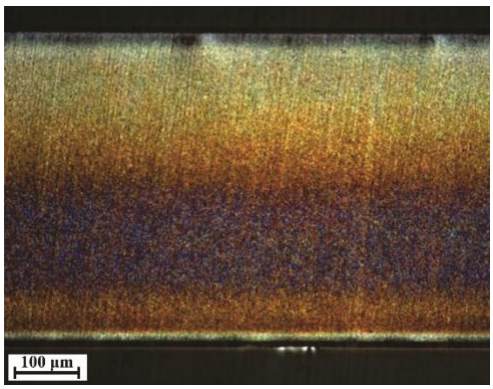


Figure 1: Polarized optical microscopic image of of cross-section of the iPP foil.

References:

1. Housmans, J. W., et al. (2009) Structure–property relations in molded, nucleated isotactic polypropylene, *Polymer*, **50**, 2304–2319,
2. Kumaraswamy, G., Kornfield, J. A., Yeh, F. and Hsiao, B. S. (2002) Shear-Enhanced Crystallization in Isotactic Polypropylene. 3. Evidence for a Kinetic Pathway to Nucleation, *Macromolecules*, 35, 1762–1769
3. MIHELČIČ, M., et al. (2022) Influence of stabilization additive on rheological, thermal and mechanical properties of recycled polypropylene, *Polymers*, 14, 5438.

Ammonia triggered self-healing of an ozone cracked high strength ionomeric elastomer

Srikanth Billa,[1*] Sangram K Rath,[1]
[1]Polymer Division, Naval Materials Research Laboratory, Ambernath, Maharashtra 421506, India
Corresponding author email: srheeb91@gmail.com

Abstract:
Ionomers are known to exhibit thermally activated self-healing by virtue of the thermoreversibility of their ionic associations. However, the upper bound of the extent of their self-healing shares a trade-off relationship with their initial strengths, as is the case with all classes of polymers. In the present study, we report a remarkable 100 % self-healing efficiency for an Ozone cracked ionically cross-linked carboxylated nitrile rubber (XNBR) having an initial strength of 23 MPa. This was accomplished by a two-step process of ex-situ ammonia vapor exposure of the vulcanizates followed by thermal activation. Fourier Transform Infrared Spectroscopy (FTIR) was used to delineate the ammonia induced alterations in the ionic associations and phase morphology of the cross-linked elastomers. Dynamic mechanical analysis (DMA) was used to understand the modified segmental dynamics of the networks upon exposure to ammonia. These studies together provided mechanistic insights into the remarkable healing ability of the robust commercially used ionomeric elastomers. The thermo-reversibility of ammonia induced altered ionic associations and phase morphology is proposed as the mechanistic origins of the observed self-healing of the high strength ionomeric elastomers. We posit that this approach is a new and effective addition to the field of self- healing chemistries.
Key Words: Self-healing, ionomeric elastomer, XNBR, ammonia vapor

References:

1. Yang, Ying, and Marek W. Urban. "Self-healing polymeric materials." Chemical Society Reviews 42.17 (2013): 7446-7467.
2. Li, B., Cao, P. F., Saito, T., & Sokolov, A. P. (2022). Intrinsically Self-Healing Polymers: From Mechanistic Insight to Current Challenges. Chemical Reviews.
3. Hohlbein, N., Shaaban, A., Bras, A. R., Pyckhout-Hintzen, W., & Schmidt, A. M. (2015). Self-healing dynamic bond-based rubbers: understanding the mechanisms in ionomeric elastomer model systems. Physical Chemistry Chemical Physics, 17(32), 21005- 00n bc 21017.

Numerical Simulation of Thermal Frontal Polymerization in Polymer Composites: The Role of Nanoparticle Fillers

M.Lang [1,*], C.Schmidleitner [1,2], P.Fuchs [1], E.Rossegger [1]
[1] Polymer Competence Center Leoben GmbH (PCCL), Sauraugasse 1, 8700 Leoben, Austria
[2] Institute for Chemistry and Technology of Materials, University of Technology of Graz, NAWI Graz, Stremayrgasse 9, 8010 Graz

Abstract:
Given the global priority of sustainability and waste reduction, polymer composites play an important role in enabling high-performance, light-weight structures and increasing product lifespans by decades due to corrosion resistance and durability. At the same time, innovative curing and polymerization processes must exhibit improved efficiencies and reduced environmental impact. In this context, frontal polymerization (FP) has emerged as a low-energy alternative that enables rapid and energy-efficient manufacturing of composites compared to conventional processes, thus providing a promising strategy to address sustainability challenges [1].

FP is a self-driven cure process, where an initial stimulus (e.g., thermal or photo) induces a localized reaction zone, the so-called "polymerization front", which can propagate through the entire system without requiring further energy input (see Figure 1) [2].

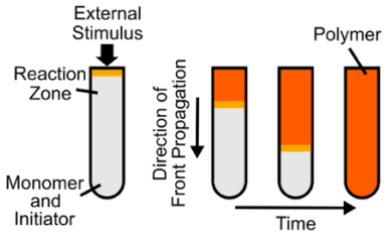


Figure 1: Schematic representation of the FP reaction technique.

Successful FP requires a delicate balance of reaction rates, exothermicity, and efficient heat transport into unpolymerized media while minimizing losses to the surroundings, see Figure 2. A substantial heat loss to the surroundings is expected to affect the key characteristics of the polymerization front.
In this context, sustaining FP in composites, using highly thermally conductive fillers, is challenging due to the increased energy dissipation and reduced availability of exothermic energy as the volume fraction of the resin decreases with increasing filler content [3].
In this work, a numerical study ,focusing on the thermal FP-based manufacturing of bisphenol A diglycidyl ether (BADGE) filled with Fe_3O_4 nanoparticles, is presented. The simulation provides insight into the thermo-chemical process and into the impact of different particle filling degrees on the key characteristics of thermal frontal polymerization (i.e., maximum attainable degree of cure, maximum temperature, front shape, and front speed).

Keywords: thermal frontal polymerization, polymer composites, nanoparticle fillers, polymerization front, heat loss

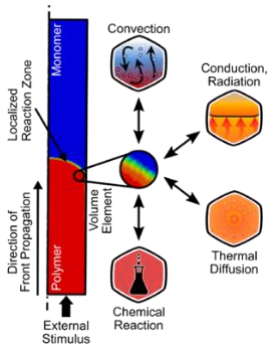


Figure 2: Heat conservation for a control volume across the front in a FP reaction.

References:

1. Robertson, I. D., Yourdkhani, M., Centellas, P. J., Aw, J. E., Ivanoff, D. G., Goli, E., ... & White, S. R. (2018). Rapid energy-efficient manufacturing of polymers and composites via frontal polymerization. *Nature*, *557*(7704), 223-227.
2. Centellas, P., Garg, M., Chen, Z., Zhang, X., Parikh, N., Geubelle, P., & Sottos, N. (2023). Energy-efficient manufacturing of multifunctional vascularized composites. *Journal of composite materials*, *57*(4), 581-592.
3. Zhang, Z., Liu, R., Li, W., Liu, Y., Pei, Z., Qiu, J., & Wang, S. (2021). Frontal polymerization-assisted 3D printing of short carbon fibers/dicyclopentadiene composites. *Journal of Manufacturing Processes*, *71*, 753-762.

Challenges and solutions to assess the real true stress – true strain response of pure and recycled polymers under large strains

P. Hao [1,*], C. Siebers [2], K. Ragaert [2], F. A. Gilabert [1]

[1] Department of Materials, Textiles and Chemical Engineering (MaTCh), Mechanics of Materials and Structures (MMS), Ghent University, Technologiepark Zwijnaarde 46, 9052, Zwijnaarde, Belgium
[2] Circular Plastics, Department of Circular Chemical Engineering, Faculty of Science and Engineering, Maastricht University, 6162 AL Geleen, The Netherlands

Abstract:
The aim of this work is to create robust characterization techniques to guide the design of high-quality recycled plastics. The intricate task of obtaining the thermomechanical responses of pure and blended thermoplastics is addressed. In this study, blow molding and injection molding grades of HDPE (F4520) and PP (576P) were provided by SABIC, The Netherlands. A blend with 10 wt% 576P was compounded. Tensile tests equipped with a high-speed 3D stereo Digital Image Correlation (DIC) system and an infrared camera (Figure 1) were conducted adopting ISO-527/1A dog-bone specimen. However, the 'necking' effects arising from geometric nonlinearity in the specimen contribute to the nuanced characterization of tensile behavior. This is particularly relevant for highly stretchable polymers. Current approaches to determining strains in these materials do not provide a reliable measure that can be confidently used in modeling and simulation frameworks which require an accurate constitutive response of the polymer.

Polymers are widely recognized for their rate- and temperature-dependence [1, 2]. Additionally, self-heating and thermal softening are phenomena often observed at medium and high loading speeds. Building on this understanding, a consistent polymer model has been recently developed, tailored for a range of thermosets and thermoplastics [2]. This model effectively characterizes the complex yielding kinematic mechanisms in both pure and blended polymers. By employing a hybrid experimental-numerical approach, the model accurately captures the true thermomechanical response of these materials, demonstrating its utility in addressing the challenges associated with necking effects. This approach successfully tracks the dynamic yielding process in polymers, mapping local strain and temperature fields in detail. Unlike current approaches in literature, the proposed strategy confidently identifies the intrinsic response of polymers regardless factors like the size of the Digital Image Correlation (DIC) window or the dimensions of the specimen. This process is crucial for employing advanced simulation techniques in the design and application of recycled polymers. The aim is to achieve performance comparable to that of pure materials, thus enhancing the viability of recycled polymers.

Keywords: thermoplastics, recycled plastics, thermomechanical behavior, necking, FEM, self-heating.

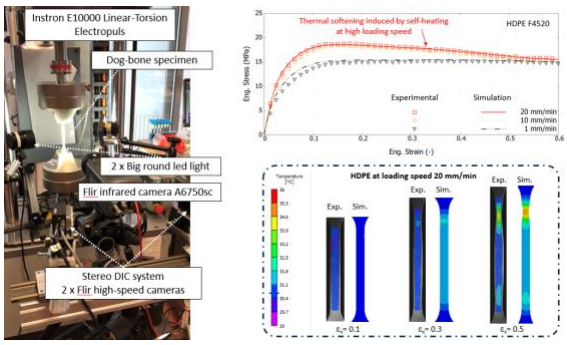


Figure 1: Instron Electropuls tensile experiment set-up using 3D stereo DIC system combined with IR camera (left) and comparison of engineering stress-stress response between experimental and simulation results along with local temperature fields at different instances (right).

References:

1. Poulain, X., Kohlman, L. W., Binienda, W., Roberts, G. D., Goldberg, R. K., Benzerga, A. A. (2013) Determination of the intrinsic behavior of polymers using digital image correlation combined with video-monitored testing, *Int. J. Solids Struct.*, 50, 1869-1878.
2. Hao, P., Dai, Z., Laheri, V., Gilabert, F. A. (2022), A unified amorphous–crystalline viscoplastic hardening law for non-isothermal modelling of thermoplastics and thermosets, *Int. J. Plast.*, 159, 103469.

Composites Session I. C: Synthesis, Processing and Characterization

Electrofluids: liquid composites as soft electrical components

Lola González-García[1,2]

[1]INM-Leibniz Institute for New Materials, Campus D2 2, 66123 – Saarbrücken, Germany
[2]Department of Materials Science and Engineering, Saarland University, Campus D2 2, 66123, Saarbrücken, Germany

Abstract

Liquid metals, printed conductive structures, or composites are today the alternatives to the classical stiff electronic components for wearables and soft robots. Here, we introduce a new concept: "Electrofluids", that consists of liquid composites of conductive (carbon- or metal-based) particles suspended in solvents with different polarity and viscosity, which conduct electricity while flowing. As in classical solid, conductive composites, electrical conductivity is ensured through the 3D percolative networks of the solid fillers. Here, however, the contacts between the particles are transient, so they can move in the liquid and rearrange under mechanical stress preserving the electrical conductivity of the material. This kind of materials allows for tailored rheoelectrical properties and find one of the niches of application in soft-robotics and wearables.

We will show how the rheoelectrical properties of the liquid composites strongly depend on a) the polarity of the solvent matrix, b) its viscosity, and c) the shape of the particles used as conductive fillers. We also tested the electrical response to uniaxial strain of electrofluids encapsulated in elastomeric tubes as a previous step for their device integration. We found out the gauge factor of the material to be dependent on the volume fraction of the filler and the matrix employed. We will exploit this behavior and discuss the use of these materials to create soft strain sensors and conductive interconnects.

Integration of electrofluids for sensor applications using 3D printing

Niclas Hautz[1,*], Dominik S. Schmidt[1], Srishti Arora[1], Sergio Lago-Garrido[1], Lola González-García [1,2]
[1] INM – Leibniz Institute for New Materials, Saarland University, 66123 Saarbrücken, Germany
[2] Department of Materials Science and Engineering, Saarland University, Campus D2 2, 66123 Saarbrücken, Germany

Abstract:
The term electrofluids is used to describe liquid composites, in which a conductive filler component forms a mechanical and an electrical network. Variations between the filler and the matrix material enable a wide range in their electrical and mechanical properties. As the filler remains suspended in the liquid matrix, the dynamic transient contacts determine the electrical response. Electrofluids have the advantage of realizing truly soft and streachable components due to their fluid or gel-like behaviour.

Here, we use different filler particle types ranging from fractals (carbon black) to sheet/flake like fillers (graphene) in combination with various polar and non-polar solvents. This allow us to create electrofluids with different unique mechanoelectrical properties. For each sample, the filler concentration was chosen to be above the percolation threshold, to ensure the formation of an electrical network.

In order to use electrofluids they have to be encapsulated. We use 3D printing to created reproducable, well-defined structures. Here, we distinguish two main processes: the printing "onto", in which the electrofluid is printed on a substrate and afterwards is covered with additional encapsulation material; and the printing "into" process, in which the electrofluid is directly printed in the uncured encapsulant. We will discuss that in both cases, the mechanical properties of the electrofluid and the encapsulant play a crucial role.

While most rheological measurements provide insights in the linear viscoelastic (LVE) region only the non-linearaties arising in the sample during 3D printing cannot be described by the linear viscoelastic moduli, as the non-linear material stress response is not a single harmonic sinusoid[1]. Therefore, the material behaviour in the large amplitude oscillatory shear (LAOS) region is of interest. Fourier-Transform (FT) rheology is a promising analysis method to obtain information in the LAOS region[2]. We carry out FT rheology on our electrofluids and use it to evaluate standard parameters like yield and flow point.

Based on these parameters printability maps are generated following the methods discussed in literature[2,3].

Finally, we demonstrate the potential of electrofluids as electric components and fabricate strain gauges using 3D printing.

Keywords: electrofluids, liquid composites, conductive suspensions, additive manufacturing, 3D printing, FT rheology, mechanoelectrical properties.

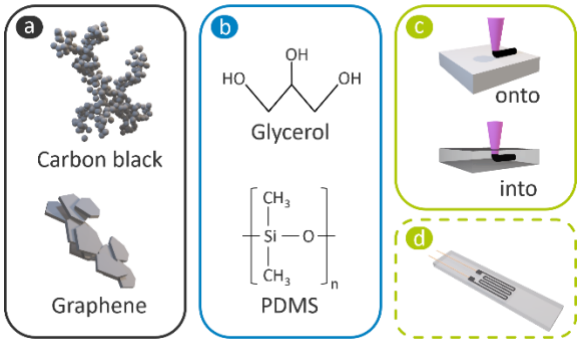


Figure 1: Comparison of different filler particles (a) and solvents (b). Scheme of the printing "onto" and "into" processes (c) and sketch of a printed stain gauge (d).

References:

1. Ewoldt, Randy H., A. E. Hosoi, and Gareth H. McKinley. "New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear." Journal of Rheology 52.6 (2008): 1427-1458.
2. García-Tuñón, Esther, et al. "Fourier-transform rheology and printability maps of complex fluids for three-dimensional printing." Physics of Fluids 35.1 (2023).
3. Corker, Andrew, et al. "3D printing with 2D colloids: Designing rheology protocols to predict 'printability'of soft-materials." Soft Matter 15.6 (2019): 1444-1456.

Cross-linking reaction of bio-based epoxy systems: a study on cure Kinetics

Pietro Di Matteo[a*], Andrea Iadarola[b], Valentina Brunella[a], Raffaele Ciardiello[b], Davide Salvatore Paolino[b], Francesco Gazza[c], Vito Guido Lambertini[c]

[a]Department of Chemistry, Università degli Studi di Torino, Via Pietro Giuria 7, Turin 10125, Italy.
[b]Department of Mechanical and Aerospace Engineering, Politecnico di Torino, C.so Duca degli Abruzzi 24, Turin 10039, Italy.
[c] Material Sustainability Engineering Department, Centro Ricerche Fiat (Stellantis), C.so Giovanni Agnelli 220, Turin 10135, Italy

Abstract:
The cure kinetic of various epoxy-novolac resin mixtures, by comprising a bisphenol epoxy, two novolac epoxy modifiers and two hardening agents, were investigated through non-isothermal differential scanning calorimetry (DSC) experiments. The development of these mixtures aimed to achieve an epoxy material with a substantial bio-based content, up to 50% in alignment with the 2050 climate neutrality objectives outlined in European Regulation (EU) 2019/631, for potential automotive applications. Friedman isoconversional method was employed to determine key kinetic parameters, such as activation energy and pre-exponential factor, providing valuable insights into the cross-linking process. Kamal Sourour model exhibited the most accurate fit for describing and predicting the kinetics of the chemical reaction. This empirical approach was employed to forecast the curing process for the specific oven curing cycle utilized. Moreover, tensile tests were carried out for evaluating tensile properties revealing promising results showcasing materials viability against conventional counterparts.
Looking ahead, future developments will focus on the integration of natural fibres, such as flax fibres, into the epoxy matrices to improve mechanical properties while further increasing the overall bio content of composites.
Overall, this investigation provides a comprehensive understanding of the cure kinetics, mechanical behaviour and thermal properties of the novel epoxy-novolac resins. These findings contribute to the development of high-performance epoxy materials with enhanced bio-based content for sustainable automotive applications.

Keywords: epoxy resin, bio-based, kinetic analysis, activation energy, curing, differential scanning calorimetry, tensile test.

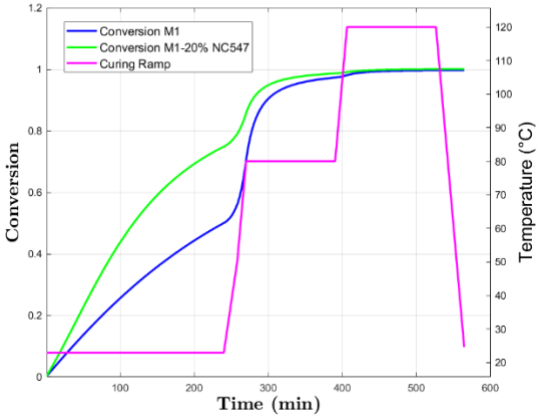


Figure 1: Kamal-Sourour model prediction for the curing cycle used for the production of bio-based epoxy resins.

References:

1. FLAMMERSHEIM, Hans-Jürgen; OPFERMANN, Johannes R. Investigation of epoxide curing reactions by differential scanning calorimetry–formal kinetic evaluation. *Macromolecular materials and engineering*, 2001, 286.3: 143-150.
2. VYAZOVKIN, Sergey, et al. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochimica acta*, 2011, 520.1-2: 1-19.
3. OZAWA, Takeo. A new method of analyzing thermogravimetric data. *Bulletin of the chemical society of Japan*, 1965, 38.11: 1881-1886.
4. VYAZOVKIN, Sergey; KOGA, Nobuyoshi; SCHICK, Christoph. Handbook of thermal analysis and calorimetry: recent advances, techniques and applications. 2018.

Pt/WO_3 Nanoparticle-Dispersed Polydimethylsiloxane Membranes for Transparent and Flexible Hydrogen Gas Leakage Sensors

Ryo Ishihara[1*], Yoshihiro Makino[1], [†] Yuki Yamaguchi[2], and Keishi Nishio[1]

[1] Department of Materials Science and Technology, Tokyo University of Science, Tokyo, Japan
[2] Department of Pure and Applied Chemistry, Tokyo University of Science, Chiba, Japan.

Abstract:

Hydrogen gas is expected to emerge as a next-generation energy source because of its high energy density and low environmental load compared with fossil fuels[1]. However, to use combustible H_2 gas safety, high-performance and safe gas leakage sensors are required. Moreover, it is desirable that the sensors can be used for leakage detection in transportation pipes and storage tanks with complicated shapes. In this study, transparent and flexible platinum-catalyst-loaded tungsten trioxide (Pt/WO_3) nanoparticle-dispersed membranes were developed as H_2 gas leakage sensors.

Pt/WO_3 exhibits a rapid and reversible color change, called gasochromism, through redox reactions with hydrogen and oxygen, even at room temperature[2, 3]. Pt/WO_3 allows rapid and inexpensive detection of the leakage of the colorless and odorless hydrogen gas by the naked eye. Because no electricity is used, we can detect H_2 gas even after a power failure. However, Pt/WO_3 nanoparticles cannot be handled easily. Consequently, flexible polymers have been used as substrate materials for the fabrication of Pt/WO_3 particle thin films using a sol-gel method[4, 5].

In this study, a novel fabrication process of hydrogen sensor based on Pt/WO_3 nanoparticles and a polymer is proposed. In this process, instead of forming Pt/WO_3 layers on the surface of existing substrates, Pt/WO_3 particles are prepared in advance and are then incorporated into a polymer membrane synthesis process. Accordingly, we can use flexible polymer materials without concerns about temperatures when fabricating Pt/WO_3. The Pt/WO_3 nanoparticles, prepared in advance, were dispersed in a precursor solution to synthesize a polymer substrate and obtain a Pt/WO_3 nanoparticle-dispersed membrane. Polydimethylsiloxane (PDMS) membrane, which is transparent, flexible, and gas-permeable, was selected as the polymer[6].

The nanoparticle-dispersed membrane with a Pt:W compositional ratio of 1:13 was transparent and exhibited a sufficient color change in response to H_2 gas. The membrane containing 0.75 wt.% of Pt/WO_3 nanoparticles exhibited high transparency and the largest transmittance change in response to H_2 gas. The heat treatment of the particles at 573 K provided sufficient crystallinity and an accessible area for a gasochromic reaction, resulting in a rapid and sensitive response to the presence of H_2 gas. The lower limit of detection of the optimized Pt/WO_3 nanoparticle-dispersed membrane by the naked eye was 0.4%, which was one-tenth of the minimum explosive concentration. Because this novel transparent and flexible membrane exhibited a clear and rapid color response to H_2 gas, it is a promising sensor for the safe and easy detection of H_2 gas leakage.

Keywords: H_2 gas leakage sensors, platinum-catalyst-loaded tungsten trioxide, transparent and flexible sensor, polydimethylsiloxane

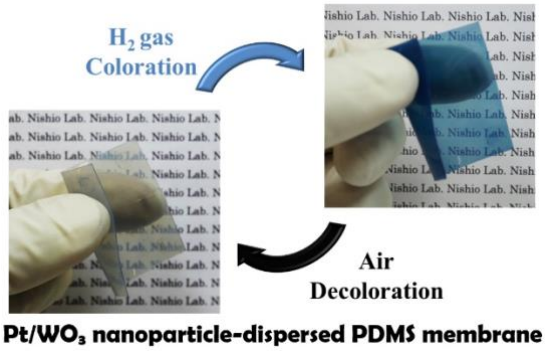


Figure 1: The Pt/WO_3 nanoparticle-dispersed PDMS membrane developed by this study. The transparent and flexible membrane exhibited a clear and rapid color response to H_2 gas.

References:

1. T. Sinigaglia *et al* (2017) *Int. J. Hydrogen Energ.*, 42, 24597.
2. H.W. Kohn *et al* (1964) *Science*, 145, 149.
3. X. Zhou et al (2018) *IEEE Sens. J.*, 18, 2652.
4. Y. Yamaguchi *et al* (2015) *Sens. Actuat. B-Chem.*, 216,394.
5. R. Ishihara *et al* (2019) *Mater. Chem. Phys.*, 226, 226.
6. J.Y. Lee *et al* (2020) *J. Membr. Sci.*, 598, 117654.

Structure and photoluminescence properties of $NiW_{1-x}Mo_xO_4$ (x = 0, 25, 50, and 75%) solid solutions: A Comprehensive Experimental and Theoretical Exploration

A.F. Gouveia[1,*], M. Assis,[1] E.O. Gomes,[1] M.T. Daldin,[2] J. Andrés[1]

[1] Department of Physical and Analytical Chemistry, University Jaume I, Castelló, Spain.
[2] Physics Department, Federal University of Sao Carlos, São Carlos, Brazil.

Abstract:
$NiW_{1-x}Mo_xO_4$ (x = 0, 25, 50, and 75%) solid solutions have been synthesized through the coprecipitation method. The samples were characterized using X-ray and neutron diffractions with Rietveld refinement, Raman spectroscopy, X-ray fluorescence, and ultraviolet-visible diffused reflectance spectroscopy. Finally, photoluminescence properties of $NiWO_4$, $NiMoO_4$, and the $NiW_{1-x}Mo_xO_4$ (x = 0, 25, 50, and 75%) crystals were explained by means of distortional effects and oxygen vacancies in $[NiO_6]$ and $[WO_6]/[MoO_6]$ clusters.
In order to complement and rationalize experimental results, first-principles calculation, at the density functional theory (DFT) level associated with B3LYP hybrid functional, were led to obtain the geometry, electronic structure, and properties of $NiWO_4$, $NiMoO_4$, and the $NiW_{1-x}Mo_xO_4$ (x = 0, 25, 50, and 75%) solid solutions. The electronic properties of $NiW_{1-x}Mo_xO_4$ (x = 0, 25, 50, and 75%) solid solutions indicate an increase in the intermediary electronic levels between valance and conduction bands with the increase in the concentration of Mo^{6+} cations in the lattice.

Keywords: $NiW_{1-x}Mo_xO_4$ solid solution, synthesis, DFT calculations, structure and photoluminescence properties.

Acknowledgment:
A.F.G. acknowledges the Generalitat Valenciana (Conselleria de Innovación, Universidades, Ciencia y Sociedad Digital) for the postdoctoral contract (CIAPOS/2021/106). J.A. acknowledges Universitat Jaume I (project UJI-B2022-56), Generalitat Valenciana (Conselleria de Innovación, Universidades, Ciencia y Sociedad Digital – project CIAICO/2021/122, and Ministerio de Ciencia e Innovación de España (project PID2022-141089NB-I00) for financially supporting this research.

Evaluation of Radiation Shielding Properties for Innovative Concrete With Oil Shale and Basalt-Boron Fiber Additives

A. Slavickas, M. Vaišnoras, E. Babilas
Laboratory of Nuclear Installation Safety, Lithuanian Energy Institute, Kaunas, Lithuania

Abstract:
Cement-based concretes are commonly used for managing radioactive waste due to their low cost and acceptable radiation shielding properties. However, the potential of using oil shale ash as an admixture in concrete for the radioactive waste packaging has been overlooked. Estonia generated millions of tons of ashes collected at landfills by burning oil shale for energy production.

In 2021, four research institutes in Latvia, Lithuania, Estonia and Norway started a cooperation project – Innovation in CONcrete DEsign for hazardous waste management applications (ICONDE) – with the aim to develop innovative concrete mixtures for the safe disposal of hazardous waste, including radioactive waste. The project promotes a circular economy by using oil shale ash, an industrial waste product created in energy production in Estonia, as a supplementary cementitious material in concrete production.

The mechanical properties of concrete will be improved by the addition of dispersed fibers. Furthermore, the use of basalt fibers infused with boron oxide will increase the material's ability to shield neutrons. These properties make the concrete mixtures suitable for radioactive waste management. A possible application for innovative concrete mixtures is the waste created during the decommissioning of nuclear power plants and other types of radioactive/hazardous waste from industry or medicine.

The waste containers used in Ignalina Nuclear Power Plant for the short-lived, low and intermediate level liquid waste were chosen for analysis in this study. Cementation is chosen for the solidification of radioactive liquid waste at the Ignalina nuclear power plant. The liquid waste is cemented and solidified into 200 l drums. Drums are stored in a concrete container with a storage capacity of 8 drums. The drums within the container will be immobilized with cemented grout before the final disposal. In this study, the cemented grout within the container is changed with the concrete with oil shale and basalt-boron fiber additives to evaluate the radiation shielding properties of innovative concrete.

This study investigates the radiation shielding properties of oil shale ash as an additive in concrete for waste packaging. Both Monaco and MAVRIC modules within SCALE 6.2.4 for radiation transport simulations were used to conduct two independent evaluations. The Monaco module is a Monte Carlo transport code for shielding applications with direct particle transport simulations. The MAVRIC module is designed for deep penetration problems as one analyzed and is based on the same Monaco module using an automated variance reduction method.

The MAVRIC module performs a radiation shielding analysis in two steps including the calculation of adjoint flux as a function of position and energy using the Denovo module (3D Cartesian geometry discrete ordinates transport code) and particle transport calculations. An importance map generated by the Denovo module is applied for biasing during Monte Carlo particle transport to accelerate Monte Carlo simulations. It enables to obtain good statistics (i.e., low relative uncertainty) in the regions of interest without sacrificing computation time.

The estimated photon flux and the relative computation efficiency were compared between Monaco and MAVRIC modules in addition to the demonstration of radiation shielding properties for concrete with oil shale and basalt-boron fiber additives in comparison with the cemented grout.

Keywords: radioactive waste, concrete, oil shale ash, basalt boron, radiation shielding modeling, Monate Carlo method, variance reduction method.

Advanced Characterization of Short Fibre Reinforced Concrete in Dynamic Regime through Hopkinson bar and X-ray inspection

Nela Krčmářová[1], Jan Šleichrt[1], Jan Falta[1], Tomáš Fíla[1]

[1] Department of Mechanics and Materials, Czech Technical University in Prague, Faculty of Transporation Sciences, Prague, Czech Republic

Abstract:
Ultra High Performance Concrete (UHPC) is a novel cementitious composite material used in wide range of applications most often in civil engineering. UHPC exhibits excellent mechanical properties and can therefore be used for the production of slender building elements with high load–bearing capacity. UHPC is considered as promising sustainable and resilient construction material with expected lifetime of up to 200 years [1, 2].
UHPC is characterised by low water-to-binder ration (w/b 0.15 – 0.25) which needs to be well controlled in order to achieve high compressive strength. Post-cracking retention, a level of ductility and tensile strength > 8 MPa is achieved thanks to adding fiber reinforcement [2].In this study the UHPC matrix was reinforced by short steel fibres (13 mm long with diameter 0.2 mm).

Figure 1 shows the samples which were drilled out from a UHPC with steel fibres reinforcement block and were in shape of prisms with diameter of 20 mm and were 65 mm long.

Figure 1: UHPFRC samples in shape of prisms which were subjected to dynamic testing using Split Hopkinson pressure bar.

Samples of UHPC reinforced by steel fibres were inspected using computed tomography before dynamic testing in order to get detail information about the inner structure of the material and fiber distribution in the samples. Dynamic testing in compressive mode of deformation was performed using Split Hopkinson pressure bar (SHPB) apparatus depicted in Fingure 3 [3]. To capture the internal damage in time of loading, fast radiography was applied based on the usage of a Flash X-ray system producing a series of short high intensive pulses. The radiographs were acquired by a scintillator panel converting to visible light and recorded by a high-speed camera. The second camera observed a scene around the sample and was placed in a similar direction as an X-ray tube.

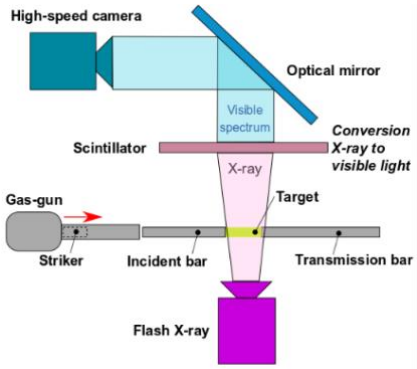


Figure 2 SHPB apparatus and principal of the measurement and flash X-ray inspection during experiment.

Keywords: ultra high performance concrete, steel fibres reinforcement, dynamic testing, split Hopkinson pressure bar, X-ray inspection, computed tomography, flash X-ray radiography.

References:

1. Jiang Du, Weina Meng, Kamal H. Khayat, Yi Bao, Pengwei Guo, Zhenghua Lyu, Adi Abu-obeidah, Hani Nassif, Hao Wang, (2021) New development of ultra-high-performance concrete (UHPC), *Composites Part B: Engineering*, 224, 109220.
2. Habel K., Viviani M., Denarié E., Brühwiler E., (2006), Development of the mechanical properties of an Ultra-High Performance Fiber Reinforced Concrete (UHPFRC), *Cement and Concrete Research*, 36, 1362-1370.
3. Krčmářová N., Falta J., Fíla T., Čítek D., Response of the Ultra high performance concrete under dynamic compressive loading, (2023) *Acta Polytechnica CTU Proceedings*, 42, pp. 51 – 54.

Empowering Environmental Sustainability Functionalized SBA-15 as a Cutting-Edge Solution for Effective Metal Uptake

M. Dulski[1], A. Strach[2], M. Wojtyniak[3], B. Chrzaszcz[1], M. Laskowska[4], P. Duda[5], J. Karczewski[6], J. Goscianska[7], A. Jankowska[7], and Ł. Laskowski[4]

[1] Institute of Materials Engineering, and Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland
[2] Doctoral School, University of Silesia, Bankowa 14, 40-032 Katowice, Poland
[3] Institute of Physics, Silesian University of Technology, Konarskiego 18A, 44-100 Gliwice, Poland
[4] Institute of Nuclear Physics Polish Academy of Sciences, 31-342 Kraków, Poland
[5] Institute of Biomaterials, and Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland
[6] Institute of Biology, Biotechnology, and Environmental Protection, Faculty of Natural Sciences, University of Silesia, Jagiellońska 28, 40-032 Katowice, Poland
[7] Adam Mickiewicz University, Department of Chemical Technology, Uniwersytetu Poznańskiego 8, 61–614 Poznań, Poland
*Corresponding Author E-mail: mateusz.dulski@us.edu.pl

Abstract

One of the most promising and modern solutions to combat environmental pollution is the development of bio-perforated, mesoporous SBA-15 silica. This material boasts an impressive surface area of approximately 800m2/g. It features structurally amorphous properties, forming uniaxially ordered hexagonal channels with a diameter of 5 nm and a length on the order of micrometers. These channels are uniformly distributed throughout the volume, allowing for high capillary properties. SBA-15 also demonstrates a neutral impact on the environment and living organisms, exhibiting no toxic or irritating effects. Furthermore, its physicochemical properties are easily adjustable through various technological processes, offering great flexibility in terms of chemical modification. This high degree of adaptability allows for the functionalization of SBA-15 with a wide range of functional groups, either on its outer or inner walls, while maintaining precise control over their concentration within the material's volume.

The significant advancement in environmental protection, as proposed by our research team, has been achieved by activating the mesopores using specific functional groups tailored for capturing specific types of metals. This functionalization involves the use of various functional groups, such as propyl-carbonate (for metal-binding I, e.g., silver), propyl-phosphate (for metal-binding II, e.g., copper), and cyclam (1,4,9,11 tetraazacyclodecane), which is capable of chelating metal chlorides like copper, chromium, cobalt, nickel, and more. Importantly, this functionalization process ensures the homogeneous distribution of these functional groups within the silica pores.

The potential of metal ion uptake has been rigorously verified using advanced techniques such as SAXS, Positron-Electron annihilation, BET (Brunauer-Emmett-Teller), and spectroscopy methods like UV-VIS spectroscopy. Time-dependent metal uptake curves have been instrumental in estimating the real-time sorption capacity of functionalized SBA-15. Mechanical studies, including Young's modulus parameters at various force levels (ranging from nN to N), have been conducted on individually prepared SBA-15 pellets to assess their stability and mechanical properties. The combined efforts of functionalizing SBA-15 and evaluating its sorption potential through various methodologies aim to pave the way for developing an entirely new class of materials with unique properties for remediating contaminated environments. This research holds the promise of making a significant and positive impact on preserving our environment and protecting human health.

Acknowledgment

M.D. and L.L. are thankful for the financial support from the National Center of Science (NCN) based on 2020/37/B/ST8/03637.

An experimental investigation of spreading behavior of carbon fiber rovings

S. Kohl [1,*], C. Marschik [1], T. Kranzl [2], M. Schnaitter [2], G. R. Berger-Weber [2]

[1] Competence Center CHASE GmbH, Hafenstraße 47-51, 4020 Linz, Austria
[2] Institute of Polymer Processing and Digital Transformation, Johannes Kepler University, Linz, Austria

Abstract:
Unidirectional (UD) fiber-reinforced thermoplastic tapes are increasingly used in lightweight applications to locally reinforce structural components in a targeted manner due to their excellent specific mechanical properties [1].

In this work, the production of UD tapes based on a continuous extrusion process is investigated. In this process, multiple fiber rovings are unwound from a creel and spread mechanically to a certain width to form a homogeneous fiber carpet (Figure 1). Subsequently, the fiber carpet is impregnated with thermoplastic polymer melt while it is pulled through an extrusion die. The polymer melt must penetrate completely between the fibers to ensure good fiber-matrix adhesion in the tape, which is essential for transferring mechanical loads in the later application. In the downstream processing steps, the tape is calibrated to the final thickness, cooled, and wound up.

An integral step of the process is fiber spreading. A perfectly spread and homogeneous fiber carpet is crucial for achieving a complete fiber impregnation and moreover an adequate tape quality. Various spreading techniques [2-5] can be used to spread rovings from their initial to the required width. In this work, we systematically examined the inputs affecting fiber spreading by deflection. This method causes the outer roving filaments to experience higher stresses. To reduce these stresses, the filaments adopt smaller radii, resulting in a widening of the roving.

For this purpose, a test rig was developed to investigate fiber spreading under near-process conditions. Using a carbon fiber roving, a large number of spreading tests was carried out, in which the roving was guided over deflection rods and the roving width was recorded using cameras before and after spreading. During these experiments, (i) the number of rods, (ii) the rod radius, (iii) the rod immersion depth, and (iv) the roving take-off speed were varied.

The results of the experiments can be used to optimize the spreading configuration in the production of UD tapes.

Keywords: UD tapes, carbon fibers, fiber spreading, spreading by deflection

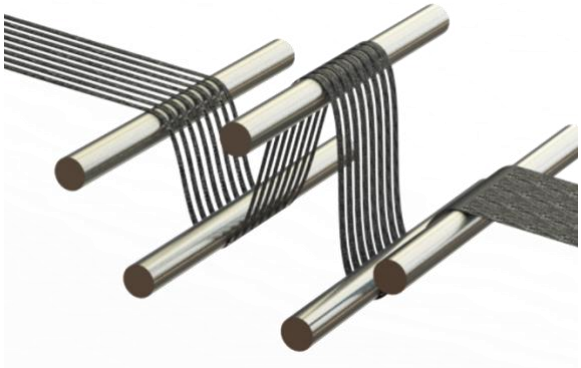


Figure 1: Schematic representation of the mechanical fiber spreading process by deflection of several fiber rovings.

References:

1. Kropka M., Muehlbacher M., Neumeyer T., Altstaedt V. (2017) From UD-tape to final part – a comprehensive approach towards thermoplastic composites, *Procedia CIRP*, 66, 96-100.
2. Lifke JL. (2000) Method and apparatus for spreading fiber bundles, US Patent 6049956.
3. Peritt JM. (1993) Electrostatic fiber spreader including a corona discharge device, US Patent 5200620.
4. Newell JA and Puzianowski AA. (1999) Development of a pneumatic spreading system for Kevlar-Based Sic-Precursor carbon fibre tows, *High Perform Poly*, 11, 197–203.
5. Akase D. (2000) Method and apparatus for opening reinforcing fiber bundle and method of manufacturing Prepreg, US Patent 6094791.

A new optical method for surface quality analyses of thermoplastic composite parts

J. Birtha [1,*], E. Kobler [1], C. Marschik[1], K. Straka[2], G. Steinbichler[2]

[1] Competence Center CHASE GmbH, Hafenstraße 47-51, 4020, Linz Austria
[2] Johannes Kepler University Linz, Institute of Polymer Injection Molding and Process Automation, Altenberger strasse 69, 4040 Linz, Austria

Abstract:
During the processing of fiber-reinforced thermoplastic composites, surface defects such as in-plane fiber waviness and surface grooves can occur. These defects have a detrimental effect on the surface quality and mechanical performance of components [1,2]. Being able to quantify surface quality requires adequate measurement systems, which moreover help to investigate the relationship between processing parameters and critical quality attributes and ultimately optimize process conditions.
We propose an optical measurement approach based on a monochrome line scan camera to analyzing the surface of flat composite parts. The camera is mounted on a rail and moves horizontally at a constant speed over a fixed distance while scanning the subjacent component. To ensure constant lightning conditions, an LED light strip is attached to the camera. The system is designed to operate without interference from ambient light, allowing measurements of parts with a maximum size of 500 x 500 mm. It achieves a ~24 µm/pixel resolution and provides user-independent and reproducible results. The recorded images are analyzed using OrientationJ, a plugin for an image analysis software, which can analyze the gradient tensor in a local neighborhood [3]. One output is a color-coded local dominant orientation image (see Figure 1). In addition, the tool can be used to measure orientation and isotropy properties of an image, including (i) standard deviation of orientation, which assesses fiber orientation variation, (ii) coherency, which determines the presence of a dominant direction in the local structure, (iii) and gradient energy, which measures region homogeneity [4]. Using these metrics, we performed measurements of surface quality in various thermoplastic composite plates, including a polycarbonate/carbon fiber (PC/CF) plate, a PC/CF plate consolidated with a polyetherimide (PEI) foil, and a polyaryletherketone (PAEK) plate. Our study shows that the new measurement system can quantitatively assess surface defects and fiber waviness in thermoplastic composite plates in a non-destructive, quick, and effective manner.

Keywords: Thermoplastic composites, surface quality, fiber waviness, optical measurement system, surface defects, OrientationJ.

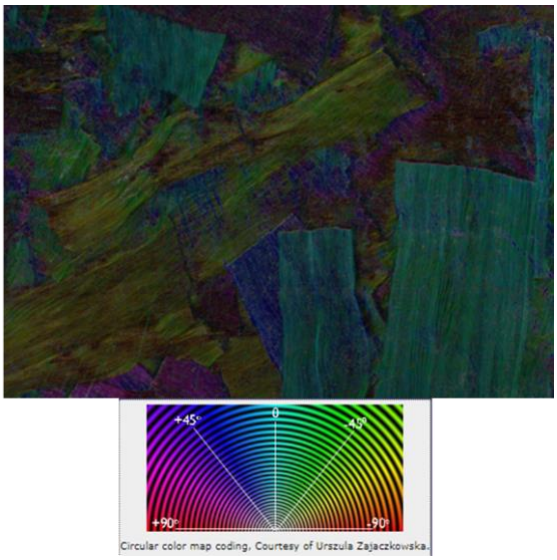


Figure 1: Optical image of a thermoplastic composite plate surface. The colors represent the fiber orientations.

References:

1. Kulkarni, P., Mali K. D., Singh S. (2020) An overview of the formation of fibre waviness and its effect on the mechanical performance of fibre reinforced polymer composites, *Composites Part A*, 137, 106013.
2. Sitohang R.D.R., Grouve W.J.B., Warnet L.L., Akkerman R. (2021) Effect of in-plane fiber waviness defects on the compressive properties of quasi-isotropic thermoplastic composites, *Composite Structures*, 272, 114166.
3. https://bigwww.epfl.ch/demo/orientationj/ (visited: 02.11.2023).
4. Püspöki Z., Storath M., Sage D., Unser M. (2016) Transforms and Operators for Directional Bioimage Analysis: A Survey, *In: Focus on Bio-Image Informatics*, 219, 69-93.

Inline Quality Assurance of Glass-Fiber-Reinforced Unidirectional Thermoplastic Tapes using Optical Coherence Tomography

M. Wenninger [1*], C. Marschik [1], G. Berger-Weber [2]

[1] Competence Center CHASE GmbH, Hafenstraße 47-51, 4020 Linz, Austria
[2] Institute of Polymer Processing and Digital Transformation, Johannes Kepler University, Linz, Austria

Abstract:
Optical coherence tomography (OCT), originally developed for biomedical diagnosis, has been demonstrated to be a powerful non-destructive and non-invasive measurement method for the detection of common defects in glass-fiber reinforced polymer composites. While previous studies have focused mainly on the use of OCT in the analysis of thermoset composites, we were able to show that OCT can be used to quickly detect typical defects (e.g., gaps, fiber breakages, bad edges or dry fiber regions) in thermoplastic UD tapes at high resolution in offline experiments. OCT was integrated into an industrial tape production line and optimal settings were derived experimentally for the inline detection of dry fiber regions to find an optimal balance between accuracy and data size using a stationary Polycarbonate (PC) / glass-fiber (GF) tape by varying the A-scan sampling rate, A-scan averaging and OCT transverse travel velocity.
Here we present the inline monitoring of moving tapes over a range of industrially relevant take-off speeds. Microscopy was used for validation in both cases. A fast and robust statistical analysis of B-scans was developed that visualizes the quality of full-cross sections for potential use in a real-time setting.
Within an industrially relevant production speed range of up to 15 m/min, we are thus now able to investigate 120 mm wide (and potentially wider) UD tapes inline at a transverse resolution of 22 µm, producing only 21 MB of data per measurement.

Keywords: Thermoplastic UD tapes, optical coherence tomography, unidirectional, glass-fiber reinforced thermoplastics, inline, quality assurance, non-destructive testing, defect detection

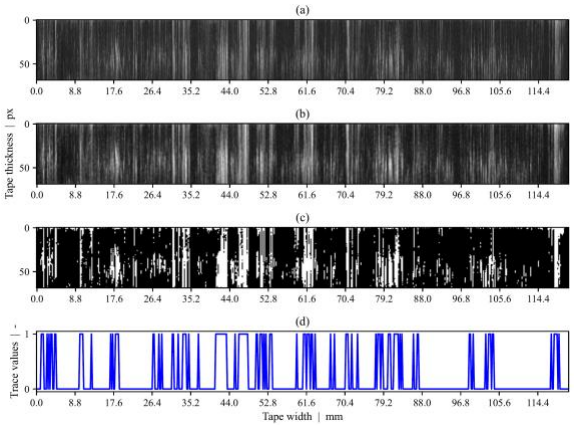


Figure 1: Full-cross sectional quality assessment of a B-scan recorded at 1 m/min tape take-off speed explaining the data processing steps to obtain a representative trace along the complete tape width that indicates dry fiber regions (peak values = 1) and thus allows for statistical analysis of dry region counts and sizes.

References:

1. Dunkers, J.P. et al., Imaging of Composite Defects and Damage Using Optical Coherence Tomography, *Advancing with Composites* (2000)
2. Stifter, D. et al., Investigation of polymer and polymer/fibre composite materials with optical coherence tomography. *Measurement Science and Technology* (2008)

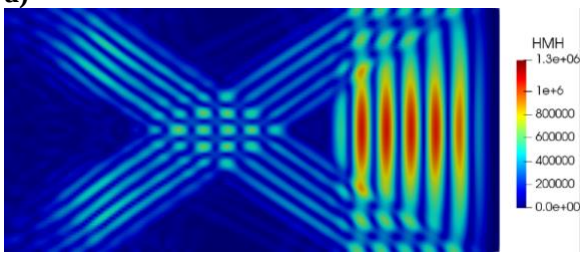
Stress wave attenuation in bi-material 3D printed metallic structures

R. Kolman[1,2,*], R. Dvořák[1,3], M. Mračko[1], A. Berezovski[4], M. Kylar[1,3], V. Kotek[1,3]
[1] Institute of Thermomechanics of the CAS, v. v. i., Praha 8, Czech Republic
[2] The College of Polytechnics Jihlava, Czech Republic
[3]CTU in Prague, Faculty of Transportation, Praha 1, Czech Republic
[4]Tallinn University of Technology, Tallinn, Estonia

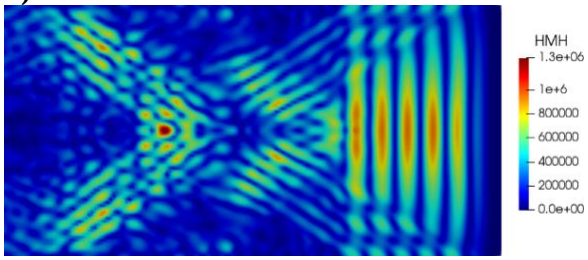
Abstract:
Additive manufacturing technologies enable the creation of components with extremely complex shapes. Such structures have a wide range of applications in a variety of industrial fields. Structures suitable for elastic wave attenuation are required in precise engineering, space engineering, and many areas of mechanical engineering to reduce unwanted system vibrations. In that contribution, we study the wave propagation in bimaterial 3D printed structures and the elevel of stress wave attenuation is control by the topology of material distribution. Elastic stress wave attenuation in two-dimensional bi-material composite structures is studied theoretically (Ref. 1) and numerically by finite element method (Ref. 2,3). The explicit finite element method is used to simulate pulse propagation in various compositions with special attention to spurious stress wave propagation in heterogeneous structures (Ref. 4). The effect of the frequency and wavelength of pulses on wave attenuation has been analyzed and also criteria for stress attenuation is analyzed.

Keywords: elastic wave propagation, finite element method, bi-material composites, 3D printing, stress attenuation

a)



b)



c)

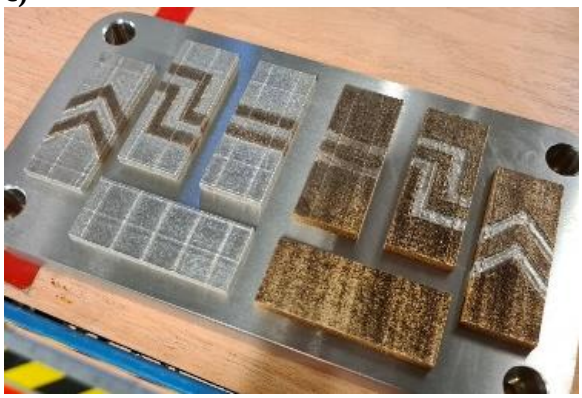


Figure 1: FEM simulation of Stress fields (a) in homogenous 2D body; (b) in heterogeneous 2D body from two materials with V-shaped interfaces; (c) examples of multimaterial plane samples 1.4404 + CuSn10 with similar V-shaped interface.

References:

1. Bacigalupo, A., Lepidi, M., (2018) Acoustic wave polarization and energy flow in periodic beam lattice materials. *International Journal of Solids and Structures* 147, 183-203.
2. Hughes, T. J. R. (2000) The Finite Element Method: Linear Static and Dynamic Finite Element Analysis. Dover Publication.
3. Mračko, M., Kober, J., Kolman, R., Převorovský, Z., Tkachuk, A., Plešek, J. (2021). Finite element method based computational time reversal in elastodynamics: Refocusing, reconstruction and its numerical sensitivity. *Mathematics and Computers in Simulation*, 189, 163-190.
4. Dvořák, R., Kolman, R., Mračko, M., Kopačka, J., Fíla, T., Jiroušek, O., Falta, J., Neuhäuserová, M., Rada, V., Adámek, V., González, J.A. (2023) Energy-conserving interface dynamics with asynchronous direct time integration employing arbitrary time steps, Computer Methods in Applied *Mechanics and Engineering*, 413, 116110.

Erosion Characteristics of SCR Material Under Diverse Temperature Conditions: An Experimental and Computational Inquiry

S. Rajath [1], N D Shivakumar [1]

[1]Department of Design and Manufacturing, Indian Institute of Science, Bangalore, 560012, India

Abstract:
This investigation focuses on enhancing the erosion resistance of V_2O_5–TiO_2 Selective Catalytic Reduction (SCR) plate catalyst composite while upholding optimal De-NO_x efficiency requisite for thermal power plants in high ash/dust environments. These components are prone to failure due to the erosive wear of their surface by silica sand particles in the fly ash present in the flue gases. The study provides the possible characterization experiments to evaluate the ceramic matrix composite and the findings hold importance in choosing between different Plate samples. The results of abrasion experiments have followed the model developed by Iain Finnie. In further study, the erosion rate was obtained both experimentally and numerically by varying parameters such as the velocity of abrading particles, impact angle, and testing temperature, i.e., at room temperature and at 350°C, which is the actual working temperature of the SCR composite. The Finnie erosion model was used to determine the material scaling coefficient (K) and the velocity exponent (n) empirically, which are required for simulations. CFD simulations were carried out with the exact experimental conditions to determine the erosion rate numerically. Increasing the velocity of erosive particles led to an exponential increase in the rate of erosion. Furthermore, with a temperature increase to 350°C, the erosion rate nearly doubled. Using these erosion characteristic data, the erosion process can be simulated under the same working conditions as the SCR product, and the life of the catalyst plates can be predicted.

Keywords: Ceramic matrix composite, NO_x Reduction, Erosion behavior, Finnie model, Discrete phase modeling

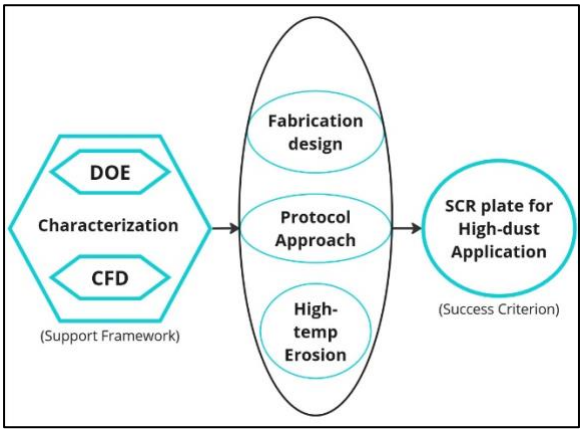


Figure 1: Design Research Methodology Impact Model for tailoring SCR plate catalyst composite suitable for high dust/ash power plant conditions.

References:

1. Wiatros-Motyka M (2018). NOx control for high-ash coal-fired power plants in India. Clean Energy, 3(1), pp.24-33.
2. Protocol for Laboratory Testing of SCR Catalyst: 2nd Edition. Accessed from: https://www.epri.com/#/pages/product/1014256/?lang=en-US
3. Halima Hadžiahmetović, Nedim Hodžić, Damir Kahrimanović, Ejub Džaferović (2014). Computational fluid dynamics (CFD) based erosion prediction model in elbows. *Tehnički vjesnik*, 21, 275-282

Method of localized Lagrange multipliers for coupling of 1D and 3D finite elements

R. Dvořák [1,2,*], J.A. Gonzalez [3], R. Kolman [2], O. Jiroušek [1]

[1] Czech technical university, Faculty of Transportation Sciences, Department of Mechanics and Materials; Na Florenci 25, Praha 1, 110 00, Czech Rep.
[2] Institute of Thermomechanics of the CAS, v. v. i., Dolejškova 1402/5, 182 00 Praha 8, Czech Rep.
[3] Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Camino de los Descubrimientos s/n, Seville E-41092, Spain

Abstract:
The contribution presents a method for domain decomposition of finite-element models using Localized Lagrange Multipliers (LLM) [1, 2, 3]. The LLM decomposition, in contrast to the conventional Mortar method, is characterized by the existence of an interface that is described by additional degrees of freedom - displacements in the statics problem, and additionally velocity and acceleration in the dynamics problem. At this interface, kinematic continuity and force balance of the localized fields of the multipliers of each subdomain are enforced. The suitability of the LLM for parallel computations and actual implementation is shown. Furthermore, the application of the method to the problem of a 3D printed fiber composite sample is outlined. The matrix is described by 3D finite elements, whereas 1D elements are used to describe the filaments. The process of decomposing the model into a 3D matrix and 1D filaments and relating them to each other by the kinematic continuity equation and the equilibrium equation of the localized multiplier fields is described.

Keywords: finite element method, domain decomposition, localized Lagrange multipliers, coupling of 3D and 1D elements, 3D printed fiber composites

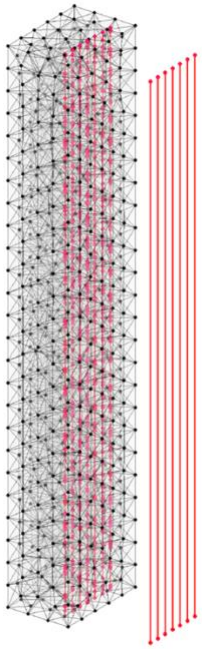


Figure 1: Figure illustrating the 1D element fibers in 3D element matrix

References:

1. K. C. Park, C. A. Felippa, A variational principle for the formulation of partitioned structural systems, International Journal for Numerical Methods in Engineering 47 (2000) 395–418.
2. K. C. Park, C. Felippa, G. Rebel, Interfacing nonmatching fem meshes: the zero moment rule, Trends in Computational Structural Mechanics (01 2001).
3. K. C. Park, C. Felippa, G. Rebel, A simple algorithm for localized construction of non-matching structural interfaces, International Journal for Numerical Methods in Engineering 53 (2002) 2117 – 2142. doi:10.1002/nme.374.125

Multiscale modelling of composite pressure vessels

L. Bouhala*, A. Laachachi, A. Karatrantos
Material Research and Technology, Luxembourg Institute of Science and Technology, Luxembourg

Abstract:
Compressed gas storage of hydrogen has emerged as the preferred option for fuel cell vehicles and diverse applications such as road transport and aviation. However, designers face mounting challenges in crafting secure and efficient composite overwrapped pressure vessels (COPVs) for hydrogen storage. One obstacle involves creating precise software, incorporating advanced finite element models (FEM) that account for factors in the filament winding process and the development of robust models for the dome region. Another challenge lies in formulating predictive behavior and failure models to ensure optimal structural integrity for COPVs. In this study, FEM is employed to model COPVs based on enhanced resin properties infused with nanofillers. The properties of the resulting composite are thoroughly characterized through experimental methods or inverse engineering and subsequently utilized as inputs in the numerical model. The study culminates in the proposal of a novel design for type-IV hydrogen composite pressure vessels, accompanied by a comparative analysis between the conventional composite material and the upgraded version. Molecular dynamics simulations played a pivotal role in facilitating the dispersion of nano-fillers within the pristine epoxy resin, complemented by integration with higher-scale models like finite element models. Additionally, various experimental characterizations were carried out to acquire insights into the properties of the newly developed composite.This paves the way for future advancements in this critical field.

Keywords: nano-fillers, epoxy resin, carbon fibers, molecular dynamics, finite element method, multiscale modelling, chacterization, high pressure vessels, simulation.

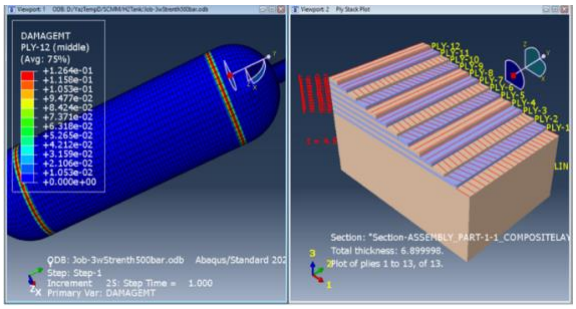


Figure 1: Figure illustrating the damage response in the matrix at ply 12 of a type-3 composite pressure vessel, in the right hand side we see the stacking sequence, plies orientation, thicknesses of the plies and of the aluminium liner.

References:

1. Comparative analysis of numerical methods for modeling composite pressure vessels, Lyazid Bouhala, Yao Koutsawa, Argyrios Karatrantos, Claus Bayreuth, Composite Structures, submitted.
2. From Ionic Nanoparticle Organic Hybrids to Ionic Nanocomposites: Structure, Dynamics, and Properties: A Review, Karatrantos, A.V., Mugemana, C., Bouhala, L., Clarke, N., Kröger, M., Nanomaterials, 2023, 13(1), 2

3Bs Materials Session I. D: Synthesis, Processing and Characterization

Combinatorial Synthesis of polymeric non-viral nanovectors for gene delivery: use of Box Behnken design and Response Surface Methodology

S. Schirinzi[1,2,*], Giuseppe Gigli[1,2], I. E. Palamà[2], G. Maiorano[2]
[1] Physics and Mathematics, University of Salento, Lecce, Italy
[2] CNR-Institute of Nanotechnology (NANOTEC), Lecce, Italy

Abstract:
T cell engineering to express CAR *via* viral vectors such as lentiviral and retroviral vectors[1] is characterised by high costs and safety issues.
Non-viral nanovectors offer a safe solution for immune cell engineering by being non-integrating vectors, thus excluding oncogenic transformation and clonal expansion.
So far, the production of nanoparticles (NPs) for immune cell engineering has proved challenging, and high transfection efficiency is still a goal to be achieved[2].
For this reason, the development of efficient non-viral nanovectors requires in-depth studies of their interactions at the cellular level in order to gain principles of design for suitable nanoparticles (NPs).
For this reason, the correlation of factors that affect the behaviour of NPs in terms of physical-chemical properties and biological responses could represent a successful approach for producing efficient delivery systems.
In this frame, Box-Behnken response surface design is a considerably efficient and cost-effective method respect to other conventional combinatorial synthesis methods[3].
In this study, the combinatorial synthesis of polymeric NPs for gene delivery employs Box-Behnken is based on 3 factors and 3 levels, thus allowing the design of appropriate experiments by subdividing the nanoparticles into different populations according to N/P ratio. Some specific materials in the synthesis showed better results at higher concentrations (*e.g.* PVA), while others performed better at lower concentrations (*e.g.* PCL) with dissimilar responses of % encapsulation, mean size, surface charge, polydispersity index (PdI), cell uptake, cell viability and transfection efficiency (Fig.1). The optimised NPs resulted with a hydordinamic radius about 230 nm, a PdI of 0.15, an encapsulation efficiency up to 40%, high cell uptake, and excellent biocompatibility. Therefore, the Box-Behnken design method resulted in providing desired delivery systems by optimising proper experimental factors.
The key question that we would like to experimentally address regards the importance of the parameters that influence NP structure on cell uptake,the release of the encapsulated genetic material, and biological activity.
However, further characterisation studies will be required to obtain a structural correlation with the transfection response.

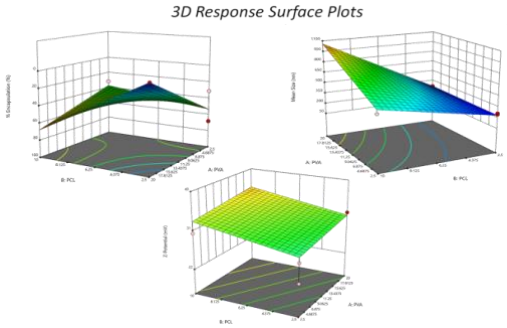


Figure 1: Three-dimensional response surface plots showing the effects of independent variables on particle size, loading efficiency and Z-potential for NPs belonging to group N/P=2.

Keywords: gene delivery, non-viral nanovectors, combinatorial syntheses, poliplex, CAR-T therapy, biopolimers.

Acknowledgements: This study was supported by EU funding within the MUR PNRR "National Center for Gene Therapy and Drugs based on RNA Technology", Life-Science Hub–Terapie Avanzate, "Tecnopolo per la medicina di precisione" (TecnoMed Puglia) - Regione Puglia and project PON ARS01_00906 "TITAN - Nanotecnologie per l'immunoterapia dei tumori".

References:

1. Zhang, H., et al. (2020). Engineering better chimeric antigen receptor T cells. Experimental Hematology & Oncology, 9(1), 1-13.
2. Smith, et al. (2017). In situ programming of leukaemia-specific T cells using synthetic DNA nanocarriers. *Nature nanotechnology*, *12*(8), 813-820.
3. Ding, Y., et al. (2016). Box–Behnken design for the optimization of nanoscale retrograded starch formation by high-power ultrasonication. LWT-Food Science and Technology, 67, 206-213.

Improving Comfort and Performance of Contact Lenses Through Hydrophilic Polyphenolic Coatings

P. Demian[1], D. Nagaya[2], K. Lee[3], G. A. Lee[3], K. Iwai[2], D. Hasegawa[2], M. Baba[2], P. B. Messersmith[3], Roeya Refaei[4], M. Lamrani[1,2*]

[1]MeniconR&D Innovation Centre, MeniconCo., Ltd., Nagoya (Japan), Geneva branch, Switzerland
[2]MeniconCo.; Ltd, Nagoya, Japan
[3]Bioengineering and Materials Science and Engineering Departments, University of California, Berkeley, USA
[4]Laboratory of LAMSE, Faculty of Sciences and Techniques of Tangier, B.P. 416, Tangier 90000, Morocco

Abstract:
Contact lens comfort is a significant concern for wearers, with surface properties playing a crucial role in comfort levels. Traditional approaches to enhance contact lens comfort by increasing hydrophilicity often lead to an imbalance between hydrophilic and hydrophobic components, resulting in adverse reactions. To address this, we propose two approaches for increasing lens hydrophilicity, both based on the chemistry of phenolic molecules.
The first approach involves a co-deposition technique, a universal method applicable to various existing lens types, promising increased hydrophilicity and improved overall comfort. Additionally, the study introduces a second approach employing the subsequent deposition of two layers to fabricate functionalized coatings on rigid contact lenses. Leveraging the chemistry of polyphenolic compounds, the initial layer is polyphenol-based, while the secondary layer, consisting of either a peptoid or a polysaccharide, exhibits notable hydrophilicity, biocompatibility, and non-toxicity. This sequential deposition method allows for a versatile selection of molecules to be grafted onto the secondary layer, providing options for achieving specific functional properties such as antimicrobial or antiviral effects. Results obtained from this dual-layer deposition approach showcase promising enhancements in terms of hydrophilicity, biocompatibility, and durability of the resultant coatings.
Together, these approaches offer a comprehensive solution to address comfort and functionality issues in contact lenses by leveraging the chemistry of phenolic coatings.

Keywords: protein folding, nanoporous sol-gel glasses, silica-based biomaterials, circular dichroism spectroscopy, surface hydration, crowding effects, micropatterning, biomedical applications.

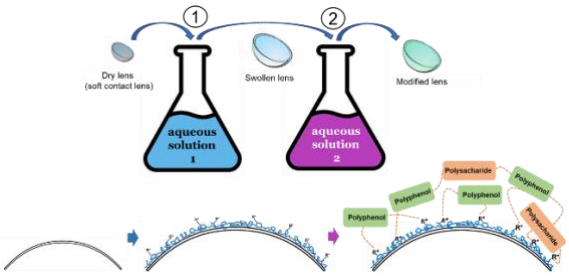


Figure 1: Figure illustrating the two-step co-deposition process of contact lens modification with phenolic compounds and polysaccharides.

References:

1. Lee, H., Dellatore, S. M., Miller, W. M., & Messersmith, P. B. (2007). Mussel-inspired surface chemistry for multifunctional coatings. *science*, *318*(5849), 426-430.
2. Li, P., Poon, Y. F., Li, W., Zhu, H. Y., Yeap, S. H., Cao, Y., ... & Chan-Park, M. B. (2011). A polycationic antimicrobial and biocompatible hydrogel with microbe membrane suctioning ability. *Nature materials*, *10*(2), 149-156.

Gallic Acid Loaded-Poly (Lactic Acid) Electrospun Fibers for Bone Tissue Engineering

N. Sribungngaw[1], P. Naruphontjirakul[1], P. Namchaiw[1] and K. Ngamkham1[1]
[1]Biological Engineering Program, Faculty of Engineering, King Mongut's University of Technology Thonburi, Bangkok, Thailand.

Abstract:
The main property of bioactive scaffold is not only to provide an extracellular matrix but also to accelerate tissue regeneration. In light of this, the addition of other bioactive compounds to the scaffolds becomes a key method to increase their potential. For this work, PLA nanofibrous scaffolds incorporated with various concentrations of gallic acid (GA) (0, 2.5, 5, and 10 mg/ml) were prepared by electrospinning. The scaffold properties were assessed through SEM imaging, GA releasing assay, and degradation assay. SEM imaging revealed that the incorporation of GA did not have a discernible impact on the average fiber diameter and morphology. In addition, the release of GA increased with respect to GA content. Short-term degradation assays indicated that the weight of the scaffolds reduced over time but still remained after day 28. Furthermore, we assessed the in vitro biological activities of the scaffolds using the MC3T3-E1 cell line, including cytotoxicity, cell adhesion, ALP activity, and calcium deposition. In terms of cytotoxicity, no significant cytotoxic effects were observed through MTT assay, and the cells were able to adhere to the scaffold after 21 days. Crucially, the evaluation of ALP activity and calcium formation revealed a positive correlation with increasing GA content. In summary, the study suggests that PLA electrospun fibers incorporated with GA hold promise for enhancing bone formation, highlighting their potential as bioactive scaffolds for bone regenerative applications.

Keywords: Poly (lactic acid) electrospun fiber, Gallic acid (GA), Bone tissue engineering, Nanofibrous scaffold

Engineered anisotropic interlocking strategy for interface toughening in 3D printed bi-material thermoplastic polymers

L. Farràs-Tasias [1], J. Topard [2,3], S. Panier[3], F. A. Gilabert [1*], F. H. Marchesini [1]
[1] Department of Materials, Textiles, and Chemical Engineering, Ghent University, Campus Ardoyen, Thecnologiepark-Zwijnaarde, Belgium
[2] UniLaSalle Amiens, Amiens, France
[3] Laboratoire des Technologies Innovantes, Avenue des Facultés – Le Bailly, Université de Picardie Jules Verne, Amiens, France

Abstract:
This study explores the innovative application of bi-material thermoplastic 3D printing, utilizing the distinct characteristics of Polylactic acid (PLA) and Thermoplastic Polyurethane (TPU) in Additive Manufacturing (AM). PLA is valued for its lower environmental impact compared to other polymers with similar mechanical responses, while TPU is known for its significant elasticity and deformability. This combination enables the creation of components that can bend, stretch, or compress, which is particularly beneficial for advanced applications in soft robotics (such as robotic limbs that mimic biological movements), medical prosthetics (combining rigidity and flexibility to provide natural movement and comfort for patients), and sports goods (integrating impact resistance with comfort for helmets, pads, and guards), among others.

The research specifically addresses the issue of weak interfaces between PLA and TPU in Fused Filament Fabrication (FFF), a frequent cause of mechanical failure in such materials. To counter this, the study introduces a variety of interlocking flat interfaces between PLA and TPU, created using multi-nozzle 3D printing. These interfaces are thoughtfully designed with precise raster directions and material pairings, creating mechanically bonded zones that significantly improve toughness. By strategically orienting these interlockings, the design effectively prevents crack propagation during debonding, thus enhancing the durability of the structures. The innovative design of these interfaces leads to an increase in toughness by up to two orders of magnitude. This advancement paves the way for the development of meta-structure mechanisms with a wide range of improved mechanical properties.

Keywords: Multi-material 3D printing, inter-locking interface, mechanical bonding, flat interface, interface toughening

References:

1. Darnal, A., Shahid, Z., Deshpande, H., Kim, J., Muliana, A., (2023) Tuning mechanical properties of 3D printed composites with PLA: TPU programmable filaments, *Composite Structures*, 318, 117075.
2. Altuntas, U., Coker, D., Yavas, D., (2023) Creating tougher interfaces via suture morphology in 3D-printed multi-material polymer composites by fused filament fabrication, *Additive manufacturing*, 61, 103359.

Mesoporous bioactive glass nanoparticles doped with cobalt and boron for theragnostic applications.

M.Vitázková [1*], F. Kurtuldu [1], N.Mutlu [1], E.Vidomanová[1], Z.Vargas[1], M.Michálek[1]
[1] FunGlass, Alexander Dubček University of Trenčín, 911 50 Trenčín, Slovakia

Abstract:
The increasing field of theragnostics has instigated intense exploration into multifunctional nanomaterials, particularly mesoporous bioactive glass nanoparticles (MBGNs), which hold immense promise for integrated diagnostic and therapeutic applications. This study investigates the nuanced influence of cobalt (Co) and boron (B) on the properties of MBGNs, aiming to elucidate their impact on structural, chemical, and biological aspects for potential theragnostic applications. The synthesized nanoparticles [1]underwent comprehensive characterization employing advanced techniques. X-ray diffraction (XRD) was employed to recognize structural changes induced by Co and B incorporation while scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provided complex details regarding morphological alterations. Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were utilized to unravel changes in the chemical composition, offering insights into the surface functional groups and elemental states. Inductively coupled plasma optical emission spectrometry (ICP-OES) quantified the elemental composition, establishing the extent of Co and B integration. To assess the bioactivity of the modified MBGNs, their ability to induce hydroxyapatite-like crystal formation was evaluated. Furthermore, antibacterial efficacy against Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) was investigated, shedding light on the potential of these nanoparticles for combating bacterial infections. Additionally, the impact of Co and B modifications on cellular behavior was studied using MG-63 (osteosarcoma) and HDFa (human dermal fibroblast) cell lines. Cell viability assays provided crucial information regarding the biocompatibility and cytotoxicity profiles of the modified MBGNs.This multifaceted investigation yields a nuanced understanding of how the introduction of Co and B influences the physicochemical properties of MBGNs. These insights not only contribute to the fundamental knowledge of nanomaterial design but also pave the way for the development of advanced theragnostic platforms, showcasing the potential of Co- and B-modified MBGNs on angiogenesis and osteogenesis [2] in revolutionizing personalized medicine as well as the very understanding of the impact of these ions on cell biology.

Keywords: boron, cytocompatibility, cobalt, mesoporous bioactive glass nanoparticles, theragnostic

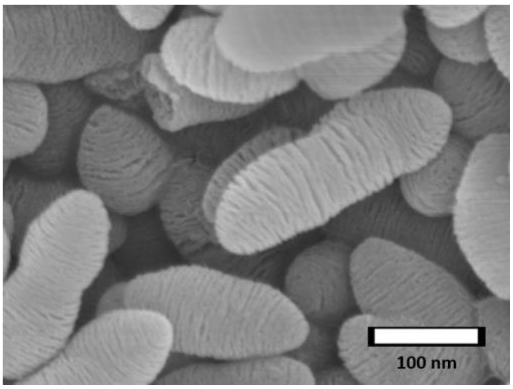


Figure 1: The Figure illustrating the well-dispersed co-doped mesoporous bioactive glass nanoparticles shows the nonuniform worm-like porosity with spherical and pineal particle shape.

ACKNOWLEDGMENT

This study was carried out in the framework of the project FunGlass which has received funding from the European Union´s Horizon 2020 research and innovation programme under grant agreement No 739566. The financial support of this work by the grants SAS-MOST JRP 2023 and APVV-20-0322 is gratefully acknowledged.

References:

1. Zheng, K. & Boccaccini, A. R. Sol-gel processing of bioactive glass nanoparticles: A review. *Adv. Colloid Interface Sci.* **249**, 363–373 (2017).
2. Chen, S. *et al.* Multi-targeted B and Co co-doped 45S5 bioactive glasses with angiogenic potential for bone regeneration. *Mater. Sci. Eng. C* **112**, 110909 (2020)

Spray dried drug loaded zein microparticles for active wound healing

Chiara Gnoccchi[1,2,*], Martina Lenzuni[3], Fabrizio Fiorentini[1], Danila Merino[4], Maria Summa[5], Rosalia Bertorelli[5], Giulia Suarato[6], Athanassia Athanassiou[1]

[1]Smart Materials, IIT, Genoa, Italy - [2] DIBRIS, University of Genoa, Italy - [3] DICCA, University of Genoa, Italy – [4]SusBioComp, POLYMAT, San Sebastian, Spain - [5]Translational Pharmacology, IIT, Genoa, Italy - [6] CNR-IEIIT, Italy

Abstract:
Treating wounds, regardless of the type, is a challenge that doctors and health care workers face in their everyday life. The normal healing process encompasses numerous molecular and cellular mechanisms, from inflammation to regeneration of the damaged tissues. Every single step requires a precise sequence of biochemical events and the active participation of specific cells and molecules. Yet, in chronic wounds the inflammation process does not evolve in standard times; instead, the cascade of the subsequent events that lead to the healing is delayed [1]. This condition rises the chances for the wound to be infected by dangerous pathogens. Therefore, an ideal dressing should support the wound during its healing process, following the dynamics of tissue repair, while, at the same time, preventing the initial inflammatory phase from lasting too long. One strategy can be the release of anti-inflammatory and anti-bacterial compounds to protect the lesion from a likely bacterial contamination. Within this frame, zein proteins represent a promising material. Their large availability alongside with their slow degradation rate in aqueous milieus make them particularly suitable for this kind of application, especially when combined with naturally derived anti-inflammatory drugs [2].
In this study, we fabricated zein microparticles via spray drying, blank and loaded with a type of chemically modified curcumin presenting anti-inflammatory and antioxidant properties. Spray drying is a widely used process to transform a solution, suspension, or emulsion into a powder. The technique consists in the atomization of a solution, the evaporation of the solvent and eventually the separation of the powder from the drying gas. Spray-drying offers the advantages of tailoring both particle attributes (e.g., particle size, specific surface area, morphology) and powder properties (e.g., flowability, compressibility, and bulk density), therefore it guarantees a high reproducibility of the whole process.
During the optimization of the fabrication process, different surfactants were studied, to stabilize the solution and to maximize the yield. The so obtained formulations were chemically and physically characterized, in terms of morphology, size, zeta potential and atomic composition. Tests about the degradation rate of the microparticles showed a slow and controlled degradation mechanism. Therefore, also the release behavior of the system has been studied, alongside its antioxidant properties in vitro on human keratynocytes and its antibacterial properties on *Escherichia Coli*.

Keywords: wound healing, biomaterials, zein, mCUR, antioxidant

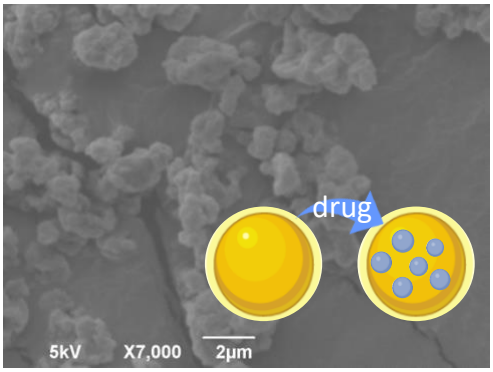


Figure 1: SEM image of the spray dried microparticles with a schematic that shows drug encapsulation.

References:

1. Sorg, H.; Tilkorn, D. J.; Hager, S.; Hauser, J.; Mirastschijski, U., Skin wound healing: an update on the current knowledge and concepts. *European Surgical Research* **2017,** *58* (1-2), 81-94.
2. Jaski, A. C.; Schmitz, F.; Horta, R. P.; Cadorin, L.; da Silva, B. J. G.; Andreaus, J.; Paes, M. C. D.; Riegel-Vidotti, I. C.; Zimmermann, L. M., Zein-a plant-based material of growing importance: New perspectives for innovative uses. *Industrial Crops and Products* **2022,** *186*, 115250.

Complex composites based on collagen scaffold as wound dressings

M. Deaconu [1,2,*], A.-M. Brezoiu [2], A.-M. Prelipcean [3], R. Mitran [4], C. Matei [2], D. Berger [2]

[1] CAMPUS Research Institute, National University of Science and Technology Politehnica Bucharest, Bucharest, Romania
[2] Faculty of Chemical Engineering and Biotechnologies, National University of Science and Technology Politehnica Bucharest, Bucharest, Romania
[3] National Institute of R&D for Biological Sciences, Bucharest, Romania
[4] "Ilie Murgulescu" Institute of Physical Chemistry, Bucharest, Romania

Abstract:
Our study introduces composite materials based on collagen scaffolds that have the potential to be used as wound dressings that could assist and aid the multiple issues related to wound healing, like antibacterial infections, anti-inflammatory effects, enhanced stability of bioactive ingrdients, and stimulation of cellular proliferation. The complex composites consist of an antibacterial agent encapsulated in mesoporous silica nanoparticles (MSN), which were included in a collagen scaffold.
Polyphenolic extracts were chosen as antibacterial agents, due to their demonstrated antibacterial activity against Gram-positive and Gram-negative bacteria, but also good biocompatibility towards HaCaT skin cells and anti-inflammatory effects. MSN functionalized with organic groups were used as reservoir for the bioactive component, the polyphenolic extract, which was encapsulated to enhance its stability over time. Collagen scaffolds have been approved by the Food and Drug Administration for use in different clinical applications [1]. As a protein, collagen could represent a challenge when used in biomedical applications due to its low thermal and chemical stability. Our approach regarding the thermal stability of the collagen scaffold consisted of both physical and chemical modification of the scaffold. The introduction of functionalized MSN demonstrated an enhancement of the thermal stability of the scaffold due to the electrostatic interactions between the surface of the silica nanoparticles and the amino acids in the collagen, without interfering with the triple helix structure of the protein [2]. The second method proposed for the enhancement of thermal stability was the introduction of zinc ions into collagen scaffold. The collagen structure was not disturbed by the presence of zinc ions. Furthermore, zinc has anti-inflammatory properties and stimulates cell motility [3]. The composites enhanced fibroblast mobility and showed promising results for their use in developing effective wound dressings.

Keywords: collagen scaffold, mesoporous silica nanoparticles, polyphenolic extract, wound healing.

Acknowledgements: This work was financially supported by the UEFISCDI National Funding Agency through the project PCE no. 117/2022.

References:

1. Sorushanova, A., Delgado, L.M., Wu, Z., Shologu, N., Kshirsagar, A., Raghunath, R., Mullen, A.M., Bayon, Y., Pandit, A., Raghunath, M., Zeugolis, D.I. (2019) The collagen suprafamily: From biosynthesis to advanced biomaterial development, *Adv. Mater.*, 31, 1801651.
2. Deaconu, M., Prelipcean, A.-M., Brezoiu, A.-M., Mitran, R.-A., Matei, C., Berger, D. (2023) Novel collagen-polyphenols-loaded silica composites for topical application, *Pharmaceutics*, 15, 312.
3. Tapiero, H., Tew, K.D. (2003) Trace elements in human physiology and pathology: Zinc and metallothioneins, *Biomed. Pharmacother.*, 57, 399–411.

Functional characterization of *Hermetia illucens*-derived chitosans for wound healing applications

M. Giani[1*], B, Vigani[1], G. Sandri[1], A. Guarnieri[2], P. Falabella[2], S. Rossi[1]
[1] Department of Drug Sciences, University of Pavia, Pavia, Italy
[2] Department of Sciences, University of Basilicata, Potenza, Italy

Abstract:
Chitosan (CS) is a biocompatible natural chitin-derived polymer composed of β(1-4)-D-glucosamine and N-acetyl-D-glucosamine monomers. Numerous beneficial effects for human health have been attributed to chitosan. In particular, due to its antioxidant and antimicrobial properties, CS is one of the most investigated bopolymers for wound healing applications. Although commercial CS is mostly obtained from marine crustacean chitin, this source has several drawbacks including seasonal supply limitation and its dependence on environmental conditions. Therefore, alternative CS sources are needed, such as chitin from insects. Among them, the black soldier fly (*Hermetia illucens* L. (Diptera: Stratiomyidae)) stands out as a promising candidate [1]. The aims of the present project are: i) the investigation of the functional properties and the bioactivity of CS obtained from this unlimited source (CS*h*) in comparison with those of a commercial CS from marine crustacean chitin (CS*m*), ii) the development of sponge-like scaffolds based CS*h* intended for wound healing applications.
Bleached and unbleached CS*h* were obtained from *Hermetia illucens* pupal exuviae, which are side streams from bioconverter farms. They were compared with a commercial CS*m* of similar molecular weight.
Unbleached CS*h* showed, when hydrated in acetic acid 1% v/v, rheological properties comparable to those of CS*m*. In particular for concentration higher than 4% w/v, unbleached CS*h* was characterized by loss tangent values lower than 1, indicating a marked prevalence of the elastic behaviour on the viscous one. Such behaviour suggests that CS*h* is a good candidate for the preparation of wound dressings that, after the exudate uptake, protect the wound bed from external stresses.
In *vitro* tests performed on human dermal fibroblasts pointed out that all the three CS were biocompatible and significantly enhanced fibroblasts proliferation; unbleached CS*h* was the most effective one (135 ±6 % cell viability). It also showed the highest antioxidant potential, reducing the oxidative stress caused by hydrogen peroxide to fibroblasts: cells treated with unbleached CS*h* and exposed to the oxidant agent presented viability values of up to 83(±4)% vs 50(±2)% observed for untreated cells.
The highest antioxidant potential of unbleached CS*h* could be due to the presence in the sample of melanin, well-known for its antioxidant properties, that forms complexes with chitosan [2].
Considering the promising properties showed by *CSh*, sponge-like dressings were obtained by frreze-drying CS*h* solutions [3] and characterized for: i) morphology (SEM); ii) capability to absorb a medium mimicking wound exudate; iii) mechanical properties before and after hydration; iv) rheological properties of the gel formed upon hydration; v) in vitro bioadhesion and biodegradation, vi) capability to support fibroblast migration and proliferation.
In conclusion, this research highlights the great potential of *Hermetia illucens* as a valuable alternative source of chitosan with respect to marine crustaceans.

Keywords: chitosan, *Hermetia illucens*, wound healing, sponge-like dressings

References:

1. Triunfo, M., Tafi, E., Guarnieri, A., Salvia, R., Scieuzo, C., Hahn, T., Zibek, S., Gagliardini, A., Panariello, L., Coltelli, M.B., De Bonis, A., Falabella, P. (2022). Characterization of chitin and chitosan derived from *Hermetia illucens*, a further step in a circular economy process. *Sci Rep.*, 12(1):6613. https://doi.org/10.1038/s41598-022-10423-5
2. Khayrova, A., Lopatin, S., Varlamov, V. (2021). Obtaining chitin, chitosan and their melanin complexes from insects. *Int J Biol Macromol.*, 167:1319-1328. doi: 10.1016/j.ijbiomac.2020.11.086.
3. Valentino, C., Vigani, B., Zucca, G., Ruggeri, M., Boselli, C., Icaro Cornaglia, A., Malavasi, L., Sandri, G., Rossi, S. (2023). Formulation development of collagen/chitosan-based porous scaffolds for skin wounds repair and regeneration. *J Biol Macromol* 242:125000

Novel antibacterial coating: functionalization with bovine serum albumin and silver

C.Reggio[1], S. Spriano[1], A. C .Scalia[2], A. Cochis[2]
[1]DISAT, Politecnico di Torino, Turin, Italy
[2] Università del Piemonte Orientale, Novara, Italy

Abstract:
Avoid infection due the bacterial adhesion on a bone implant is a challenge for many researchers, here it was engineered a novel coating by using Bovine Serum Albumin (BSA) and silver on a Ti6Al4V titanium alloy Chemical Treated (CT) and the same smooth alloy (Ti64). Silver can have an antibacterial action but also a cytotoxic effect, and our purpose was to investigate the mechanism of antibacterial action and cytotoxicity of samples directly functionalized with silver or using a pre-adsorption of BSA to bind silver [1]. A direct functionalization was performed in 5ml of 0.01M $AgNO_3$ for 2h in dark tubes at RT, obtaining Ti64_Ag and CT_Ag. Ti64_BSA_Ag and CT_BSA_Ag were obtained by first adsorbing BSA on the substrate and then functionalizing with $AgNO_3$. The analyses performed include FESEM images, XPS, analysis of silver release in water and D-MEM, halo inhibition zone test with S. Epidemidis (non-pathogenic), direct and indirect cytocompatibility test with mesenchymal cells, and antibacterial test with S. Aureus (pathogenic - ISO 22196).

The FESEM images showed nanoparticles of different dimensions on Ti64_Ag and Ti64_BSA_Ag, but they were not visible on CT_Ag and CT_BSA_Ag because of the nanotexturing of the surface. The XPS results showed that the presence of BSA increased the quantity of silver on both substrates. The halo inhibition zone test, performed with S. Epidemidis, showed that Ti64_Ag and Ti64_BSA_Ag had not an antibacterial effect. On the contrary, CT_BSA_Ag showed the highest effect against bacteria with respect to all samples, with a well-defined inhibition halo. A small halo was observed around CT_Ag. The results were in agreement with the release tests, where Ti64_Ag and Ti64_BSA_Ag had not a significant release of silver while it was observed on CT_Ag and CT_BSA_Ag. The direct antibacterial test showed Ti64_BSA_Ag, CT_Ag, and CT_BSA_Ag had antibacterial activity against S. Aureus. The indirect cytocompatibility cell test showed the cells were alive and spread when cultured for 24h or 48h in a D-MEM conditioned with the release solutions of different samples for 1-3-7 days. This evidenced that the release of silver was below the cytotoxicity threshold for all samples. Unfortunately, the direct cytocompatibility test failed, Ti64_BSA_Ag, CT_Ag, and CT_BSA_Ag were cytotoxic. This was probably due to the formation of silver nanoparticles, confirmed by the High Resolution of XPS silver spectra. The role of ion release and direct contact of cells and bacteria with silver nanoparticles on the antibacterial action and cytocompatibility is discussed case by case.

Keywords: Silver, Bovine Serum Albumin, Titanium alloy, Surface modification, Antibacterial action, surface characterization, Coatings, XPS

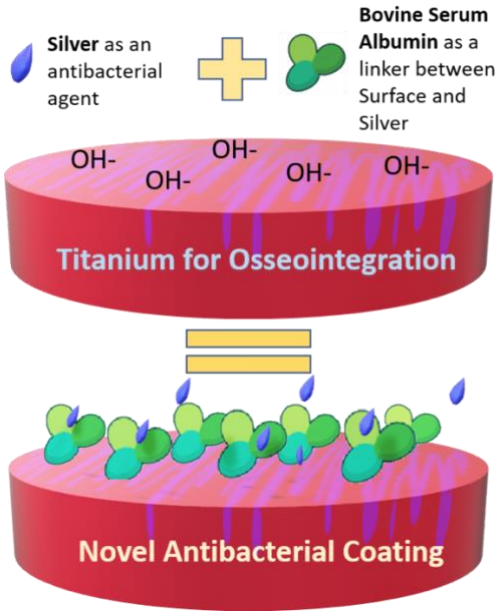


Figure 1: Figure illustrating the main actors involved in the surface modification: the chemically treated titanium, silver as an antibacterial agent, and BSA that was absorbed on the titanium used to chemically bind silver.

References:

1. Barberi, J. et al. (2022). Albumin and fibronectin adsorption on treated titanium surfaces for osseointegration: An advanced investigation. Appl Surf Sci 599, 154023

Nanostructured Multi-Responsive Coatings for Tuning Surface Properties

Suzanne Giasson*[1,2], Alberto Guerron[2]

[1,2] Laboratory of Engineering and Dynamics of Stimuli-Responsive Surfaces, Faculty of Pharmacie[1] and Department of Chemistry[2)], Université de Montréal, Québec, Canada.
*Corresponding author: suzanne.giasson@umontreal.ca

Abstract

Stimuli-responsive polymer coatings can be used as functional elements in nanotechnologies such as valves in microfluidic devices, as membranes in biomedical engineering, as substrates for culture of biological tissues or in developing nanomaterials for targeted therapies in different diseases. However, such coatings usually suffer from major shortcomings such as lack of selectivity and poor environmental stability. The talk will present multi-responsive hierarchical and hybrid polymer-based coatings aiming to overcome some of these limitations.

Hierarchical polymer coatings, consisting of two-dimensional arrays of thermo-responsive cationic PNIPAM-based microgels and surface-functionalized with non-responsive or pH-responsive polymers, was covalently grafted to substrates to tune independently the surface chemistry and the elasticity of the surface using different stimuli. The characteristic dimensions (i.e. layer thickness) and surface properties (i.e. adhesion, friction) of the microgel coatings were assessed using the Surface Forces Apparatus.

The ability to independently control the swelling and surface properties using temperature and pH as triggers was investigated for microgels in aqueous suspension and microgels immobilized on substrates.[1] Polymer chain grafting did not impede the ability of cationic PNIPAM microgels to undergo a volume phase transition above the VPTT, either in suspension

or immobilized on a substrate. Due to the presence of amino groups throughout the entirety of the microgel polymer network, the swelling behavior was also pH dependent. However, the thermo-responsive swelling was more significant than the pH-triggered one. The microgels functionalized with PEG exhibited the most promising behavior. Indeed, the thermo-triggered swelling of microgel-co-PEG did not give rise

to changes in the microgel surface properties (i.e., surface potential and adhesion) within a wide range of pH values. It was possible for the immobilized microgel-co-PEG to undergo a volume transition (swelling/shrinking) with no change in adhesion, suggesting that the surface of the thermo-responsivemicrogels remains rather hydrophilic above the VPTT. This work confirms the possibility of tuning the swelling behavior of microgels without changing the adhesive properties. Responsive surfaces whose swelling properties can be reversibly and externally altered over space and time regardless of the surface chemistry are very innovative and will enable revolutionary advances in technologies, particularly in biomedical surface engineering [2] and microfluidics where advanced assembly of functional components are increasingly required.

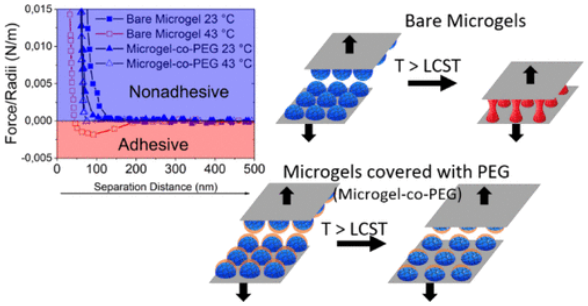


Figure 1: Illustration of the Concept for Independent Control of Swelling and Surface Properties Using Thermo-Responsive PNIPAM Microgels Surface-Functionalized with (A) pH-Insensitive PEG and (B) pH-Sensitive PDMAEMA.

References

1. Guerron A. et al., S " Multiresponsive Microgels: Toward an Independent Tuning of Swelling and Surface Properties" Langmuir 2021, 37 (38) 11212–11221.
2. Guerron A. et al., "Selectively triggered cell detachment from poly(N-isopropylacrylamide) microgel functionalized substrates." Colloids and Surfaces B: Biointerfaces, 2022, 217, p.112699

Mechanical Characterization of Electrospun Tubular Scaffolds with Randomly Distributed PLA/PCL Bicomponent Fibers

J. Oztemur [1,*], S. Ozdemir [1], H. Sezgin [1], I. Yalcin-Enis [1]

[1] Textile Engineering, Istanbul Technical University, Istanbul, Turkey

Abstract:
Cardiovascular diseases remain a leading cause of morbidity and mortality worldwide, necessitating innovative solutions to address the challenges posed by compromised blood vessels. Small caliber vascular grafts (<6 mm) play a pivotal role in cardiovascular interventions, offering crucial support for revascularization procedures, bypass surgeries, and other therapeutic strategies [1]. Optimizing the mechanical properties of vascular grafts is essential for achieving successful clinical outcomes, improving patient quality of life, and addressing the challenges associated with vascular diseases and bypass procedures.

Advances in biomaterial selection and scaffold design contribute to the development of grafts with tailored mechanical characteristics, bringing closer to the realization of highly effective and durable vascular replacements [2]. Polylactic acid (PLA), derived from renewable resources, boasts notable biocompatibility and biodegradability, with sufficient mechanical strength for load-bearing in vascular grafts whereas, polycaprolactone (PCL) offers a prolonged degradation profile, enhanced flexibility, and ductility. In addition, electrospinning method allows for precise control over fiber diameter and alignment, crucial for mimicking the intricate architecture of the native extracellular matrix. The bicomponent PLA and PCL fibers produced using coaxial electrospinning achieves a synergistic balance, addressing limitations of single-component materials, such as PLA's brittleness and PCL's lower mechanical properties [3].

This study employes the mechanical behaviors of small caliber tubular scaffolds with randomly distributed bicomponent PLA and PCL fibers. Furhermore, the study focuses on the effect of polymer type in the core and shell part of bicomponent fibers on key mechanical parameters, to assess the suitability of these scaffolds for vascular applications.

Keywords: vascular grafts, biomaterials, PLA, PCL, co-axial electrospinning, mechanical behavior, bicomponent fibers

References:

1. Oztemur, J., Ozdemir, S., Sezgin, H., & Yalcin-Enis, I. (2023). Hydrogel-based vascular grafts: State of art. In S. Thomas, B. Sharma, P. Jain, & S. Shekhar (Eds.), *Sustainable Hydrogels* (1st ed., pp. 397–442). Elsevier.
2. Ozdemir, S., Yalcin-enis, I., Yalcinkaya, B., & Yalcinkaya, F. (2022). An Investigation of the Constructional Design Components Affecting the Mechanical Response and Cellular Activity of Electrospun Vascular Grafts. *Membranes*, *12*(929).
3. Oztemur, J., & Yalcin-Enis, I. (2021). Development of biodegradable webs of PLA/PCL blends prepared via electrospinning: Morphological, chemical, and thermal characterization. *Journal of Biomedical Materials Research - Part B Applied Biomaterials*, *109*(11), 1844–1856. https://doi.org/10.1002/jbm.b.34846

Fibroblast Growth Factor 21 Adsorption on Polyelectrolyte Layers: Modeling and Experimental Studies

A. Michna [1*], Piotr Batys [1], Maria Dąbkowska [2], Bogusław Kowalski [2], Agata Pomorska [1], Monika Wasilewska [1], Zbigniew Adamczyk [1]

[1] Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland

[2] Independent Laboratory of Pharmacokinetic and Clinical Pharmacy, Pomeranian Medical University, Szczecin, Poland

Abstract:
A secreted endocrine hormone, fibroblast growth factor 21 (FGF 21), is responsible for lowering blood glucose and improving blood lipid profiles. Thus, it is a promising therapeutic target for metabolic diseases such as type 2 diabetes, obesity, and non-alcoholic steatohepatitis. However, FGF 21 molecules have a limited scope of application due to their short half-life (0.5–1.5 h) in vivo and instability in vitro. Physicochemical characterization of FGF 21 in solution was performed using both theoretical calculations (MD) and an experimental method (multi-angle dynamic light scattering, MADLS). This allowed for a more straightforward interpretation of experimental results, including the determination of FGF 21 adsorption and desorption kinetics on/from biocompatible polyelectrolyte layers, which have not been previously described in the literature. Poly(diallyldimethylammonium chloride) (PDADMAC, cationic) and anionic polyelectrolytes: hyaluronic acid sodium salt and heparin sodium salt were applied for forming the layers. The adsorption/ desorption kinetics of FGF 21 were monitored by optical waveguide light spectroscopy (OWLS), quartz crystal microbalance with dissipation (QCM-D), streaming potential measurements (SPM), and atomic force microscopy (AFM). Furthermore, the impact of the PDADMAC/FGF 21 complex on the viability of two cell lines (Chinese hamster ovary cell line and mouse connective tissue fibroblasts) was also determined. The globular molecular shape of FGF 21 was confirmed, and its size and the cross-section area were established. The dependence of the nominal charge of the protein on pH was calculated, and an isoelectric point of 5.3 was found. The tendency of FGF 21 to form dimers in bulk was also revealed by MD and MADLS. It was found that the hormone irreversibly adsorbed onto polycation-covered silica, whereas its adsorption on the negatively charged substrate was much smaller. It was also observed that FGF 21 is not toxic to either of the examined cell lines, while PDADMAC alone reduces cell viability. We also reported that the PDADMAC-FGF 21 complex was less toxic to the cells than PDADMAC alone. One can expect that the formation of stable FGF 21-biocompatible polycation complexes will extend the half-life of the growth factor in its active state and can also affect cell viability, especially that of fibroblasts, their adhesion, and proliferation.

Acknowledgments: This work was financially supported by the National Science Centre, Poland, Opus Project, 2018/31/B/ST8/03277.

Keywords: fibroblast growth factor 21; polyelectrolytes, poly(diallyldimethylammonium chloride); molecular dynamics modeling; adsorption of growth factor; optical waveguide lightmode spectroscopy; streaming potential measurements; quartz crystal microbalance; viability; fibroblasts; cell line.

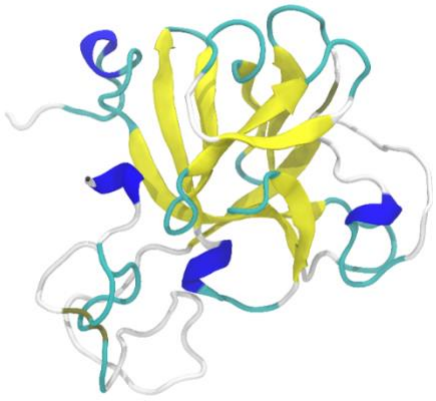


Figure 1: Snapshot of the FGF 21 molecules in 0.01 M, molecular dynamic (MD) modeling

References:

1. Wasilewska, M., Dąbkowska, M., Pomorska, A., Batys, P., Kowalski, B., Michna, A., & Adamczyk, Z. (2023). Mechanisms of Fibroblast Growth Factor 21 Adsorption on Macroion Layers: Molecular Dynamics Modeling and Kinetic Measurements, *Biomolecules*, 13(12), 1709.

Glass Fiber-reinforced Bio-derived Polybenzoxazine Composites for Medical Application

C. Jubsilp [1,*], P. Mora [1], S. Rimdusit [2]
[1] Department of Chemical Engineering, Factulty of Engineering, Srinakharinwirot University, Nakhonnayok 26120, Thailand
[2] Center of Excellence in Polymeric Materials for Medical Practice Devices, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand

Abstract:
Fiber reinforced polymer composite materials (FRPs) are widely used in several applications especially in medical application that requires varied performance characteristics including good mechanical and thermal property, flame retardance, corrosion resistance, x-ray transparency or opaqueness. In addition, the environmental concerns are considered in recent years, the medical devices produced from bio-based components are greatly developed. Therefore, glass fiber-reinforced bio-derived polybenzoxazine composites were prepared in this work. The effects of the glass fiber contents on chemical, mechanical, thermal properties was evaluated. Stress distributions by Finite element analysis (FEA) of the tooth model restored with the the composite was also investigated. It was found that mechanical property of the composites was improved with increasing glass fiber content due to reinforcing effect of the glass fiber and good interfacial adhesion between bio-derived polybenzoxazine matrix and the glass fiber. The addition of glass fiber into bio-derived polybenzazine was found to enhance thermal stability and flame retardant of the composites. The thermal expansion of the obtained composites was reduced with an increase of glass fiber content. Maximum stress by FEA of the tooth model restored with the bio-derived polybenzoxazine composite post was expected showing in dentin, which could play important role in protecting root fractures. By demonstrating favorable properties and performance, the bio-derived polybenzoxazine composite maintains significant potential for medical application like a dental fiber post.

Keywords: bio-based polymer, reinforcing fiber, eco-friendly materials, mechanical property, biomedical applications.

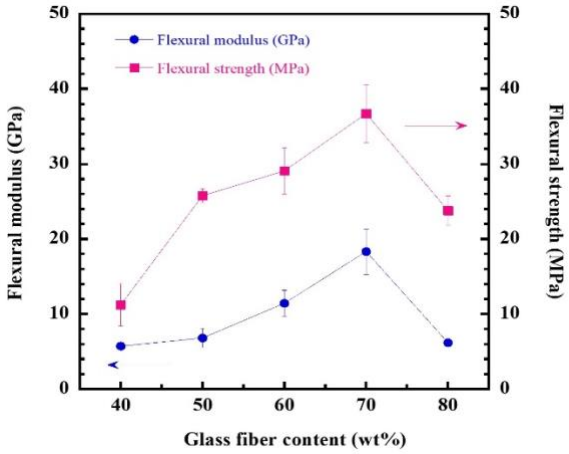


Figure 1: Figure shows flexural modulus and strength of the glass fiber-reinforced bio-derived polybenzoxazine composites with various glass fiber contents. An increase of flexural modulus and strength with increasing glass fiber content was observed. In addition, it was found that the maximum flexural modulus was belonged to the bio-derived polybenzoxazine composite reinforced with 70 wt% glass fiber, i.e., 18.3 GPa. This value was agreed to the current concept of restoring materials for teeth having elastic modulus close to dentin's, i.e., 18.6 GPa. It is expected that the fracture risk of the remaining tooth structure would be potentially decreased.

References:

1. Mora, P., Nunwong, C., Sriromreun, P., Kaewsriprom, P., Srisorrachatr, U., Rimdusit, S. (2022) High performance composites based on highly filled glass fiber-reinforced polybenzoxazine for post application, *Polymers*, 14, 4321.
2. Pegoretti, A., Fambri, L., Zappini, G., Bianchetti, M. (2002) Finite element analysis of a glass fibre reinforced composite endodontic post, *Biomaterials*, 23, 2667-2682.

Synthesis and evaluation of poly(propylene fumarate)-grafted graphene oxide as nanofiller for porous scaffolds

*Andreea Madalina Pandele
Advanced Polymer Materials Group, University Politehnica of Bucharest, 1-7 Gheorghe Polizu St., 011061, Bucharest, Romania, 2 "Costin Nenitzescu" Department of Organic Chemistry, University Politehnica of Bucharest, 1-7 Gheorghe Polizu St., 011061, Bucharest, Romania
*pandele.m.a@gmail.com

Abstract:
In an effort to obtain porous scaffolds with improved mechanical properties and biocompatibility, the current study discusses nanocomposite materials based on poly(propylene fumarate)/N-vinyl pyrrolidone(PPF/NVP) networks reinforced with polymer-modified graphene oxide (GO@PPF). The GO@PPF nanofiller was synthesized through a facile and convenient surface esterification reaction, and the successfull functionalization was demonstrated by complementary techniques such as FT-IR, XPS, TGA and TEM. The PPF/NVP/GO@PPF porous scaffolds obtainedusing NaCl as porogen were further characterized in terms of morphology, mechanical properties, sol fraction, and in vitro degradability.SEM and nanoCT examinations of NaCl-leached samples revealednetworks of interconnected pores, fairly uniform in size and shape.We show that the incorporation of GO@PPFin the polymer matrix leads to a significant enhancement in mechanical properties, which we attribute to the formation of denser and more homogenous networks, as suggested by a decreased sol fraction for the scaffolds containing a higher amount of GO@PPF. Moreover, the surface of mineralized PPF/NVP/GO@PPG scaffolds is uniformly covered in hydroxyapatite-like crystals having a morphology and Ca/P ratio similar to bone tissue. Furthermore, the preliminary biocompatibility assessment revealed a good interaction between PPF/PVP/GO@PPF scaffolds and murine pre-osteoblasts in terms of cell viability and proliferation..

Keywords: porous scaffolds, polymer-grafted graphene oxide hybrid materials, poly(propylene fumarate) composites

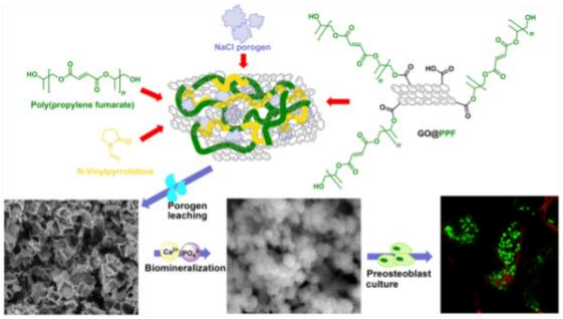


Figure 1: Synthesis of porous scaffolds

Table 1. Total porosity and structure thickness of the composites

Sample	Total porosity (%)	Pore wall thickness (µm)
PPF/PVP	80	27
PPF/PVP/GO@PPF 0.25 wt.%	83	14
PPF/PVP/GO@PPF 0.5 wt.%	83	17
PPF/PVP/GO@PPF 1 wt.%	83	17

Acknowledgements
This work was supported by a grant of the Ministry of Research, Innovation 602and Digitization, CNCS-UEFISCDI, project number PN-III-P1-1.1-TE-2021-1107, within PNCDI III, TE 110/2022-POLYREB.The nanoCT equipment was funded by the European Regional Development Fund through Competitiveness Operational Program 2014-2020, Priority axis 1, Project No. P_36_611, MySMIS code 107066, Innovative Technologies for Materials Quality Assurance in Health, Energy and Environmental – Center for Innovative Manufacturing Solutions of Smart Biomaterials and Biomedical Surfaces – INOVABIOMED.

Polymers / Composites / 3Bs Materials 2024 Session II. A

Polymers and Green Chemistry: Materials for a Circular Economy

J.H.Clark
Circa Renewable Chemistry Institute, Green Chemistry Centre of Excellence, University of York, York YO10 5DD, UK; Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai 200438, China; and Addible Ltd., ACDAL, Allenwood, Ireland.

Abstract:
There is an irresistible drive across the globe towards a so-called Circular Economy. In Europe for example, an increasing amount of policy and funding is designed to progress the transition from our traditional unsustainable linear economy to a circular and sustainable one. In practice this means that we should seek to keep all resources working with little "leakage" and thus little need for the use of virgin resources. Processes to achieve this must not in themselves be harmful to us or the environment and when new resources are to be used, they should be based on sustainable feedstocks including recycled materials. In the case of polymers, the principles of Green Chemistry apply, and green chemical technologies can be used to do the real work.

We can and should view this in a holistic way typically using a simple lifecycle approach to check on all the key elements in a materials lifetime (Figure 1).

In the simplest feedstock case, the polymer would be a natural material such as a starch or cellulose and in practice this is a viable option. However, we prefer to have a wider range of material properties than nature provides and thus we have created a library of synthetic polymers. To make these compatible with the circular economy model, we should build up such synthetic polymers using natural monomers. In practice this normally means bio-based monomers which are obtained from biomass. Here we look to the biorefinery as a source of such small molecules and there are already some successful examples. These include lactic acid and bio-ethene although the latter only addresses the feedstock questions since the main environmental impact of polyethylene is in its end-of-life. Like with conventional PE, bio-PE has a low-cost abundant feedstock (bioethanol, which can now be made greener by 2nd generation feedstocks like sugarcane bagasse). Even in the case of lactic acid, we need to be aware of the second feedstock question – if it's derived from a food grade feedstock then it may cause "harm" (e.g. by increasing the price of corn). As biorefineries become more common and more efficient, we can anticipate a growing number of useful bio-based monomers.

The processing step(s) may or may note be problematic. If it involves especially hazardous chemical reactions or is very wasteful, it does need attention to be compatible with a true circular economy.

The product stage including use and fate, can be the most difficult to be circular economy compatible. While polymers were not generally considered to present toxicity problems, the rapid build of (micro)plastics in the environment is now being seen as a threat to the eco-system. The problem is complex and needs a multi-actor approach, but technology can help by ensuring product biodegradability and/or recyclability. The former would appear to rule out many of the most important polymers including PE and PP and we need to move towards as many eco-friendly and efficient alternatives as possible. Recyclability is proving very troublesome largely because we have made our polymer-containing articles of society like packaging complex by design. Here we both need to seek clever green chemistry solutions to recycling real materials and we need to reconsider the design of those materials.

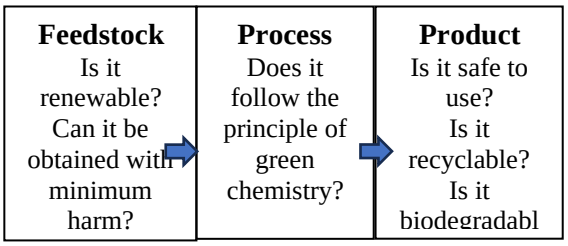


Figure 1: Figure illustrating the key steps in the lifecycle of a polymer including the questions that need to be checked to help move the material into a circular economy.

Keywords: Green chemistry; circular economy

References

1. Kümmerer, K., Clark, J.H. & Zuin, V.G. (2020). Rethinking chemistry for a circular economy. *Science*, 367(6476), 369-370.
2. Clark, J.H. (2022). Using green chemistry to progress a circular fashion industry. *Current Opinion in Green and Sustainable Chemistry*, 38, 100685.

Stimulating Biomaterial Innovation: Why the Hip Implant Has Not Changed Since 1967

Thomas J. Webster
School of Biomedical Engineering and Health Science, Hebei University of Technology, China; Division of Pre-College and Undergraduate Studies, Brown University, Providence, RI; School of Engineering, Saveetha University, Chennai, India

Abstract

The Charnley hip implant has not changed significantly since 1967 and still represents the most common hip implant. This is despite current failure rates ranging from 10 – 15%[1]. Clearly to get beyond such failure rates, we need to new ideas in orthopedics.

Nanotechnology is now found in almost every aspect of life, from the liposomes that carry vaccines for COVID-19 to coatings placed on floors to reduce wear. Over the past 20 years, the use of nanotechnology in medicine has grown from the unknown to now significantly helping to prevent, diagnosis, and treat numerous diseases. This includes the use of nanomaterials for orthopedic implants. This talk will cover the extensive efforts that have been used to commercialize such nanomaterials used as orthopedic implants to help real human patients as well as present the future directions needed for the field to continue to grow.

Numerous nanomaterials, nanoparticles, and nanotextures have been synthesized[1]. For example, off-the-shelf titanium implants were modified through anodization to possess nanoscale surface roughness (Figure 1)[2,3].

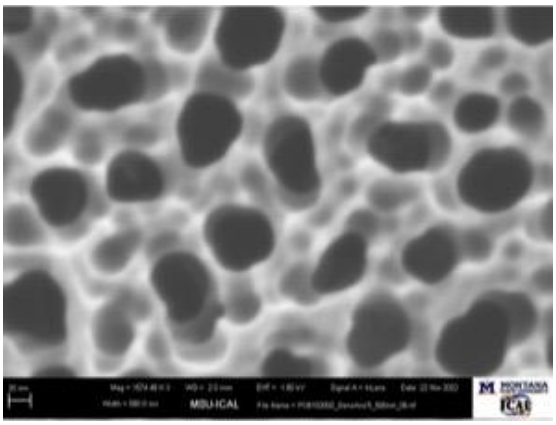


Figure 1: Nanotextured titanium implants which have shown zero cases of implant failure after implantation into 30,000 patients over the past 5 years (traditional orthopedic implant failure ranges from 10 – 15%)[3].

In vitro and in vivo studies have demonstrated that such nanotextured titanium implants inhibit bacteria, limit inflammation, and promote bone growth. Moreover, such materials have recently been commercialization and have now been implanted in over 30,000 patients over the past 5 years with no cases of implant failures (according to the Maude database where such failures are required to be reported: no infection, no bone non-unions, and no chronic inflammation).

When created at the nanoscale, the surfaces of titanium based implants can inhibit bacteria colonization without the use of antibiotics. This is significant due to the increasing concern with using antibiotics to kill bacteria and the emergence of antibiotic resistant bacteria. In fact, the Centers for Disease Control (CDC) in the U.S. has predicted that one person every three seconds will die from an antibiotic resistant bacteria by 2050. These nanotextured surfaces have proven to reduce bacteria spreading and not promote antibiotic resistant bacteria since antibiotics are not needed. Further, these nanotextured surfaces limit chronic inflammation which results in the formation of soft fibrous tissue, not hard bony tissue, around orthopedic implants. Again, this has been accomplished without using anti-inflammatories or drugs. Lastly, such nanotextured surfaces promote new bone growth.

This is all achieved through the control of surface energy via nanotextured surfaces. Such control allows us to selectively adsorb and promote the bioactivity of proteins known to inhibit bacteria, promote osteoblast (bone forming cell), and limit inflammatory cell functions. In this manner, nanotexturing surfaces provides a significant advance over the Charnley implant originally designed in 1967, which has not significantly changed since its inception.

References:

1. L. Weng and T.J. Webster (2012), *Nanotechnology* **23(48)**: 485105. [2]H. Liu and T.J. Webster (2007), *Biomaterials* **28(2)**: 354-369. [3]J.T. Seil and T.J. Webster, (2012) *International Journal of Nanomedicine* **7**: 2767-2781.

The Role of Nanofiller Geometry in the Reinforcement of Polymerbased Nanocomposites

Robert J. Young [1*], Z. Li [2], M. Liu [1]
[1] National Graphene Institute and Department of Materials, University of Manchester, Manchester M13 9PL, UK
[2] College of Aerospace Engineering, Chongqing University, Chongqing 400044, China

Abstract:
The role of the nanofiller geometry upon the Young's modulus and toughness of polymer nanocomposites has been studied through the analysis of published literature data. The types of filler considered have been nanoparticles such as carbon black (CB), graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs) reinforcing elastomers, an example of a soft polymer and epoxy resins, an example of a rigid polymer. The Young's modulus data of CB-reinforced nanocomposites is shown to follow the conventional theories for particulate reinforcement. The experimental Young's modulus data for the GNPs and CNTs have been analysed successfully using a combination of the rule of mixtures and shear lag theory. It is shown that as long as the Young's modulus of the nanofiller is very much higher than that of the polymer matrix, the Young's modulus of the nanocomposite depends only upon the volume fraction, orientation and aspect ratio of the nanofiller. The failure of the nanocomposites has been analysed in terms of the tear strength of elastomer nanocomposites and fracture toughness of the epoxy nanocomposites. It is shown that the toughening of the CB reinforced nanocomposites can be modelled using crack pinning theory whereby the propagation of the cracks is impeded by the nanoparticles in the polymer matrix acting as obstacles. It is further shown that the tear strength of the elastomer nanocomposites and fracture strength of the epoxy nanocomposites reinforced with GNPs and CNTs is controlled by nanoparticle pull-out but in the case of elastomers matrices other toughening mechanisms such as cavitation or voiding may also be induced. Overall, it is demonstrated that the best reinforcement is obtained using CNT nanofillers although there can be challenges in maintaining the aspect ratio of long CNTs through avoiding bending and aggregation at high volume fractions. Although the examples analysed in this present study are for carbon-based nanofillers, it is anticipated that the findings will be applicable to all geometries and types of rigid nanofiller particles in nanocomposites.

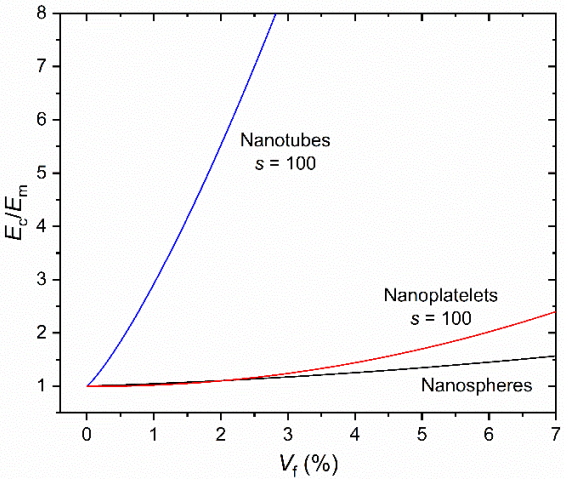


Figure: Predicted dependence of the normalised Young's modulus of a nanocomposite, E_c/E_m, upon the volume fraction of the nanofiller, V_f, where E_c is the modulus of the nancomposite and E_m is the modulus of the matrix. The illustration is for nanospheres and randomly-oriented nanoplatelets and nanotubes, both with an aspect ratio of 100. It can be seen that the best reinforcement is found for nanotubes but this can only be realized as long as they remain straight and untangled.

References:

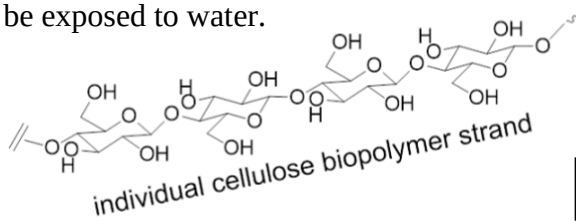
1. Zheling Li, Mufeng Liu and Robert J Young, (2024) Dependence of the Reinforcement of Polymer-Based Nanocomposites upon the Nanofiller Geometry, *Nano Materials Science*, in press.
2. Dimitrios G Papageorgiou, Ian A Kinloch, Robert J Young, (2017) Mechanical Properties of Graphene and Graphene-based Nanocomposites, *Progress in Materials Science* 90, 75-127.

Keywords: Carbon nanomaterials; elastomers; epoxy resins; Young's modulus; fracture toughness; modelling.

Molecular raincoats are better that coatings: enabling water-resistant biocomposites

J. Andrew[1], P. Ramadoss[2], G.R. Stephenson[1&2,*]
[1] Cellexcel Ltd, Enterprise Centre, Norwich Research Park, Norwich, NR4 7TJ, UK
[2] School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, UK

Abstract:
Cellulose is the ubiquitous biopolymer that holds up trees. It is also the strength-giving molecule that contributes to the utility of biocomposites when cellulosic fabrics are used to replace glass and carbon fibres in composite structural materials. Cellulose, however, degrades when it gets wet, and consequently biocomposites made from resin and cellulosic fabrics are not typically used in components for external applications, where they may be exposed to water.



This lecture presents Cellexcel's molecular-scale approach to improving the resistance to water uptake by cellulosic fabrics. By this, we aim to improve durability and increase operational life-times, delaying the onset of problems such as the appearance of surface blemishes, or cracking due to wicking. These changes in 'Cellexcellent™' materials will open up new markets for biocomposites. Cellexcel is working with partner companies to bring these opportunities to fruition. The Cellexcel approach is based on a simple principal - a molecular scale approach, not a materials-scale approach. If it is cellulose that is the source of strength, it is the molecule cellulose that should be protected.
If water ingress between the cellulose strands in crystalline cellulose (Figure 1[1]) causes wicking and swelling, then a 'molecular raincoat' (Figure 2) should address the problem. The lecture will explain the huge range of scales encountered (Figure 1) between the visible strands in woven fabrics, the microscopic cellulosic macrofibrils, the submicroscopic chains of microfibrilated cellulose

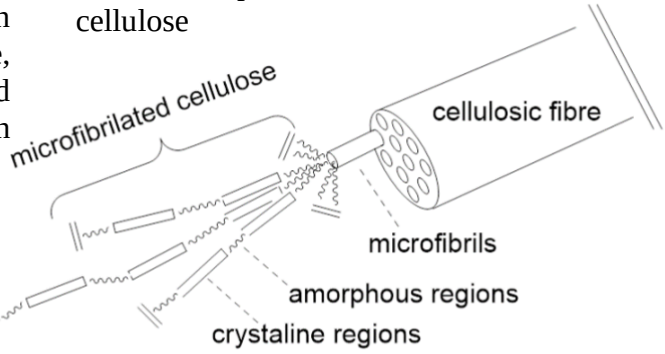


Figure 1

within them, and the nanoscale molecular biopolymers themselves.

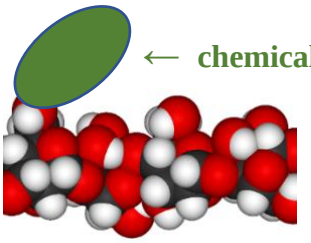


Figure 2

This is where Cellexcel's chemistry happens. The commercial and environmental benefits that result from this molecular-scale modification will also be discussed.

Keywords: water-resistant biocomposite, cellulose modification, embedded CO_2.

Reference: [1] Lavoine, N., Desloges, I., Dufresne, A., Bras, J. (2012), Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review *Carbohydr. Polym.*, 90, 735–764.

Polymers / Composites 2024
Session II. B

Fire-safe Strategies on Fiber Reinforced Polymer Composites: Progress and Challenge

De-Yi Wang
IMDEA Materials Institute, C/Eric Kandel, 2, 28906 Getafe, Madrid, Spain
Email: deyi.wang@imdea.org

Abstract:
Energy efficiency and environmental sustainability are promoting the replacement of traditional metal-based structures with fiber-reinforced polymer composites in aviation, e-mobility as well as marine industries. The lightweight and high-strength properties of polymer composites bring fascinating new choices of materials design while inevitably imparting issues regarding safety design, especially in terms of fire spread and high-temperature structural loading due to the polymer's inherent ignitability and flammability. In this work, a detailed case study was carried out to investigate the influence of fire protective coating on the fire safety and post-fire mechanical properties of FRPs with an ingeniously designed coating bilayer composition. Combustion behavior study showed that the bilayer substantially postpones the decomposition of polymer matrix. Fire resistance tests showed good thermal insulation capabilities with no burn-through for 20mins for protected composite panels. Furthermore, the tensile strength of protected composite coupons was screened and showed a retention of 79% original tensile strength compared to nearly 0% of that for pristine coupons when both suffered120s of heat/fire attack. The investigations results with a proposed mechanism offered a detailed explanation to the enhanced post-fire strength contributed by our coating layers. In addition, main flame-retardant strategies on natural fiber reinforced polymer composites (NFCs) are also summarized and reviewed, with special focus on their interaction with polymer matrix in fire behavior.

Keywords: flame retardancy, fiber reinforced polymer composites, mechanical properties, glass fiber reinforced composites, natural fiber reinforced composites, post-fire mechanical properties, fire behavious

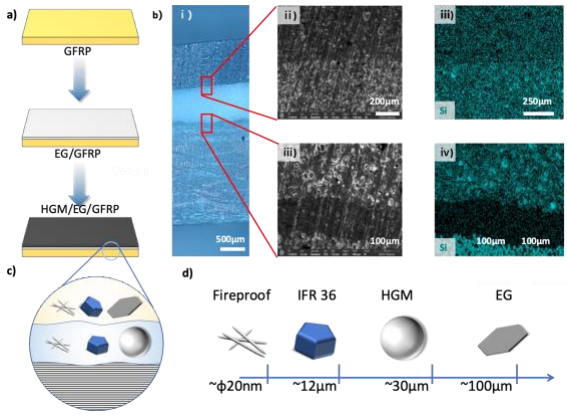


Figure 1: a), c) schematic illustration for the application of bilayer on the substrate of GFRP and b) components inside of coating layers. b) optical image (i) for the cross-section of coated GFRP. SEM (ii) and EDS images (iii) for the boundary between EG layer and the HGM layer. SEM (v) and EDS images (vi) for the boundary between the HGM layer and GFRP matrix. d) Size comparison of different fillers used in the formulation.

References:

1. Ao, X., Vázquez-López, A., Mocerino, D., González, D., Wang, D.Y.(2024) Flame retardancy and fire mechanical properties for natural fiber/polymer composite: A review, *Composites Part B: Engineering*, 268, 111069.
2. Ao, X., Xiao, J., Hobson, J., de la Vega, J., Yin, G., Puertas Cuadron M.L., Esteban Cubillo, A., González, C., Wang, D.Y. (2023) Bilayer Coating Strategy for Glass Fiber Reinforced Polymer Composites Toward Superior Fire Safety and Post-fire Mechanical Properties, *Composites Communications*, 44, 101763.

BIO-IGNITION Project: Development of Innovative Fire-Retardant Additives from Renewable Resources Compatible with Various Polymers in Construction, Automotive and Railway Sectors

A. González-Jiménez [1,*], J.V. Izquierdo [1], B. Galindo [1]
[1] AIMPLAS - Technological Institute of Plastics

Abstract:
The BIO-IGNITION project focuses on pioneering advancements in fire retardant technology by developing novel additives derived from renewable resources. These additives are designed to be compatible with a range of commonly used polymers in sectors such as construction[1], automotive, railway, and electrical-electronic industries. The primary goal is to enhance the fire resistance of polymers, addressing the inherent flammability issues associated with materials widely employed in these sectors.[2]

The project's overall objective involves extensive research on the development of new fire-retardant additives sourced from natural materials, evaluating their compatibility with various polymer bases, including thermoplastics and thermosetting polymers. The research also aims to assess the fire behavior of these new developments and their suitability for diverse industrial applications.

Polymers, despite their versatility and lightweight properties, pose significant fire safety challenges. The incorporation of fire-retardant additives is essential to improve flame retardancy, particularly in critical sectors such as construction and transportation. The project builds upon AIMPLAS's previous research on bio-based solutions to enhance fire resistance sustainably.

The project introduces a unique approach by studying the synergies between a bio-based additive developed in a prior project and the integration of different metal carbide-based nanoparticles. The envisioned benefits include enhanced gas absorption during combustion, particularly crucial in sectors like aerospace and railway, where low smoke emission is a key safety concern.

Evaluation in the project encompasses metal carbides and metal-organic frameworks (MOFs), synthesized in the previous phase. The focus is on achieving both environmental improvements and enhancing the competitiveness of plastic-related industries.

Results achieved include the successful synthesis of a fire-retardant additive based on phytic acid from seeds and chitosan obtained from crustaceans. This additive demonstrated improved fire resistance properties in polypropylene and epoxy, materials widely used in automotive, aeronautics, construction, and railway industries.

The project's innovative aspects extend to the incorporation of synergistic agents to enhance the thermal stability of bio-based additives. The synthesis of these compounds is carried out using mechanochemistry, providing a more competitive and sustainable production method.

The evaluation of developed materials includes a comprehensive analysis of their fire behavior, physical-mechanical properties, and specific tests tailored to industry requirements. Key findings indicate promising improvements in flame resistance, with some variations in properties based on additive proportions.

In conclusion, the BIO-IGNITION project represents a pioneering effort to revolutionize fire retardant technologies using renewable resources. The successful synthesis and evaluation of innovative additives demonstrate the project's potential to contribute significantly to the safety and sustainability of polymers used in critical industrial sectors.

Keywords: Composites, Flame-retardant additives, Sustainable Materials, Bio-Based Solutions

References:

1. Shen, J. et al. (2022), The flame-retardant mechanisms and preparation of polymer composites and their potential application in construction engineering, *Polymers,* 14(1), 82
2. Araaby, S. et al. (2021) Recent advances in carbon-based nanomaterials for flame retardant polymers and composites, *Composites Part B: Engineering* 212, 108675.

Smart ethylene-octene copolymer nanocomposites with hybrid MWCNT- Fe_3O_4 fillers: development, properties and applications

Janis Zicans* [1], Remo Merijs-Meri[1], Ingars Reinholds[2], Tatjana Ivanova[1]
[1]Faculty of Natural Sciences and Technology, Riga Technical University, Riga, Latvia
[2]Faculty of Chemistry, University of Latvia, Riga, Latvia

Abstract:
Sensors, actuators and other smart devices require use of advanced materials demonstrating change of certain physical properties under the influence of external fields, such as electromegnetic field. Response behaviour of so called smart materials may be improved by hybridization. For an example, by modifying a polymer matrix with nanofillers of different aspect ratios or chemical functionalities may endow unique set of properties to the resulting composite thus enhancing its application potential. Thus co-synthesyzed hybrid fillers from carbon nanotubes (MWCNTs) and iron(II, III) oxide (Fe_3O_4) may be used to tailor electrical and magnetic properties to a polymer composite. The current research is devoted to development and characterization of smart ethylene-octene (EOC) nanocomposites with magnetite (Fe_3O_4), multi-wall carbon nanotube (MWCNT) and MWCNT/Fe_3O_4 hybrid fillers. In the first stage of the research a method of functionalization of multi-wall carbon nanotubes (MWCNT) with magnetite (Fe_3O_4) has been acquired to obtain MWCNT- Fe_3O_4 hybrids at different proportionality ratios of the ingredients. In the second stage of the research a method of development of the hybrid filler modified ethylene-octene copolymer (EOC) masterbatches is used to obtain thermoplastic EOC-MWCNT/Fe_3O_4 composites. Structural, mechanical, thermal, electrical and magnetic properties of the obtained hybrid nanocomposites have been characterized.
It has been revealed that the highest stiffness, thermal stability and electrical conductivity of the nanocomposites may be achieved by introducing MWCNT containing nanofillers in the EOC matrix. However, by increasing Fe_3O_4 content in the hybrid nanofiller leads to improved thermal conductivity and magnetic properties of the investigated nanocomposite. Use of MWCNT/30Fe_3O_4 hybrid filler ensures considerable increment of EOC nanocomposite's electrical conductivity and moderate increment of its thermal conductivity, which is important for development of innovative thermoelectric devices [1].

Keywords: electrically conductive, magnetic filler, masterbatch synhesis, melt compounding, thermoplastic composite, properties.

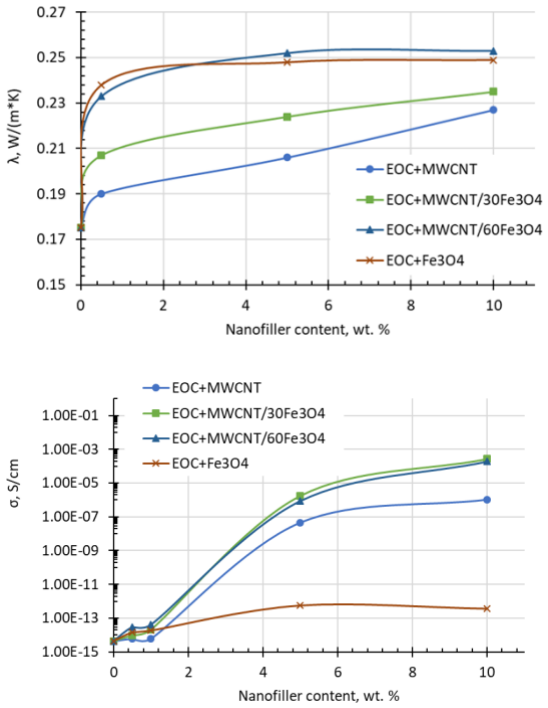


Figure 1: Figure illustrating the change in thermal and electrical conductivity of the investigated thermoplastic composites.

References:

1. Y. Wang, L. Yang, X.-L. Shi, X. Shi, L. Chen, M.S. Dargusch, J. Zou, Z.-G. Chen, Adv. Mater., 2019, 31(29), 1807916.

Surface and mechanical properties of polymer nanocomposite PVDF-HFP/PVP/SiO_2 with anti-fouling properties

Urška Gradišar Centa[1*], Meta Sterniša[2] and Lidija Slemenik Perše[1]
[1] Laboratory for Experimental Mechanics, Faculty of Mechanical Engineering, University of Ljubljana, Aškerčeva cesta 6, 1000 Ljubljana, Slovenia
[2] Department of Food Science and Technology, Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia

Abstract:
Nanoparticles of silicon dioxide (SiO_2) are used as structural materials in various fields such as microelectronics, food and pharmaceutical industries, biomedical research, catalytic technology, and sensing [1]. In addition, silica is one of the most abundant components of the earth's crust and the main component of sand and can be obtained from food waste or plants. Crystalline and amorphous silica occurs in nature. SiO_2 improves the mechanical properties of composite materials and can enhance the antimicrobial activity of functionalized materials [2], which are designed to prevent bacterial colonization of surfaces – a basic survival mechanism that provides microorganisms with advantages such as better access to nutitional sources, improved interactions, and greater stability.
Given the increasing problem of antimicrobial resistance due to exposure of bacteria to many different antimicrobial agents, solutions are being sought to prevent bacterial colonization of surfaces by altering surface properties such as surface charge, wettability, roughness, topography, and stiffness (Figure 1)[3].

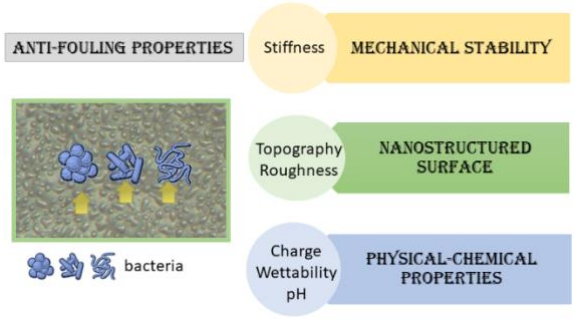


Figure 1. Schematic representation of surface properties that can contribute to anti-fouling activity.

Numerous polymers and their blends offer a wide range of possibilities for the development of such materials. In the present work, we have studied the addition of silica nanofiller in polymer nanocomposite, based on the combination of the polymers PVDF-HFP (poly(vinylidene fluoride-co-hexafluoropropylene)) and PVP (polyvinylpyrrolidone). PVDF-HFP/PVP blend has previously been shown to improve surface properties [4] and to be a good carrier for antimicrobial MoO_3 nanowires [5].
The mesoporous silica with high specific surface area was used as a nanofiller for the preparation of polymer nanocomposites PVDF-HFP/PVP/SiO_2 with different ratios between the components. The nanocomposites were prepared by the solution casting method.
The nanocomposites were characterized in terms of their surface and mechanical properties – optical microscopy, differential scanning calorimetry (DSC), nanoindentation, wettability and dissolution dynamics measurements were performed. Considering the most favorable properties compared to polymer blends alone, we investigated the anti-fouling activity on two bacterial strains, Gram-positive *S. aureus* and Gram-negative *E. coli*.

Keywords: Polymer nanocomposite; silica; bacterial colonization; anti-fouling properties.

References:

1. Nayl A. A. et al., (2022) Recent progress in the applications of silica-based nanoparticles, *RSC Advances*, 12, 13706–13726.
2. Tian B. et al., (2021) Antibacterial applications and safety issues of silica-based materials: A review, *Int J Appl Ceram Technol.* 18, 289-301.
3. Babutan, I. et al., (2021) Antimicrobial Polymeric Structures Assembled on Surfaces, *Polymers*, 13(10), 1552.
4. Gradišer Centa, U. et al., (2022) The effect of PVP on thermal, mechanical, and dielectric properties in PVDF-HFP/PVP thin film, Coatings, 12, 1241.
5. Gradišar Centa, U. et al., (2020) Novel nanostructured and antimicrobial PVDF-HF/PVP/MoO_3 composite, *Surface Innovations*, 9(5), 256–266,

Effect of a Nanocellulose on the Optical and Mechanical Properties of Flax Pulp

Josef Bárta[1], Kateřina Hájková[1], Adam Sikora[1]
[1] Faculty of Forestry and Wood Sciences, Czech University of Life Sciences Prague, Kamýcká 129, 165 00 Prague, Czechia

Abstract:
In the interest of our times, novel or modified materials are studied to create and enhance today's materials. Flax pulp is used because of its higher mechanical properties. This paper modified this material with the addition of nanocellulose to determine/assess the possibility of increasing some of the properties. Mechanical examinations assessed differences in properties, such as tensile strength, breaking length, and tensile energy absorption. For further determination, an optical examination was performed to evaluate colour differences in individual materials produced in this work. Different types of applications were compared to paper without the addition of nanocellulose. Specifically, nanocellulose was added to pulp mass and applied to a paper by spraying, coating, and lastly by using ultrasound. Results for mechanical properties are best for application form of spraying in terms of least use nanocellulose (3.5%) and the highest mechanical properties in most cases compared to reference paper product. The colour difference is the highest for those applications, where nanocellulose addition was more sufficient for two-layer coating, spraying, and using ultrasound. Data from this work serve as an extension to nanocellulose utilization for paper products, whether it may enhance specific properties of modified material.

Keywords: modified paper, nanocellulose, soda flax pulp, tensile strength, colour difference

Effect of Solvent Additives on Polyelectrolyte Physicochemical Properties and Complexation

P. Batys [1*], M. Morga [1], M. Khavani [2], T. Kastinen [2,3], I. Leszczyńska[1,4], S. M. Lalwani[5], C. I. Eneh[5], J. L. Lutkenhaus [5,6], M. Sammalkorpi [2,3]

[1] Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Krakow, Poland

[2]Department of Chemistry and Materials Science, and [3]Department of Bioproducts and Biosystems, Aalto University, Finland

[4]Department of Materials Engineering, University of Applied Sciences, Tarnow, Poland

[5]Artie McFerrin Department of Chemical Engineering, Texas A&M University, and [6]Department of Materials Science and Engineering, Texas A&M University, College Station, Texas, USA

Abstract:

The effect of solvent additives on aqueous solutions of polyelectrolytes, such as poly(styrenesulfonate) (PSS), poly(diallyldimethylammonium) (PDADMA), poly-L-lysine (PLL) and poly-L-glutamic acid (PGA) and their complexation interactions are examined here via molecular dynamics simulations, interconnected laser Doppler velocimetry, and quartz crystal microbalance with dissipation. It is found that urea and ethanol have significant, yet opposite influences on polyelectrolyte solvation and interactions.[1] Notably, ethanol is systematically depleted from solvating the charge groups but condenses at the hydrophobic backbone of PSS. As a consequence of the poorer solvation environment for the ionic groups, ethanol significantly increases the extent of counterion condensation. On the other hand, urea readily solvates both, PSS and PDADMA and replaces water in solvation. For PSS, urea causes disruption of the hydrogen bonding of the PSS headgroup with water. In PSS–PDADMA complexation, these differences influence changes in the binding configurations relative to the case of pure water. Specifically, added ethanol leads to loosening of the complex caused by the enhancement of counterion condensation; added urea pushes polyelectrolyte chains further apart because of the formation of a persistent solvation shell. In total, we find that the effects of urea and ethanol rise from changes in the microscopic-level solvation environment and conformation resulting from solvating water being replaced by the additive. The differences cannot be explained purely via considering relative permittivity and continuum level electrostatic screening. Taken together, the findings could bear significance in tuning polyelectrolyte materials' mechanical and swelling characteristics via solution additives.

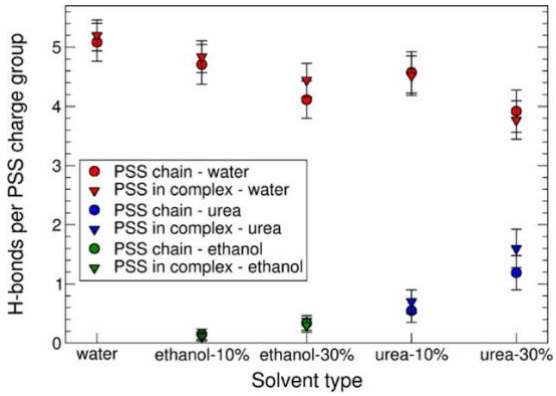


Figure 1: Calculated average number of hydrogen bonds between PSS and water, ethanol, or urea molecules for the PE single chains (circles) and complexes (triangles).

Keywords: solvent additives, polyelectrolytes, polyelectrolyte complexes and multilayers, molecular dynamics method.

Acknowledgements: The study was supported by the National Science Centre Research Grant Sonata, UMO 2018/31/ D/ST5/01866, the Academy of Finland by Centres of Excellence Programme (2022–2029, LIBER) under project no. 34611, and the U.S. National Science Foundation, grant No. 1905732.

References:

1. M. Khavani, P. Batys, S. M. Lalwani, C. I. Eneh, A. Leino, J. L. Lutkenhaus, M. Sammalkorpi, *Macromolecules* 2022 55 (8), 3140-3150

Influence of external factors on the structure of poly-L-lysine (PLL) and poly-L-glutamic acid (PGA) and formation of PLL/PGA complexes

M. Morga [1*], A. Harmat [2,3], T. Kastinen [2,3], , P. Bonarek[5], D. Lupa[6], D. Kosior [1], Z. Adamczyk [1], Jodie L. Lutkenhaus [7,8], , M. Sammalkorpi [2,3] , P. Batys [1]

[1] Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Krakow, Poland
[2]Department of Chemistry and Materials Science, and [3]Department of Bioproducts and Biosystems,
[5]Department of Physical Biochemistry, Jagiellonian University, Krakow, Poland
[6]Faculty of Physics, Astronomy, and Applied Computer Science, M. Smoluchowski Institute of Physics, Jagiellonian University, Krakow, Poland
[7]Artie McFerrin Department of Chemical Engineering, Texas A&M University, and [8]Department of Materials Science and Engineering, Texas A&M University, College Station, Texas, USA

Abstract:
The biocompatible and stimuli-responsive polypeptides such as poly-L-lysine (PLL) and poly-L-glutamic acid (PGA) are desirable in biomedical applications. Despite the extensive experimental effort, the fundamental physicochemical properties of PPs in aqueous solutions and the mechanisms of their adsorption at solid/liquid interfaces remain largely unknown. A combination of dynamic light scattering (DLS), laser Doppler velocimetry (LDV) and the circular dichroism (CD) were applied to assess the hydrodynamic diameter, the charge of the molecules and their secondary structures, according to ionic strength and pH changes. Molecular dynamics simulations reveal the associated intra- and intermolecular binding changes in terms of intrinsic vs. extrinsic charge compensation, the role of hydrogen bonding, and secondary structure changes, aiding in the interpretation of the experimental data. To enrich the knowledge in constructing smart polymer materials of controlled coverage, structure, viscoelastic and electrokinetic properties, based on naturally occurring polyaminoacids, the effect of pH on poly-L-lysine and poly-L-glutamic acid adsorption on silica surface was investigated experimentally, via streaming potential and QCM-D methods, and complemented by molecular dynamics (MD) modeling and random sequential adsorption (RSA). These results show that not only pH provides a means to control complex formation but also that the associated changes in the secondary structure and binding conformation can be systematically used to control materials assembly. This gives access to rational design of peptide materials via pH control and furtherly their interactions with biomolecules such as proteins, enzymes etc.

Keywords: polypeptides, physicochemical characteristics of polypeptides, polypeptide complexation, DLS, LDV, circular dichroism, PLL/PGA complexation, PLL/PGA bilayers

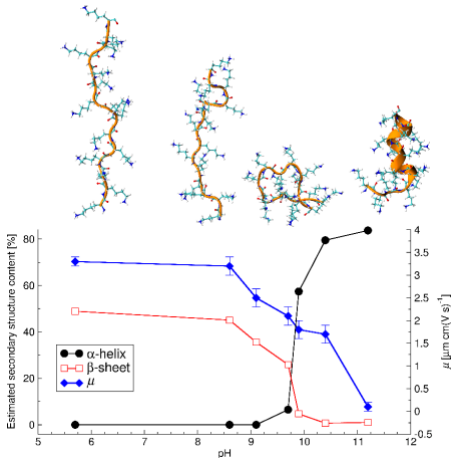


Figure 1: The experimentally determined dependence of PLL secondary structure content and the electrophoretic mobility (μ) on pH, for I = 10^{-2} M NaCl, T = 298 K. The snapshots present the AMBER99SB*-ILDNP force field predicted configurations for the corresponding pHs.

Acknowledgements: The study was supported by the National Science Centre Research Grant Sonata, UMO 2018/31/ D/ST5/01866, the Academy of Finland by Centres of Excellence Programme (2022–2029, LIBER) under project no. 34611, and the U.S. National Science Foundation, grant No. 1905732.

The effect of copper flakes surface modification on physical properties of conductive polymer composites

M. Mihelčič [1], A. Oseli, Lidija Slemenik Perše [1*]

[1] Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia

Abstract:
Conductive Polymer Composites (CPCs) are usually composed of a non-conductive (isolating) polymer matrix, and conductive fillers, which can be metallic (copper, silver, gold, etc.), carbon-based (carbon black, graphene, CNT, etc.), ceramic (BN, TiC, MXene, etc.) or metal-coated (with or without metal core). Due to various positive properties of polymer matrix, such as flexibility, low cost, low density, corrosion resistance, high specific strength, as well as the production of complex shapes through various environmentally friendly technologies, such as 3D printing, injection molding and compression molding, CPCs are gaining scientific interest in various research areas and applications [1]. On the other hand, the addition of fillers leads to the improvement of the mechanical, thermal, optical and electrical properties of the polymer. However, in order to achieve high conductivity, the selection of a filler is of great importance. The most promising fillers, achieving electrical conductivity as high as 10^7 S/m, are undoubtedly metal fillers, among which the copper flakes represent a leading conductor material for electronic applications due to their high electrical and thermal conductivity, low cost and low electron migration. However, Cu flakes are very prone to oxidation in ambient conditions, which results in reduced conductivity. In order to use Cu flakes for the production of conductive polymer products and their long-term use, it is therefore necessary to protect the surface of Cu flakes from oxidation. For this purpose, the surface modification of Cu flakes with various materials, such as silver and silica, has shown to be very successful [2-3]. However, it is not known, how the surface modification contributes to the establishment of the network, which indirectly but significantly affects functional properties such as mechanical reinforcement and electrical conductivity.
The presented study was therefore focused on surface modification of Cu-based flakes and its effect on rheological, thermal, mechanical and electrical properties. For the study, three different types of copper-based fillers flakes were used: uncoated copper, silver-coated copper and silica-coated copper flakes. The conductive polymer composites were prepared by incorporating the flakes in low-density polyethylene matrix material at various volume fractions (from 10 to 40 volume %) by using twin-screw extruder. The effects of copper surface modification was studied by rheological, thermal, mechanical and conductive properties. The results showed that surface modification of Cu-flakes significantly affects geometrical and electrical percolation thresholds.

Keywords: conductive polymer composites, copper flakes, silver coating, silica coating percolation threshold, electrical conductivity, rheological properties, thermal properties, mechanical properties, electrical properties.

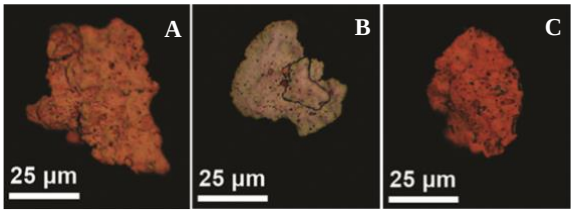


Figure 1: Figure illustrating copper surface modification of copper-based flakes used for conductive polymer composites: A) uncoated; b) silver-coated; c) silica-coated Cu flakes.

References:

1. Oseli, A.; Tomković, T.; Hatzikiriakos, S.G.; Vesel, A.; Arzenšek, M.; Rojac, T.; Mihelčič, M.; Slemenik Perše, L. (2023) Carbon nanotube network formation and configuration/morphology on reinforcing and conductive performance of polymer-based nanocomposites. *Compos. Sci. Technol.*, 237, 110010.
2. Kim, T.H.; Kim, H.; Jang, H.J.; Lee, N.; Nam, K.H.; Chung, D.; Lee, S. (2021) Improvement of the thermal stability of dendritic silver-coated copper microparticles by surface modification based on molecular self-assembly. *Nano Converg.*, 8, 15.
3. Yokoyama, S.; Takahashi, H.; Itoh, T.; Motomiya, K.; Tohji, K. Surface modification of Cu metal particles by the chemical reaction between the surface oxide layer and a halogen surfactant. (2014) J. Phys. Chem. Solids, 75, 68–73.

Chemically degradable thermoset matrix for recycling structural polymer composites

J.W. Yi*, S.W. Kim, J.W. Lee, J.S. Kim, M.K. Um
Carbon Composites Department, Korea Institute of Materials Science (KIMS), Changwon, South Korea

Abstract:
Fiber-reinforced thermoset composites have been considered as one of the promising lightweight materials for structural parts. Recently, automotive and wind turbine industry have set up a mass production system of the composite parts. One of the remarkable issues with regard to the applications is how to recycle the composites, especially with thermoset matrix. For a long time, many researchers have reported the recycling methods such as mechanical chopping, pyrolysis, chemical dissolution process and etc. However, they have some limitations on dealing with the composites in large quantities by an eco-friendly method. Therefore, there is a demand for developing a thermoset matrix resin which can be easily decomposed by a water-based solution as well as have comparable mechanical properties and chemical resistances. In this work, we estimate a new epoxy resin exhibiting a chemically degradable and mechanically robust property. The commercially available resin system consists of general epoxy resins, degradable epoxy resins, additive and hardener. In particular, the hydrophilic additive is added in order to obtain a bi-continuous phase in which one phase can play a role as a water channel. Through the channel, the water-based decomposing solution can be efficiently penetrated inside the resin. In addition, the stability of the continuous phase structure can provide good mechanical properties. Tensile, flexural and thermal properties for the resin and corresponding composite were measured. The degradability was measured by weighing the mass loss of the resin after immersing it in an aqueous decomposing solution at 100℃ for 3 hours. Experimental results showed that the resin system could be decomposed up to nearly 100% at such conditions and had excellent mechanical properties. TEM images indicated that the bi-continuous phase structure was formed during the curing reaction. Effect of the chemical structure and loading content of the hydrophilic additive will be discussed.

Keywords: composites, thermoset matrix, degradable epoxy resins, recycle, mechanical properties, bicontinuous phase,

Polymer-infiltrated zirconia ceramic networks with biodegradable and bioactive biocomposites produced by additive manufacturing

Gemma Fargas[1,2], Ernesto J. Pujol[3], Belén Begines[5], Yadir Torres[2], Luis Llanes[1,2], Ana Alcudia[4]

[1]Departament de Ciència i Enginyeria de Materials, Universitat Politècnica de Catalunya, Campus Diagonal Besòs - EEBE, Barcelona, Spain
[2]Barcelona Research Center for Multiscale Science and Engineering, Universitat Politècnica de Catalunya, Campus Diagonal Besòs (EEBE), Barcelona, Spain.
[3]Departamento de Ingeniería y Ciencia de Los Materiales y del Transporte, Escuela Técnica Superior De Ingeniería, Universidad De Sevilla, Sevilla, Spain
[4]Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad de Sevilla; C/ Profesor García González, 2. 41012, Sevilla, Spain.

Abstract:
In this work, controlled porous zirconia parts have been produced by Direct Ink Writing to enhance osseointegration by infiltrating a biodegradable and bioactive biocomposite. In doing so, the cubic geometry of pieces was obtained by perpendicular layer-by-layer deposition of yttrium-stabilized tetragonal zirconia polycrystal (3Y-TZP) and Pluronic® hydrogel ceramic paste. The specimens were prepared by robocasting assembly with 40% infill, as feed setup. Poly-ε-caprolactone (PCL), polyvinyl alcohol (PVA) (with a weight ratio of 50/50), and hydroxyapatite nanopowder (nHA) were employed to infiltrate the pores of the 3D-printed ceramic structure. The microtomography proved the homogeneous distribution of pores throughout the completely printed part. Degradation of the infiltrated scaffolds was performed in PBS solution. In this media, the formation of apatite at the surface was studied by thin-film X-ray diffraction (TF-XRD). The analysis pointed out an increase in nHA peaks, which is usually associated with osseointegration promotion. Moreover, The assessment of the mechanical properties was carried out at micro and macro scales by instrumented micro indentation and uniaxial compression tests, respectively. The results revealed that the zirconia scaffold without polymer infiltration displays lower mechanical integrity and strength resistance compared to infiltrated scaffolds.

Keywords: polymer infiltrated ceramic networks, zirconia scaffolds, biodegradable, bioactive, biocomposites, direct ink writing, additive manufacturing.

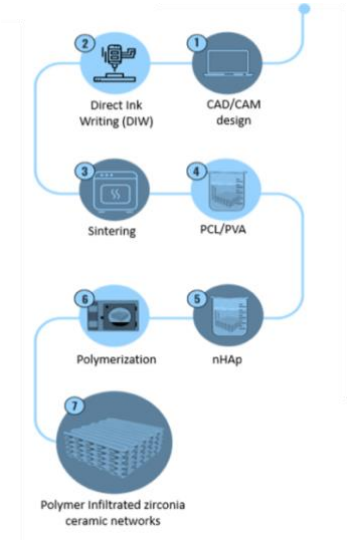


Figure 1: Figure illustrating the overall process to produce the polymer-infiltrated zirconia ceramic network: Processing steps: (1) CAD/CAM 3D design of cubic geometry, (2) Zig-zag filament layer-by-layer deposition by DIW. Postprocessing steps: (3) Drying and sintering processes. (4,5) Sequential steps for the infiltration of PVA, PCL copolymers, and nHAp particles, (6) Polymerization process, and (7) produced sample.

References:

1. Hodásova, L., Sans, J., Molina, B., Alemán, C., Llanes, L., Fargas, G., Armelin, E., (2021) Polymer infiltrated ceramic networks with biocompatible adhesive and 3D-printed highly porous scaffolds Additive Manufacturing 39, 101850.
2. M. K. Sodeyama, H. Ikeda, Y. Nagamatsu, C. Masaki, R. Hosokawa, and H. Shimizu, (2021), Printable PICN Composite

3Bs Materials Session II. C: Biomaterials Synthesis, Processing and Characterization Biobased and Biomimetic Materials / Bio interfaces / Biomaterials applications

Anti-infection Strategies Applied to Design Coating Materials for Stable and Biodegradable Biomedical Implants

Julietta V. Rau

Istituto di Struttura della Materia, Consiglio Nazionale delle Richerche, ISM-CNR, Via del Fosso del Cavaliere, 100 – 00133 Rome, Italy

Abstract:
In the next future, a significant increase in the demand for biomedical implants is projected due to population ageing and the rise in life expectancy. Currently, the primary requirements for implants include effective osteointegration, long-term stability, and antimicrobial surface capable of combating infections. To meet these objectives, metallic implants are coated with biomimetic functional ceramic biomaterials, substantially enhancing the properties of metals. This process creates a suitable bone-material interface, ultimately leading to better integration into the surrounding bone tissue. Recent findings related to biomaterials with multiple functional properties, designed as coatings on titanium and biodegradable metal alloy implants, will be presented. In the case of Mg and Zn alloy implants, the focus is on controlling their degradation rate and their bioactivity characteristics. The developed coating materials mainly consist of multi-substituted calcium phosphate materials containing trace ions with therapeutic functions, which stimulate the natural tissue response.
A crucial aspect of biomedical implants is the development of their antimicrobial characteristics – a challenging issue for sustainable medical practices, aiming to avoid the extensive use of antibiotics [1].
In this study, the synthesis of antimicrobial materials and the development of antimicrobial surfaces were conducted, and a comprehensive characterization was carried out. The structural, morphological, and mechanical features, wetting contact angle, surface topography, and behaviour in model media will be discussed. The results obtained for ion-doped calcium phosphate bioceramics will be demonstrated. These materials exhibit a wide range of specific functional properties, from antibacterial to magnetic. *In vitro* bioactivity, cell and microbiology test data, focusing on material-cell interactions, will be presented.
The specific objectives of the research are as follows:
1) Develop and synthesize a novel material with antibacterial characteristics – multi-substituted tricalcium phosphate (TCP), containing Cu2+, Mn2+, and Zn2+ ions and deposit it onto Ti and biodegradable implant materials.
2) Design, realize, and characterize optimal nanopatterning of the implant surface with the aim of maximizing its bactericidal effect, preventing biofilm formation, and promoting osteoblast cell attachment and proliferation.
3) Evaluate the *in vitro* antibacterial properties of the newly developed implants against clinically relevant bacteria. Assess *in vitro* osteoblast cell proliferation, viability, toxicity, and osteoinductive properties of the developed implants.
4) Study *in vivo* the osteointegration, the antibacterial properties, and the effects on cells in a vertebra tail defect mice model.
The specific objectives of the research are summarized in Fig. 1.
To conclude, nanostructured antimicrobial materials show promise for tissue replacement and regeneration, ensuring the required structural, chemical, morphological, and mechanical characteristics while enhancing the performance of medical implant devices.

Keywords: antibacterial, antimicrobial, coatings, biomedical implants, biodegradable biomedical implants.

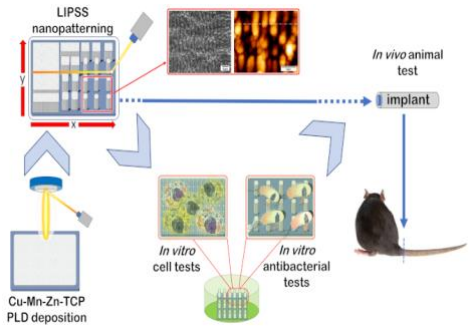


Figure 1: schemaric representation of the main objectives of the research.

Reference:

1. Fosca, M., Streza, A., Antoniac, I.V., Vadalà, G., and Rau, J.V. (2023) Ion-doped calcium phosphate based coatings with antibacterial properties, *J. Function. Biomat.*, 15(5), 250 (45 pages). https://doi.org/10.3390/jfb14050250

$CaCO_3$ Ceramics - A Bioresorbable Bone Grafting Material

S. Umemoto [1, 3], H. Unuma [2*], T. Furusawa [2], T. Goto [3,4], T. Sekino [3]
[1] Shiraishi Central Laboratories Co., Ltd., Amagasaki, Japan
[2] Graduate School of Science and Engineering, Yamagata University, Yonezawa, Japan
[3] SANKEN, Osaka University, Suita, Japan
[4] Institute for Advanced Co-Creation Studies, Osaka University, Suita, Japan

Abstract:
Bioresorbable bone grafting materials made from natural marine coral ($CaCO_3$) are clinically used [1]. If $CaCO_3$ powders can be sintered into coral-like structure, however, it would eliminate the need to harvest natural coral, avoiding damage to the marine environment and the risk of contamination with impurity elements. The present authors found that monodisperse calcium powder (ca. 150 nm) manufactured by Shiraishi Group can be sintered to almost full density at ambient pressure in a CO_2 atmosphere. Based on this finding, a SiO_2-doped $CaCO_3$ porous ceramics - an artificial coral - was prepared and its *in vivo* behavior was evaluated using a rat calvarium defect model.

A slurry containing $CaCO_3$ (calcite) powder, SiO_2 sol with 0.6 mass% of $CaCO_3$, and appropriate amounts of a diamine and a diepoxide was prepared, to which a foaming agent was added. The slurry was whisked, gelatinized at 80 °C, dried, and dewaxed before being sintered at 800 °C for 1 hour in a flow of CO_2 to obtain a sintered body with 89% porosity. The porous ceramics was pulverized into granules 1-2 mm in diameter.

The *in vivo* tests were conducted in a perfectly authenticated facility accredited by AAALAC International. Twenty-four male SD rats, 11 weeks of age, were used. A bone defect, 5mm in diameter was made in the center of the calvarium. Either the test substance, $CaCO_3$ granules, or control, β-TCP granules, was implanted in the defect. The experimental sections were retrieved at 6 and 12 weeks postoperative, sliced into thin sections 3.5 μm in average thickness, decalcified, and stained with hematoxylin-eosin.

Figure 1 shows histological pictures at 12 weeks postoperative. When $CaCO_3$ granules were implanted, now bone formation was clearly recognized within and around the granules. Bone maturation has proceeded evenly within the granules. On the other hand, when β-TCP granules were implanted, bone formation and maturation proceeded locally. Image analysis revealed no significant difference in the new bone area between $CaCO_3$- and β-TCP implantation.

Porous $CaCO_3$ ceramics should be able to be optimized with respect to porosity and pore size to maximize its bone regeneration ability, avoiding any risks of environmental and contamination issues.

Keywords: bioresorbable, calcium carbonate, porous ceramics, sintering, bone formation, *in vivo*

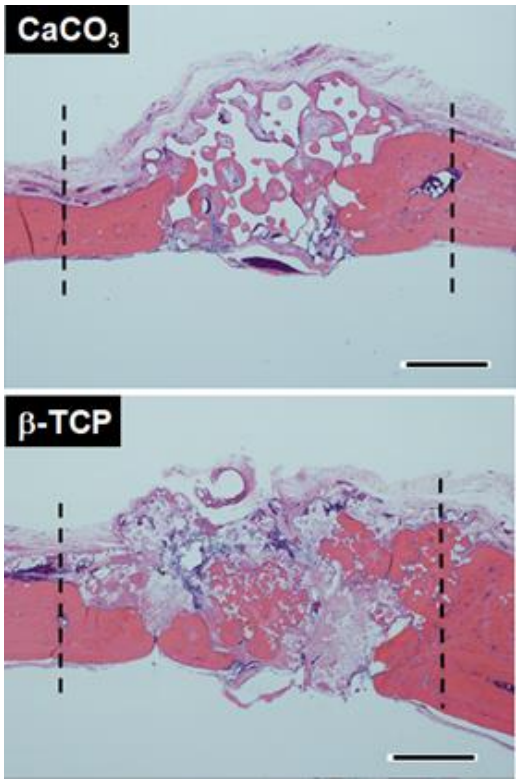


Figure 1: Histological pictures of the bone defects implanted with $CaCO_3$ and β-TCP at 12 weeks postoperative. dotted lines show the initial positions of the bone defects. Scale : 1 mm.

References:

1. Demers, C., Reggie Hamdy, C., Corsi, K., Chellat, F., Tabrizian, M., Yahia, L. (2002) Natural coral exoskeleton as a bone graft substitute: A review, *Bio-Med. Mater. Eng*., 12, 15-35.

Bio-based flexural structures based on epoxidized plant oils

A. Solt-Rindler [1,2,*], J. Janesch [1,2], L. Dumschat[1,2], O. Vay[1,2], C. Hansmann[1,2]
[1] Competence Center for Wood Composites & Wood Chemistry, Wood Material Technologies, Altenberger Straße 69, 4040 Linz, Austria
[2] University of Natural Resources and Life Science (BOKU), Department of Material Sciences and Process Engineering, Institute of Wood Technology and Renewable Materials, Konrad Lorenz-Straße 24, 3430, Tulln an der Donau, Austria

Abstract:
Bio-based flexible structures have gained popularity in the textile and automotive industries in recent years as promising alternatives to animal-based materials due to concerns over sustainability and animal welfare. There has been a growing interest in developing substitutes to traditionally syntethic textile structures using renewable and biodegradable materials[1]. Epoxidized plant oils, derived from vegetable sources such as linseed oils or soy oils, have emerged as a promising candidate for the production of eco-friendly flexibles[2]. The present work deals with the bulk curing of epoxidized linseed oil with the addition of hardeners in different mixing ratios. This study investigated curing agents that are currently used as softneres in petro-based plastics and are potentially renewable. Furthermore, bio-based filler materials were embedded in the matrix material to create all-new bio-based flexural composite materials. The properties and performance of epoxidized plant oil-based flexural structures are presented, including its mechanical strength, flexibility, and water resistance. Challenges concerning the manufacturing processes and techniques for incorporating epoxidized plant oils into flexural structures are discussed. An outlook on potential applications is given. Overall, the utilization of epoxidized plant oils offers a sustainable and renewable alternative to traditional synthetic materials, contributing to the development of eco-friendly and socially responsible products.

Keywords: bio-based flexible structures, epoxidized plant oils, bio-based hardener, renewable materials,

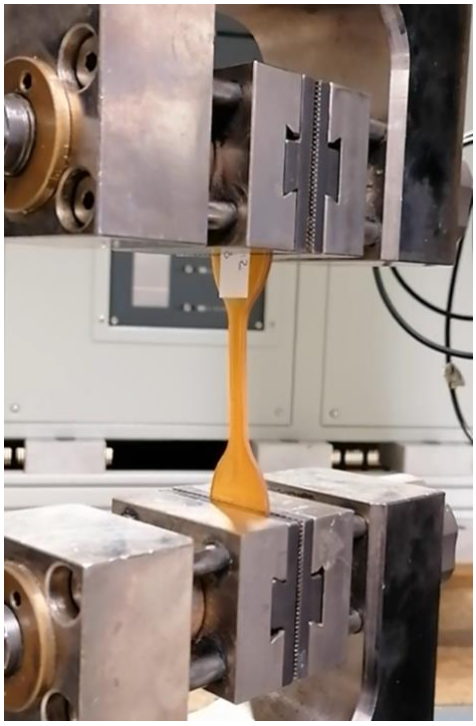


Figure 1: Tensile test of epoxidised linseed oil specimen cured with a bio-based hardener

References:

1. Meyer, M., Dietrich, S., Schulz, H. & Mondschein, A. Comparison of the technical performance of leather, artificial leather, and trendy alternatives. Coatings 11, 226 (2021).
2. Schwaiger, M. & Resch-Fauster, K. Mechanical flexible epoxy resins with 100% bio-based carbon content based on epoxidized vegetable oils. Journal of Applied Polymer Science 139, e53233 (2022).

Design of stimuli responsive antimicrobial materials based on the reversible surface grafting of trans-2-hexenal on chitosan films through imine linking

Esteve-Redondo, P.[1]., Heras-Mozos, R.[1], López de Dicastillo, C.[1], Gavara, R.[1], Hernández-Muñoz, P.[1]

[1]Instituto de Agroquímica y Tecnología de Alimentos (IATA-CSIC), Paterna, Valencia, Spain

Abstract:
Chitosan is a biopolymer which has been widely employed in the form of film to carry and release different antimicrobial volatiles by means of their physical entrapment in the polymer matrix [1]. A more sophisticated approach for the use of chitosan films as carriers of active volatiles is the employment of reversible covalent linkages based on click chemistry.
The objective of this research has been the application of reversible imine linkages for the stabilization of food grade naturally-occurring antimicrobial trans-2-hexenal on the surface of chitosan films. Imine links can be hydrolyzed under mildly acidic conditions allowing the release of the previously anchored volatile. Therefore, trans-2-hexenal was covalently attached to primary amine groups of chitosan films, the reaction was carried out in solid/liquid medium, and main reaction parameters such as trans-2-hexenal:chitosan film weight ratio, temperature and the use of HCl as catalyst were optimized by employing response surface methodology (RSM) in order to obtain trans-2-hexenal-imine-chitosan conjugates to prevent the formation of undesired bonds and side reactions. The release of trans-2-hexenal from the films was also studied in different acidic media, and their antimicrobial activity against *Penicillium expansum* and *Escherichia coli* was evaluated.
It was conversely observed that reaction without catalyst and temperatures below 25 °C resulted in films with high volatile release and therefore, great antifungal properties. Whereas, mild reaction temperatures and the presence of a catalyst gave rise to crosslinked chitosan films and low release of the volatile. Additional conjugated Michael addition of amino groups of chitosan to the α,β-unsaturation of trans-2-hexenal together with formation of imines led to a highly crosslinked structure under specific reaction parameters (Figure 1).

Keywords: biopolymer, click chemistry, antimicrobial, natural aldehydes, imine reversibility, chitosan, trans-2-hexenal.

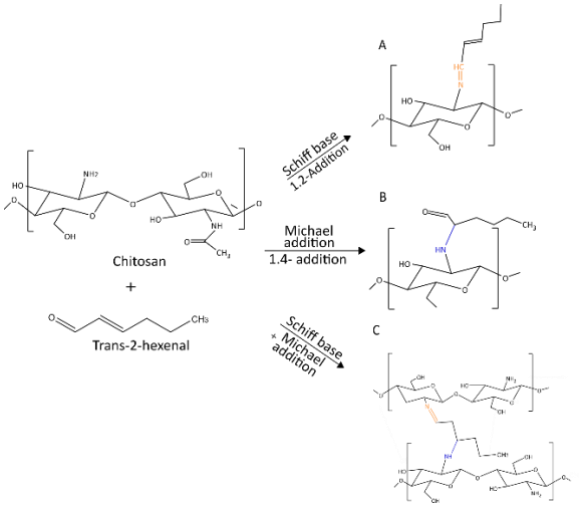


Figure 1: Scheme of possible reactions between chitosan and trans-2-hexenal

References:

1. Flórez, M., Guerra-Rodrígez, E., Cazón, P., Vázquez, M. (2022), Chitosan for food packaging: Recent advances in active and intelligent films, *Food Hydrocolloids*, 124, Part B.

Holistic approach to understand how teleost fish scales fulfill their biological function - from nano to macro structure organization

A. Petitpas [1,2], J. Veillon [1,2], L. Rubatat [1], P. Moonen [3,4], V. Pellerin [1], S.C.M. Fernandes [1,2]

[1] IPREM, Université de Pau et des Pays de l'Adour, CNRS, Pau, France
[2] MANTA chair (E2S-UPPA), Université de Pau et des Pays de l'Adour, Anglet, France
[3]LFCR, Université de Pau et des Pays de l'Adour, Pau, France
[4]DMEX, Université de Pau et des Pays de l'Adour, Pau, France

Abstract:
The United Nation's Food and Agriculture Organization (FAO) 2022 report on "The State of World Fisheries and Aquaculture" estimates that processed fish generate up to 70% of wastes [1]. Among those, fish scales represent a large portion of the waste that is not yet valorized. A better understanding of the structure from nano- to macroscale, including the composition of fish scales is then very important for the upcycling of this by-product. To this end, we chose to focus on 3 species from different environments: tilapia (*Oreochromis niloticus*) which is raised in freshwater, and salmon (*Salmo salar*) and sardine (*Sardina pilchardus*) that spend most of their life in marine water. Teleost fish scales have already been identified as composites made of Type I collagen fibers organized in layers and mineralized with hydroxyapatite [2].
We discovered these fiber orientations change within the entire surface of the fish scale. A complete mapping, using synchrotron Small Angle X-ray Scattering (SAXS), has been successfully performed on the 3 species revealing a high ordering at nanoscale and orientational heterogeneities between scale's center and edges (Figure 1). In addition, X-ray micro computed tomography (micro-CT) has shown congruent information with a thinning of the scales thickness on the edges, suggesting a decreasing number of collagen layers when the distance to the focus area increase. Furthermore, highly mineralized spots have been sighted for the first time in the internal collagen layers of the focus area of tilapia's scales. The composition of fish scales was evaluated using thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy with attenuated total reflectance mode (FTIR-ATR), scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDX), elemental analysis CHNS and amino acids analysis. Variations of collagen/mineral ratio and collagen content have been highlighted and correlated to environmental constrains as seawater and freshwater species display some differences. This study also investigated the mechanical properties of teleost fish scales with tensile tests. These results offer perspectives for valorizing teleost fish scales as source of native collagen and for mimicking the scales' 3D structure for novel materials developments.

Keywords: fish scale, collagen, hydroxyapatite, 3D structure, composition, teleost, upcycling.

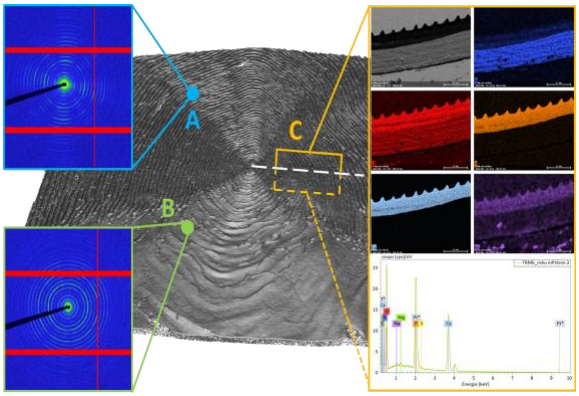


Figure 1: Combination of techniques, e.g micro-CT, SAXS and SEM-EDX, for the structural and composition analysis of a teleost fish scale - *Salmo salar*: 3D image is from micro-CT ; (A) and (B) locate two X-ray spots, anterior and posterior scale areas, with the corresponding SAXS patterns, respectively, where the X-ray beam hit for SAXS analysis ; (C) is a cross section of the anterior area observed with SEM-EDX, where the bi-layer structure collagen/mineral is visible.

References:

1. FAO, **2022,** The State of World Fisheries and Aquaculture 2022, Towards Blue Transformation, Rome.
2. Quan, H.; Yang, W.; Lapeyriere, M.; Schaible, E.; Ritchie, R.O.; Meyers, M.A. Structure and Mechanical Adaptability of a Modern Elasmoid Fish Scale from the Common Carp. *Matter* **2020**, *3*, 842–863.

Moisture Sensor Inspired by Natural Cellulosic Networks

S. D. Almeida[1], P. L. Almeida[1,2], M. H. Godinho[1], A P. C. Almeida[1,3,4*]

[1] i3N/CENIMAT, Department of Materials Science, NOVA School of Science and Technology, Caparica, Portugal
[2] Mechanical Engineering Department, Lisbon Superior Institute of Engineering, Lisbon, Portugal
[3] LAQV/Requimte, Department of Chemistry, NOVA School of Science and Technology, Caparica, Portugal
[3] iBET Instituto de Biologia Experimental e Tecnológica, Oeiras, Portugal

Abstract:
Cellulose-based materials contain many advantageous and versatile properties. While scientific research into this area has increased in the last few years, cellulose-based materials have existed for many millennia[1]. Plants can program cellulose-based dead tissues to respond to external stimuli, usually water. One of these examples is the awns of the Erodium fruit [2], which present amazing coil and uncoil motions in response to humidity. Due to its intrinsic curvature, the straight awns existing in the Erodium plants acquire the shape of a right-handed helix after leaving the fruit with the seed. When in contact with water, the awn unwinds, allowing the seed to bury in the soil. With this work, we found structures resembling the characteristics of liquid crystalline elastomers at the genesis of these movements. These movements result from anisotropic cellulose-based materials organized in layers that contract differently upon the presence of humidity.
Cellulose ribbons, if produced from liquid crystalline solutions, can also be responsive to moisture [3]. In this work stimuli-responsive cellulose-based liquid crystalline films produced by shear-casting techniques with a multi-layer design are evaluated to be used as humidity and temperature sensors. Preparation and characterization and their application as a flexible humidity and temperature sensor will be presented in this work.
Cellulose-based Nature inspired materials have significant potential for opening up new routes for the production of novel mobile soft materials with tremendous impact on intelligent textiles, energy generation, drug delivery, bio-medical and bio-sensing devices, and micro soft robotics.

Keywords: Cellulose, Bioinspired, Sensors, moisture.

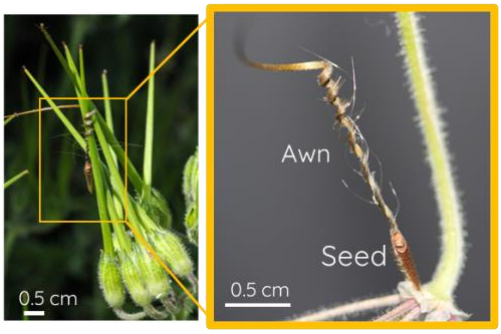


Figure 1: Erodium aws - moisture responsive hierarquical cellulose-based anisotropic natural stutures. The *Erodium* fruit has five seeds and each one is appended to an awn and attached to a central taut stem. Changes in humidity and subsequent coiling and uncoiling of the awns results in rotation ensuing self-burial of the seed.

References:

1. A. P. C. Almeida, et al., Cellulose-Based Materials: Cellulose-Based Biomimetics and Their Applications, Advanced Materials, 2018, 30(19), 1870131.
2. A.P.C. Almeida, et al. , Reversible water driven chirality inversion in cellulose-based helices isolated from *Erodium* awns, Soft Matter, 2019, 15, 2838.
3. Y. Geng, et al , A cellulose liquid crystal motor: a steam engine of the second kind, Scientific Reports, 2013, 3, 1028.

Acknowledgments
The authors acknowledge the Associate Laboratories for Green Chemistry – LAQV (UIDB/50006/2020 and UIDP/50006/2020), I.P. (FCT), and Institute of Nanostructures, Nanomodelling, and Nanofabrication – i3N (LA/P/0037/2020, UIDP/50025/2020 and UIDB/50025/2020) which are financed by national funds from FCT/MCTES and Fundação para a Ciência e a Tecnologia, I.P and European Cooperation in Science & Technology (COST) Action: CA21159 - Understanding interaction light - biological surfaces: possibility for new electronic materials and devices (PhoBioS). A. P. C. Almeida is grateful for the financial support from FCT, Portugal, through the research project grant (2022.01619.PTDC) attributed to her.

Modification of thermoplastic starch to achieve a broad range of properties in mixtures with biopolymers

I. Chodak, H. Peidayesh
Dept. Composite Mtaerials, Polymer Institute SAS, Bratislava, Slovakia

Abstract
Thermoplastic starch (TPS) is a valuable additive to a number of polymers. It is formed by plasticization of native starches, almost entirely with glycerol, although number of other plasticizers are available. The primary aim of the addition of TPS to bioplastics is usually a decrease of the price of the final product while maintaining the biodegradability of the plastics blend.
However, modification of TPS, considering its physical and ultimate properties, is in many cases rather easy and straight forward process, and a number of different procedures are used to adjusting the final properties of the TPS.
Certainly, the final effect of the addition of TPS consists not only in the price decrease but the mixture properties and possible applications depend significantly on the ultimate properties of both the matrix biopolymers and also of the TPS.
In the lecture several options for TPS modification are briefly outlined and described, starting with the selection of native starch considering the origin of the starch. The effect of various plasticizers or even their mixtures are shown using the example of glycerol and urea.
The main concern is related to reinforcement of TPS using reinforcing fillers. Among these, especially precursors of nanoparticles are the most interesting since in thta cxase usually a substantial reinforcement can be achieved with the fiierl content well below 5 wt %, so that the final material maintains its classigication as biodegradable compostable mixture according to relevant standards.
Some more advanced cases of TPS modifications will be presented, especially the effect of moisture uptake on mechanical and other physical properties of the TPS and the effect of long term storing resulting in so called retrogradation, while chemical modification consisting in starch crosslinking with citric acid or dialdehydestarch is described.
Few examples are shown of mixing TPS as the most simple glycerol plasticized additive in the blends with biodegradable polybutylene adipate terphthalate (PBAT) and the comparison of the effect of the same blends using the TPS modified by various procedures demonstrates the extent to which modification of TPS may lead to interesting and in some cases advanced biomaterials with substantial amount of TPS or even based on TPS.

Keywords: Biodegradable plastics, thermoplastic starch, reinforcement, nanoparticles

Acknowledgement:
The research was supported from the project APVV 19-0487

Bio-inspired multilayered nanocellulose-based assemblies with anisotropic properties

L. Garnier [1,*], O. Felix [1], B. Jean [2]
[1] Institut Charles Sadron (ICS – CNRS/UPR22), Strasbourg, France
[2] Centre de Recherches sur les Macromolécules Végétales (CERMAV – CNRS/UPR5301), Grenoble, France

Abstract:
Through evolutionary selection, Nature has developed nanocomposite materials with a structural complexity designed for optimal functionalities by simply assembling hard and soft elements at different length scales. Surprisingly the helical structure, probably one of the most complicated structures to assemble, is widely used in the plant and animal kingdoms to provide interesting mehanical and/or optical properties such as for example impact resistance and structural colors. These outstanding properties have attracted a wealth of research to understand their structure-properties relations at all length scales in order to design novel materials with superior performance. However, while nature masters the organization of complex nanocomposites, the development of synthetic nanocomposite materials with hierarchical architectures (e.g. helical) remains challenging due to the lack of suitable approaches for their preparation with a nanoscale precision. Recently we have introduced a new method called "Grazing Incidence Spraying" (GIS) for the in-plane alignment of anisometric nanoparticles (cellulose nanofibers or nanocrystals, metallic nanowires, …) on large areas. Its combination with the Layerby-Layer (LbL) assembly technique (Figure 1) can be used for the preparation of complex multilayer films in which composition and orientation can be controlled independently at the nanoscale in each layer. The talk will illustrate some of our recent work on the assembly of bio-inspired nanostructured materials combining hard anisometric elements like nanocelluloses with soft polymer building blocks. The preparation and anisotropic properties of these nanocomposite films differing by their composition and nanoscale architecture will be discussed as a function of building methods and conditions.

Keywords: Bio-inspired materials, nanocomposites, nanocellulose, layer-by-layer, grazing incidence spraying, helical structures, anisotropic properties

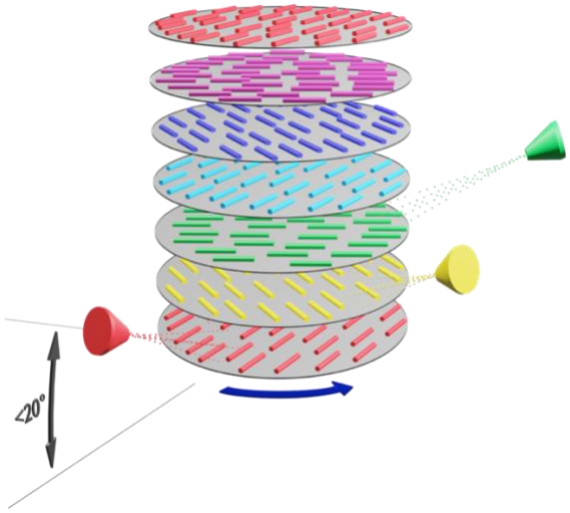


Figure 1: Combinaison of GIS and LbL assembly to prepare nanocomposites with a helical structure.

References:

1. Blell, R.; Lin, X.; Lindström, T.; Ankerfors, M.; Pauly, M.; Felix, O.; Decher, G. (2017) Generating in-Plane Orientational Order in Multilayer Films Prepared by Spray-Assisted Layer-by-Layer Assembly. *ACS Nano, 11, 84−94.*
2. Decher, G. (1997) Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites. *Science, 277, 1232-1237*
3. Merindol, R.; Diabang, S.; Mujica, R.; Le Houerou, V.; Roland, T.; Gauthier, C.; Decher, G.; Felix. O. (2020) Assembly of Anisotropic Nano-Cellulose Films Stronger than the Original Tree. *ACS Nano, 14, 16525–16534.*

Bioinspired Two Photon Polymerized Micro-Pillar Antibacterial Surfaces

G.E. Marsh [1,4*], T. Ning [2], K. Jodeiri Iran[3], R.D. Wildman[3], M.SL. Yee[,2]
[1] Swansea University Medical School, Swansea University, Swansea, United Kingdom
[2] Department of Mechanical, Manufacturing & Materials Engineering, University of Nottingham Malaysia, Malaysia
[3] Centre for Additive Manufacturing, University of Nottingham, Nottingham, United Kingdom.
[4]School of Pharmacy, University of Nottingham Malaysia, Malaysia

Abstract:
Healthcare associated infections (HAIs), incorporates all infections associated with medical interventions like surgery or from exposure to healthcare settings. However several key risk factors for developing an infection relate to the use of indwelling devices and implants. Indeed Implant-associated infections are known to account for at least 25% of all HAIs in the US[1]. In order to combat this risk, prophylactic antimicrobials are often needed, exacerbating the rise of antibiotic resistance. Therefore, there is an increasing need for surfaces that have the capability to prevent bacterial attachment and colonization.
Several studies have evaluated the ability of natural surfaces to posses anti-biofouling and antibacterial activity. The self-cleaning properties of the lotus leaf created utilizing hierarchical micro-scale papillae (5–10 μm) and nanoprotrusions is well known for its ability to generate a super-hydrophobic surface[2]. The creation of super-hydrophobic surfaces tend to resist bacterial cell attachment (Figure 1), helping to prevent biofilm formation. In this study we aim to be able to fabricate varying levels of well defined surface roughness on a series of micro-pillars on a scale comparable to the lotus leaf surface. This will allow an investigation into the effect of changing microstructure and surface roughness, on the prevention of bacterial cell adhesion.

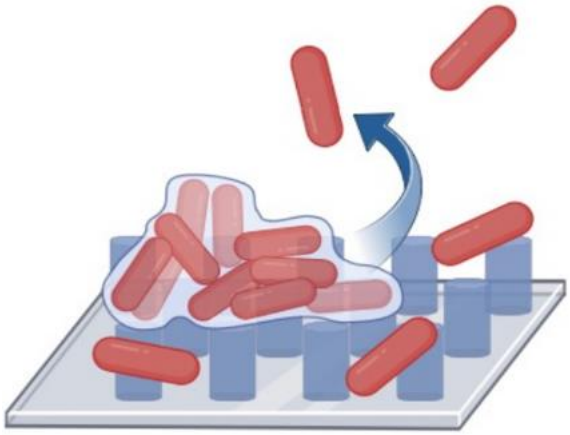


Figure 1: Schematic illustrating the concept of production of well defined micro-pillars with the ability to repel bacterial cell adhesion.

We report the ability to fabricate using two-photon polymerization (TPP), precise microscale topographies with controllable sub-micron surface roughness, heights and spacings (Figure 2).

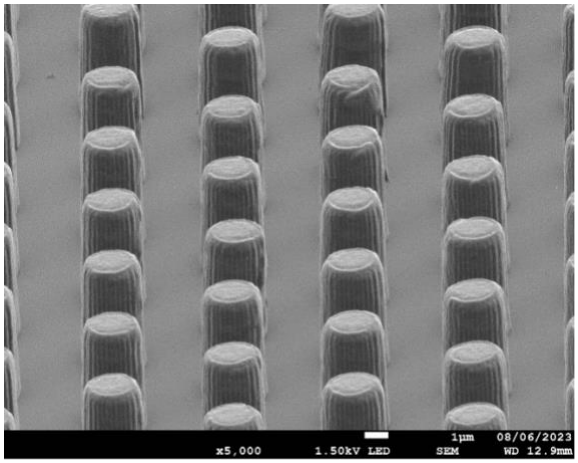


Figure 2: An SEM of TPP micropillars at X5000 magnification, demonstrating uniform height and spacing with well defined surface grooves. Scale bar = 1 μm.

These fabricated surfaces of micropillars of varying spaces, heights and surface roughness, can then be used to investigate the effect of micro-topographies on bacterial cell adhesion. In order to evaluate these properties our TPP fabricated surfaces were cultured with P. aeruginosa, a pathogenic bacteria commonly associated with HAIs. Our results showed that the TPP microstructures demonstrated intriguing antibacterial activity. This research provides the foundation for the use of well controllable surface morphology for enhanced antibacterial use within nanotechnology and biomedicine, offering a noteworthy advancement in the fight against healthcare acquired infections and antimicrobial resistance, providing support of worldwide health initiatives. It also emphasizes

the importance of precise surface roughness control to achieve these aims.

Keywords: Antibacterial, two-photon polymerization, micro-patterning, microstructures

References:

1. Kollef, MH., Torres, A,. Shorr, AF., Martin-Loeches, I., Micek, ST. (2021) Nosocomial Infection. *Crit Care Med.,* 1;49(2):169-187.
2. Dai, S., Zhang, D., Shi, Q., Han, X., Wang, S., Du, Z. (2013) Biomimetic fabrication and tunable wetting properties of three-dimensional hierarchical ZnO structures by combining soft lithography templated with lotus leaf and hydrothermal treatments *Cryst Eng Comm*, 15, (27), 5417-5424.

Evolution and characterization of Drosophila glue, a model for biomimicry

M. Monier[1], J-N. Lorenzi[1,2], F. Borne[1,3], V. Contremoulins[1], L. Mevel[1], R. Petit[1], F. Graner[4] and V. Courtier[1]

[1]Université Paris Cité, CNRS, Institut Jacques Monod, 15 rue Hélène Brion, 75005 Paris, France

[2]SMILE group, Center for Interdisciplinary Research in Biology (CIRB), Collège de France, 75006 Paris, France

[3]Department of Biological Sciences, Columbia University, New York city, New York, USA

[4]Univ. Paris Cité, CNRS, Matière et Systèmes Complexes, 75013 Paris, France

Abstract:

Bioadhesives display physico-chemical properties that enable living organisms to attach themselves to a great variety of substrates. This is the case of Drosophila glue, a bioadhesive produced during the late larval stage that enables the animal to be attached during metamorphosis as a pupa. This glue adheres to a large range of substrates: in nature Drosophila pupae are found on leaves, wood, fruits, in the soil, and in laboratory conditions, on glass, paper or plastic. The pupation substrate varies between species, suggesting they have evolved different glues. This glue is produced by the salivary glands, it dries within a few seconds, and is adhesive for several days under various humidity and temperature conditions. Being attached during metamorphosis is of crucial importance for the pupa as the animal is immobile and vulnerable to climatic conditions and predation.

So far, the precise composition and the adhesive properties of the glue had only been studied in the model species *Drosophila melanogaster*. Adhesive strength is approximately 0,2 newton for 1 mm² of glue, which corresponds to most adhesive tapes in commercial stores [1]. Moreover, this glue is biodegradable, biocompatible, reversible and could present repellent properties [2,3]. *Drosophila melanogaster* glue is made of eight glycosylated proteins, named Salivary Gland Secretion (Sgs), which form two groups. The first group (Sgs1, Sgs3, Sgs7 et Sgs8) are proteins rich in proline, serine and threonine repeats that are O-glycosylated. The second group (Sgs4, Sgs5, Sgs5bis and Eig71Ee) is composed of shorter proteins rich in cysteines [4,5].

We developed an automated adhesion force measurement and compared the adhesion properties between 25 Drosophila species. We also quantified the amount of glue secreted. Our results reveal that adhesion force evolved quickly with *D. hydei* being the most adhesive species.

Overall, our objective is to develop a future bioadhesive safe for human health and the environment.

Keywords: bioadhesion, glue, Drosophila, glycoprotein, evolution, biomaterial, biomimetics

Figure 1: Ventral view of *D. melanogaster* pupa attached to a glass slide with its own glue.

References:

1. Borne, F., Kovalev, A., Gorb, S., & Courtier-Orgogozo, V. (2020). The glue produced by Drosophila melanogaster for pupa adhesion is universal. *Journal of Experimental Biology*, *223*, jeb220608.
2. Borne, F., Prigent, S. R., Molet, M., & Courtier-Orgogozo, V. (2021). Drosophila glue protects from predation. *Proceedings of the Royal Society B*, *288*, 20210088.
3. Monier, M., & Courtier-Orgogozo, V. (2022). Drosophila glue: a promising model for bioadhesion. *Insects*, *13*(8), 734.
4. Da Lage, J. L., Thomas, G. W., Bonneau, M., & Courtier-Orgogozo, V. (2019). Evolution of salivary glue genes in Drosophila species. *BMC evolutionary biology*, *19*, 1-22.
5. Monier, M., Nuez, I., Borne, F., & Courtier-Orgogozo, V. (2023). Higher evolutionary dynamics of gene copy number for Drosophila glue genes located near short repeat sequences https://doi.org/10.21203/rs.3.rs-2495385/v2 *In revision*

Guiding Cellular Behaviour via Contact with Nature Inspired, ECM-mimetic Hierarchical Topographic Cues

A. Gope [1,*], A. Mukhopadhyay [2], R. Mukherjee[3]

[1] Advanced Technology Development Centre, Indian Institute of Technology Kharagpur, Kharagpur, India
[2] School of Medical Science and Technology, Indian Institute of Technology Kharagpur, Kharagpur, India
[3] Department of Chemical Engineering, Indian Institute of Technology Kharagpur, Kharagpur, India

Abstract: The compositional, structural, and mechanical properties of the ECM affect cellular adhesion, proliferation, migration, and differentiation, especially in the presence of growth factors and chemokines. Normal wound healing involves an interaction between cellular components, growth factors, and signalling mechanisms in close association with the surrounding and underlying healthy ECM architecture. Studies have shown that biophysical and biochemical cues of different order and scale regulate cellular proliferation, adhesion, migration, transdifferentiation, molecular expression, and apoptosis. Chemical functionalisation is widely used to modify cellular behaviour at wound site, but it is expensive and rarely investigated how the coated layer will perform in a wound mimicking environment with cellular degradation mechanisms. We replicate a few nature-inspired bio-mimicking hierarchical patterns-structures found on natural surfaces, such as the papillary microstructures on rose petals that closely resemble the skin's papillary dermis and the intricate network of Nano cuticular folds atop each micro feature, which resembles the fibrous ECM architecture, onto cross-linked PDMS substrates in a cost-effective manner. Additionally, hierarchical structures were examined in relation to PDMS substrate wetting behaviour, surface free energy, and inherent hydrophobicity. 3T3 fibroblasts, the main wound-healing cells, were cultured on flat and patterned PDMS substrates and assessed for proliferation, morphology changes in response to biophysical cues, cell-structure interaction via different adhesion regimes, and mechanotransduction. These patterns can be easily replicated onto any biopolymer and used to modify scaffold surface topography and morphology without chemical functionalization while influencing cellular behaviour.

Keywords: biophysical cues, topograpghical patterns, ECM-mimetic, PDMS, 3T3 fibroblasts, wound healing, bioscaffold, biopolymer, cell morphology, proliferation, Transdifferentiation, mechanotransduction

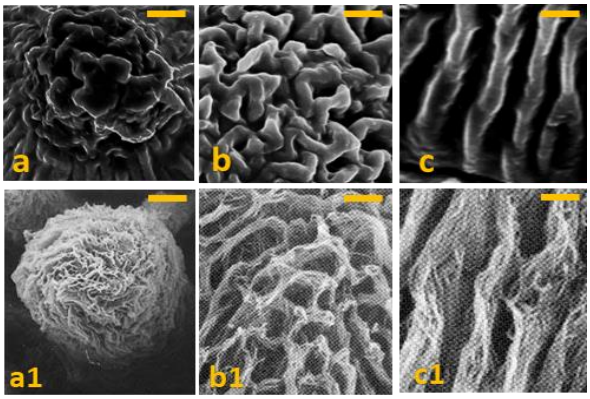


Figure 1: a, b and c represent the ECM mimetic nature inspited patterns from different sources that closely resemble the strutures of the papillary dermis and collagen network (a1, b1-c1). The resemblance of these biophysoical cues to existing architecture can help in better recruitment and further behavior of cells involved in wound healing- 3T3 fibroblasts.

References:

1. Dalby, M.J., et al., *Changes in fibroblast morphology in response to nano-columns produced by colloidal lithography*. Biomaterials, 2004. **25**(23): p. 5415-5422.
2. Mukhopadhyay, A., et al., *Modulation of Biophysical Cues in Nature Inspired Patterning of Porous Silk Fibroin Scaffold for Replenishable Controlled Drug Delivery*. Macromolecular Bioscience, 2023: p. 2300119.
3. van Kooten, T.G., J.F. Whitesides, and A.F. von Recum, *Influence of silicone (PDMS) surface texture on human skin fibroblast proliferation as determined by cell cycle analysis.* Journal of biomedical materials research, 1998. **43**(1): p. 1-14.

Polymers / Composites / 3Bs Materials Session II. D: Biobased Materials / Biopolymers / Biocomposites

Bio-based hybrid composite epoxy/NIPU foams for constructive applications

L. Gryshchuk
Tailored Thermosets and Biomaterials, Leibniz-Institut für Verbundwerkstoffe GmbH, Kaiserslautern, Germany

Abstract:
Replacement of petroleum-based materials in constructive industry with bio-based ones is necessary „Environmentally Friendly Thinking“ strategy that benefits society; reduces the impact on the environment, decreases dependence of Europe from gas and oil from non-democratic countries.
Polyurethanes (PU) and epoxies (EP) are very common materials that find many applications in various fields, such as constructive, automotive, aeronautic, etc. [1-2]. Despite the dominating of PU foams in the structural/insulation field, development of alternative materials is strong expanded during last years. Moreover, the main disadvantage of the PU synthesis is using of isocyate, diisocyanate (or poly-isocyanate). The latter is directly produced from the corresponding amine and phosgene, which is highly toxic.
In the frames of the EU-Project r-LightBioCom realize concept of phosgene-free synthesis of PU foams (NIPU) and improvement of their mechanical properties by hybridization with epoxies. One of the project´s aim is development of bio-based materials with high bio-content for structural application. Using of epoxy and NIPU allows you to avoid such difficulty as sensitivity to humidity and prolong shelf-life of the raw materials, which in turn, reduces amount of wastes and has positive influence to environment.
For development of hybrid epoxy/NIPU foam formulations were used bio-based epoxy resin SR GreenPoxy 56 and hardener SZ8525 (both from Sicomin, France) and different di- and tricyclocrbonates (Specific Polymers, France). As chemical blowing agent was used poly(methylhydrosiloxane). For increasing of the bio-content of the foams as fillers were used different bio-based and mineral fillers, such as polysaccharides, lignin, talc, diatomite, etc. Bio-based hybrid epoxy/NIPU foams were prepared using an one-step method. At first, in epoxy resin SR GreenPoxy 56 was thoroughly dispersed filler(s) in amount 0.1-7 phr, after that the appropriate amount of cyclocarbonate (0.5-5 phr) was added to the mixture and thoroughly mixed. During the dispersing was controlled the temperature of the mixture. Hardener SZ 8525 in appropriate amount was mixed together with the filled epoxy/cyclocarbonate composition. Stirring was carried out long enough for the gelation reaction to begin. After that the poly(methylhydrosiloxane) was added and all components were mixed together. Afterwards, the resultant reactive mixture was immediately transferred in open Al-mould for free-rise, kept at RT for 1 hour and then post-cured at 70°C during 4 hours. Influence of type as well as concentration of cyclocarbonate(s) and filler(s) on density, thermal and mechanical propeties of the foams were investigated.

Keywords: bio-based, epoxy, non-isocyanate polyurethane, hybrid, foam, bio-filler, mechanical properties, structural applications.

Figure 1: Cross section of hybrid epoxy/NIPU foam structural insulation panel after preparation

References:

1. Dworakowska, S., Cornille, A., Bogdał, D., Boutevin, B., & Caillol, S. (2015). Formulation of bio-based epoxy foams from epoxidized cardanol and vegetable oil amine. European Journal of Lipid Science and Technology, 117(11),1893–1902. https://doi.org/10.1002/ejlt.201500232
2. Coste, G., Berne, D., Ladmiral, V., Negrell, C., & Caillol, S. (2022). Non-isocyanate polyurethane foams based on six-membered cyclic carbonates. European Polymer Journal, 176, 111392. https://doi.org/10.1016/j.eurpolymj.2022.111392

Acknowledgements: This research was funded by the European Union under the framework of the project r-LightBioCom (HORIZON Europe, under Grant Agreement Project No 101091691)

Shape Memory Composites based on Bio-Benzoxazine/Bio-Urethane Copolymers Reinforced with Graphene with NIR Actuation Ability

S. Rimdusit [1,*], W. Jamnongpak [1], K. Charoensuk [1], and C. Jubsilp[2]
[1] Center of Excellence in Polymeric Materials for Medical Practice Devices, Department Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[2] Department of Chemical Engineering, Faculty of Engineering, Srinahkharinwirot University, Nakhonnayok 26120, Thailand

Abstract:
Shape memory polymers (SMPs) were developed from copolymerization of bio-based benzoxazine (BZ) monomer and polyurethane prepolymer (PU-prepolymer), both derived from bio-based raw materials. The bio-based BZ monomer (V-fa monomer) was synthesized through a Mannich condensation reaction using a stoichiometric amount of vanillin, paraformaldehyde, and furfurylamine. The bio-based PU-prepolymer was obtained by reacting palm oil polyol (MW = 1400 Da) with toluene diisocyanate (TDI). Curing behaviors of the poly(V-fa/Urethane), with a mass ratio of 50/50, were examined using differential scanning calorimetry. The structure of the resulting poly(V-fa/Urethane) was confirmed using Fourier transform infrared spectroscopy. Furthermore, the synthesized V-fa/Urethane copolymers with weight ratios of 70/30, 60/40, 50/50 and 40/60 were observed to exhibit shape memory behaviors which can be readily induced by Near-inferred irradiation (808 nm). The poly(V-fa/Urethane), specifically with a mass ratio of 50/50, demonstrated superior shape memory performance. It exhibited a relatively high shape memory performance i.e. shape fixity as high as 90%, shape recovery ratio up to 99%, and showed a recovery time of about 25 s. The shape memory properties were further improved with an addition of 3wt% graphene nanoplatelets (GNPs) i.e. exhibiting an improvement in shape fixity value up to 94%, and reduced shape recovery time to 16 s. In addition, our findings suggest that the 60/40 poly(V-fa/Urethane) reinforced with 3wt% GNPs possesses suitable characteristics for applications as multiple SMPs, with shape fixity values of 97% and 94%, and shape recovery values of 96% and 89% for the first and second shapes, respectively.

Keywords: shape memory polymers, nanocomposites, biobased polymers, near infrared actuation, polybenzoxazine, polyurethane, graphene.

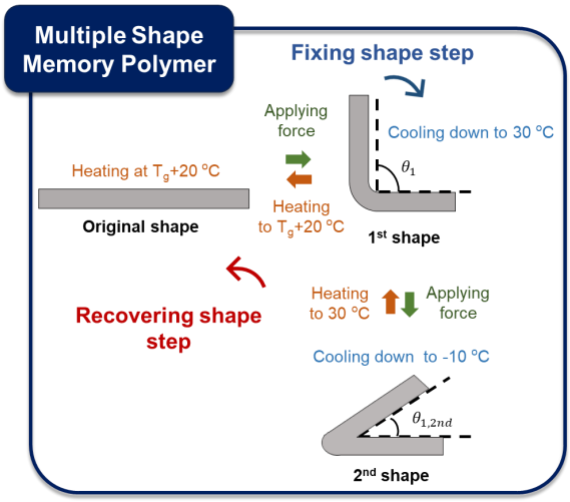


Figure 1: Figure illustrating the desired shape memory programming for multiple shape memory polymers based on bio-based benzoxazine resin and bio-based polyurethane prepolymer in this work.

References:

1. Li, T., Li, Y., Wang, X., Li, X., Sun, J. (2019), Thermally and near-infrared light-induced shape memory polymers capable of healing mechanical damage and fatigued shape memory, *ACS Appl. Mater. Interfaces*., 11, 9470-9477.
2. Prathumrat, P., Tiptipakorn, S, Rimdusit, S. (2017) Multiple-shape memory polymers from benzoxazine–urethane copolymers, *Smart Mater. Struct.*, 26, 065025.
3. Pilate, F., Toncheva, A, Dubois, P., Raquez, J.-M. (2016) Shape-memory polymers for multiple applications in the materials world, *Eur. Polym. J.*, 80, 268-294.

Impact and flexural properties of woven flax-carbon thermoplastic hybrid bio-composites

M. Bahrami [1*], M. Mehdikhani [2], Y. Swolfs [2], J. Abenojar [1,3], and M.A. Martinez [1]
[1] Materials Science and Engineering Department, IAAB, University Carlos III Madrid, Leganes, Spain
[2] Department of Materials Engineering, KU Leuven, Leuven, Belgium
[3] Mechanical Engineering Department, ICAI, Universidad Pontificia Comillas, Madrid, Spain

Abstract:
Fiber hybridization can enhance the properties of fiber-reinforced composites, especially for laminates with brittle fibers/matrices that have low resistance to dynamic loading [1-2]. This study uses drop weight low-velocity impact and three-point bending tests to examine the impact resistance and flexural properties of carbon/flax/polyamide hybrid bio-composites. Hybrid laminates were produced using woven carbon and flax fibers and a polyamide 11 matrix via hot-pressing, with flax fiber plies as inner layers and carbon plies as outer layers. In addition, non-hybrid carbon and flax fiber composites with the same matrix were produced as reference laminates to investigate the effects of hybridization. Mechanical damage was analyzed using X-ray computed tomography. The hybrid composites exhibited a positive hybrid effect with respect to impact resistance, characterized by a higher displacement at the maximum impact force. Moreover, characterization of the damage zone by X-ray microcomputed tomography confirmed the different damage mechanisms of hybrid composites compared to the non-hybrid ones. Additionally, the results revealed the advantages of hybridization in terms of flexural properties, including a higher modulus and strength compared to pure flax composites and a higher failure strain compared to pure carbon composites. These results provide valuable insights into the mechanical performance of carbon-flax hybrid composites.

Keywords: hybrid thermoplastic bio-composite, flax fibers, PA11, impact behavior, X-ray computed tomography, flexural properties.

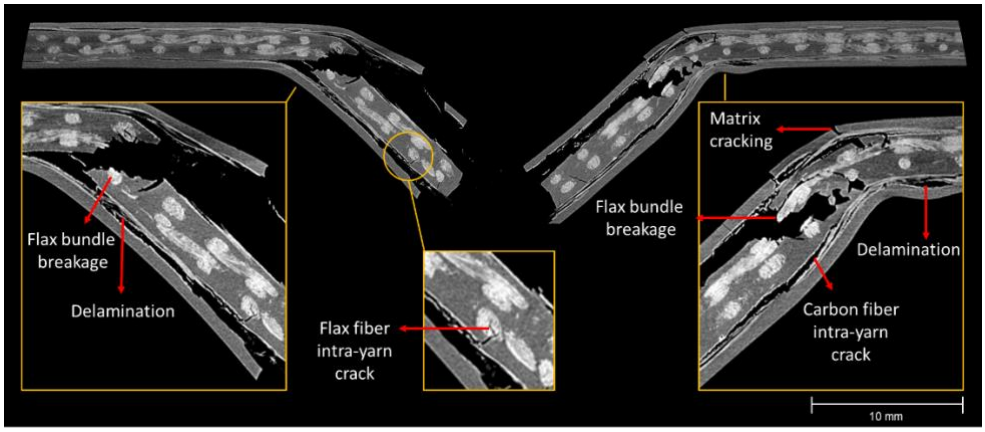


Figure 1: Micro-CT mid-width cross-sections of hybrid composite after impact.

References:

1. Wang, A., Wang, X., & Xian, G. (2020). Mechanical, low-velocity impact, and hydrothermal aging properties of flax/carbon hybrid composite plates. Polymer Testing, 90, 106759.
2. Swolfs, Y., Gorbatikh, L., & Verpoest, I. (2014). Fibre hybridisation in polymer composites: A review. Composites Part A: Applied Science and Manufacturing, 67, 181-200.

Degradation behavior of poly(lactic acid) biocomposites filled with natural materials

Marta MUSIOŁ[1], Sebastian JURCZYK[2], Wanda SIKORSKA[1], Henryk JANECZEK[1], Joanna RYDZ[1], Kolos MOLNAR[3]

[1] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34, M. Curie-Skłodowska St., 41-819 Zabrze, Poland;
[2] Łukasieiwcz Research Network – Institute for Engineering of Polymer Materials and Dyes, 55, M. Skłodowska-Curie St., 87-100 Toruń, Poland;
[3] Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, M″uegyetem rkp. 3, H-1111 Budapest, Hungary;

Abstract:
Composites made of a biodegradable polymer are becoming popular due to their eco-friendliness. Fillers added to the polymer not only enhance its properties but also make the final products more affordable. The presence of fillers is known to impact the degradation behavior of the composite (1). However, the exact nature of this impact is yet to be fully understood. Presented studies in this field are to determine how different types and amounts of fillers affect the biodegradation of composites based on biodegradable polymers. Degradation tests were conducted for the poly(lactic acid) (PLA) matrix without filler and for composites PLA with cork. The materials were incubated under industrial composting conditions and in demineralized water in laboratory conditions. The samples were placed in one of the KNEER system modules at a depth of approximately 1 m below the compost surface. In laboratory conditions, the degradation process resulted in a shrinkage effect. When composting in a 50% humidity environment, the degradation of composite materials with a larger amount of hydrophobic cork resulted in less reduction in molar mass, and no shrinkage effect. During incubation in water, the thermal stability of the samples showed slight changes as degradation products gradually formed and were eluted. This was observed through thermogravimetric analysis. After 84 days of incubation, the temperature at which the maximum rate of mass loss occurs (T_{max}) for all samples has decreased noticeably compared to its initial value before degradation. Under industrial composting conditions, the thermal properties of the samples remained stable, with no significant changes observed during degradation. The impact of cork on degradation varies depending on its quantity. Further research is necessary to understand the influecne of organic compounds found in cork on the PLA based composites degradation pathway behavior.

Keywords: biodegradable composites, PLA, natural filler, degradation test, compost

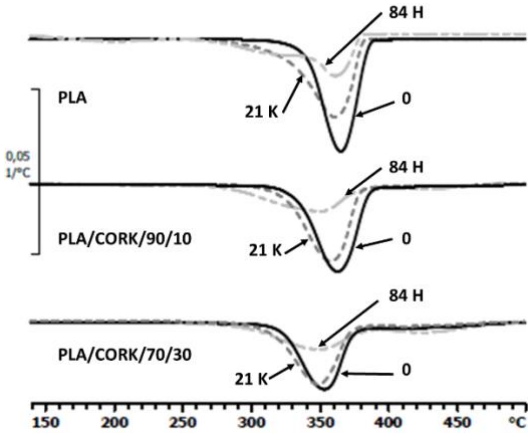


Figure 1: First-order derivative of thermal decomposition curves (DTG) of the neat PLA and composites before and after 21 days of degradation under composting conditions (21 K), and 84 days degradation in water at 70˚C (84 H).

Acknowledgements: This work was supported by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 872152, project GREEN-MAP and an international project co-financed by the program of the Minister of Science and Higher Education entitled "PMW" in the years 2020–2023; contract No. 5092/H2020/2020/2.

References:

1. Jurczyk, S., Musioł, M., Sobota, M., Klim, M., Hercog, A., Kurok, P., Janeczek, H., Rydz J. (2019) (Bio)degradable Polymeric Materials for Sustainable Future - Part 2: Degradation Studies of P(3HB-co-4HB)/Cork Composites in Environments. Polymers, 11(3), 547.

Green composites reinforced with sisal fabric: a preliminary investigation on mechanical response

C. Santulli[1], S. Boria[2,*], G. Del Bianco[2], V. Giammaria[2], M. Capretti[2], V. Castorani[3]

[1] School of Science and Technology, Geology Division, University of Camerino, Camerino, Italy
[2] School of Science and Technology, Mathematics Division, University of Camerino, Camerino, Italy
[3] HP Composites SpA, R&D Department, Ascoli Piceno, Italy

Abstract:
The growing care of the environment combined with the fight against climate change is slowly changing industrial values towards sustainable development. The demands for renewability and sustainability have led composites companies and researchers to investigate innovative green solutions. Natural fiber reinforced polymers are widely analyzed as an alternative to the use of synthetic fibers in automotive or secondary non-structural applications. The literature mainly mentions flax and hemp fabrics, which are also stacked in hybrid solutions with carbon and basalt fibers. However, other natural fibers can also be used as a reinforcement and, in this work, we pay particular attention to sisal. Sisal fiber is obtained from the leaves of the agave plant *(Agave sisalana)*, which easily grows in North and South America, Africa, Brazil, and India. As fiber, it is rough and durable, showing high resistance to damage. One of the major drawbacks of using natural fibers in composite materials is represented by the variability of their properties depending on environmental and growth conditions. Despite these disadvantages, it was demonstrated that the strength of sisal fibers is comparable to that of glass fibers.
This work aims to investigate the performance of fabric sisal laminates embedded in epoxy resin. Mechanical characterization is carried out through tensile and bending tests, to find out how sisal layers behave when are cured with epoxy resin, and whether it could be a promising raw material for composite applications. Moreover, sisal/epoxy plates are subjected to Low-Velocity Impact (LVI) tests to analyze the delamination phenomena. Experimental results are presented, and a comparative study is conducted to evaluate the acquired performance with other commonly used biodegradable natural fibers in epoxy-composites, such as the mentioned flax and hemp. This assessment seeks to ascertain and compare their reliability as prospective replacements for synthetic reinforcements, such as carbon fibers, within the context of structural composite applications.

Keywords: Natural Fiber Composites (NFC), Sisal fabric, Epoxy resin, Mechanical characterization, Low-Velocity Impact (LVI).

References:

1. Rana S.S., Kumar R., Gupta M.K. (2023) Investigation of mechanical and thermal behavior of sisal fibre reinforced polymer biocomposites. *Materials Today: Proceedings*, In Press. https://doi.org/10.1016/j.matpr.2023.06.167
2. Li Y., Mai Y.W., Ye L. (2000) Sisal fibre and its composites: a review of recent developments. *Composites Science and Technology*, Vol. 60(11), 2037-2055. https://doi.org/10.1016/S0266-3538(00)00101-9
3. Makinde-Isola B.A., Taiwo A.S., Oladele I.O., Akinwekomi A.D., Adelani S.O., Onuh L.N. (2023) Development of sustainable and biodegradable materials: A review on banana and sisal fibre based polymer composites. *Journal of Thermoplastic Composite Materials*, Vol. 0(0), 1-21. https://doi.org/10.1177/08927057231186324
4. Betelie A.A., Sinclair A.N., Kortschot M., Li Y., Redda D.T. (2019) Mechanical properties of sisal-epoxy composites as functions of fiber-to-epoxy ratio. *AIMS Materials Science*, Vol. 6(6), 985-996. https://doi.org/10.3934/matersci.2019.6.985

Development of sustainable corn derivates-based composites.

A. Cunha[1*], P. Teixeira[1], S. Gomes[1], A. Monteiro[1], N. Senhorães[1], R. Malta[1], Cristela M. Brito[2], L.F.S. Silva [3], N.M. Pereira [3], Inês Oliveira [4], Jéssica Viegas [4]

[1] CeNTI – Centre for Nanotechnology and Smart Materials, Rua Fernando Mesquita, 2785, 4760-034, Vila Nova de Famalicão, Portugal.
[2] Plásticos Futura, Lda, Rua José Alves Júnior, Cumeiras, 2430-350, Marinha Grande, Portugal
[3] SIRPLASTE-Soc. Ind. de Recuperados de Plástico S.A, Urbanização Industrial da Santeira, Lt 76, 2480-410, Porto de Mós, Portugal
[4] COPAM – Companhia Portuguesa de Amidos, S.A., Rua Deputado Pedro Botelho Neves, 2696-722, São João da Talha, Portugal.

Abstract:
The global shift towards sustainability and circular economy has become a pressing concern in recent years, due to the large amounts of post-consumer plastic waste that are discarded, causing major economic and environmental issues. Due to the complexity of the plastic value chain, with the existence of a large number of stakeholders (plastics and chemical raw material producers, converters, recyclers, waste management and treatment actors), it is of upmost importance to create an ecosystem capable to address these challenges.
The project Sustainable Plastics – Mobilizing Agenda, aims to provide a response to these challenges, contributing to the reinforcement of the economic and social importance of the plastic industry. This will foster a smart, innovative, and sustainable industry wherein design and production respect the need for re-use, repair, and recycling of plastics. The key components of circularity by material design involve the adoption of safer design concepts (i.e., polymeric materials free of hazardous chemicals, addressing micro- and nano-plastics), circular materials and resource efficiency (i.e., durable, reusable, and recyclable, drawing on alternate resources including plastic waste and biomass). In this context, the incorporation of corn derivatives into recycled or biosourced polymers has emerged as a promising alternative to replace virgin fossil-based materials. Integrating such materials allows the production of items traditionally made from non-renewable and environmentally persistent petroleum-based materials using resources that are renewable and may contribute to the degradability of the final product. Moreover, these materials can be processed and incorporated into polymeric matrices, exhibiting excellent mechanical and thermal properties while reducing waste generated by plastic products through increased biodegradation rates. Thus, the development of sustainable composites based on corn derivatives, comprising recycled polypropylene and biopolymers, will be presented. The study encompasses the formulation and comprehensive investigation of diverse blends, incorporating starch with recycled polypropylene and starch with polylactic acid (PLA). The experimental design extends to the examination of compatibility agents, antioxidants, and various types of starch, seeking to optimize the mechanical and physical characteristics of the resulting composites.

Keywords: Recycled polypropylene, biopolymers, corn derivates, starch, characterization.

This work was developed in the scope of the Project “Sustainable Plastics – Mobilizing Agenda for Sustainable Plastics”, co-financed by Recovery and Resilience Plant (RRP), through the Incentive System “Agendas for Business Innovation”.

Supercritical CO_2 impregnation of PHB-HV in submerged and non-submerged mango leaves extract

L. León[1], D. Valor[1*], I. García-Casas[1], A. Montes[1], C. Pereyra[1], E.J. Martínez de la Ossa[1]

[1] Department of Chemical Engineering and Food Technology, Faculty of Sciences, University of Cadiz, International Excellence Agrifood Campus (CeiA3), Campus Universitario Río San Pedro, 11510, Puerto Real (Cadiz), Spain
[*]diego.valor@uca.es

Abstract:
Supercritical CO_2 impregnation allows active substances to be incorporated into the polymers to minimize deterioration and extend the useful life of food products. It has been observed that biopolymers are materials with excellent potential to contain additives such as antimicrobial and antioxidant agents in their matrix, with the aim of subsequently releasing them [1]. Among the bioactive agents from natural sources, we can mention the polyphenols found in the byproducts from the mango industry *(Mangifera indica L.)* [2]. The objective of this research is to study the supercritical fluid impregnation process of the copolymer Poly(3-hydroxy-butyrate-co-3-hydroxy-valerate) (PHB-HV) immersed and non-immersed in ethanolic extracts of mango leaves. The experiments were carried out in a lab-scale high-pressure equipment supplier by Thar Tech (RESS 250 model). This equipment is equipped with a 250 mL vessel with a thermostatic jacket, a high pressure pump for CO_2, and an automatic back pressure regulator (BPR) to control the system pressure. The ethanolic extracts of mango leaves (6 mL) was introduced inside vessel. Besides, 0.10 grams of PHB-HV biopolymer sheets were deposited inside vessel, submerged and non-sumerged in mango leaves extract. The process was carried out for 1 hour in batch mode. In addition, the influence of pressure (100 - 300 bar), temperature (35 - 55 ºC) and depressurization rate (1 - 50 bar/min) on the polymers' structure and impregnation rate have been analyzed. Finally, the impregnation load percentage and the antioxidant activities of the impregnated PHB-HV sheets were determined. At the end of the assays, a slight color change was observed in the impregnated PHB-HV sheets, which was indicative that the extract penetrated into the polymer matrix. As the main result, greater impregnation was observed in those tests where the polymer was immersed in the ethanolic extracts of mango leaves during impregnation and, additionally, a strong influence of the studied variables was observed.

Keywords: Supercritical CO_2 impregnation, Poly(3-hydroxy-butyrate-co-3-hydroxy-valerate) (PHB-HV), ethanolic extracts of mango leaves.

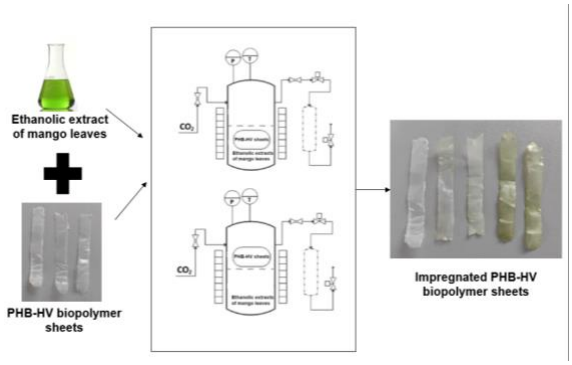


Figure 1: Illustrative diagram of the process supercritical CO_2 impregnation of PHB-HV in mango leaves extract submerged and non-submerged.

References:

1. Sutil GA, Andrade KS, Rebelatto EA, Lanza M. Effects of incorporation of pure or multicomponent active agents in biopolymers for food packaging using supercritical CO_2. Trends in Food Science & Technology. 2022;120:349-62.
2. Cejudo-Bastante C, Verano-Naranjo L, Toro-Barrios N, Pereyra C, Mantell C, Casas L. Structural Modification of Polymers Functionalized with Mango Leaf Extract by Supercritical Impregnation: Approaching of Further Food and Biomedical Applications. Polymers. 2022;14(12):2413.

Scaling-up of supercritical solvent impregnation of olive leaf extract into polypropylene films

Á. Pineda, C. Cejudo, L. Verano, N. Machado*, C. Mantell, L. Casas

Chemical Engineering and Food Technology Department, Science Faculty, Wine and Agrifood Research Institute (IVAGRO), University of Cadiz, Puerto Real, 11519, Spain

Abstract:
The agricultural by-products of the olive sector contain a large amount of antioxidant and antimicrobial compounds that can be recovered and reincorporated into a value chain. One of the technologies more used for extraction and purification of these compounds, as well as for their incorporation into the polymers, are those using high-pressure such as supercritical CO_2. Although the scaling up of the extraction process is been studied, and even applied at an industrial scale, the impregnation process has never been studied beyond than laboratory scale. As well as the extraction process, the impregnation process entails a mass-transfer process that requires an intricate balance between the solubilization power of the CO_2, and the partition coefficient of the active substance, being favored towards the polymer (1). There are several operational parameters that alter that balance, which makes difficult scaling of the process. This study is focused on the scaling up of the supercritical solvent impregnation of an antioxidant olive leaf extract (OLE) into a polypropylene film (PP). The scale-up process has been studied using three different capacities of the impregnation cell: 100 mL, 500 mL, and 2 L, maintaining constant the ratio cm^2 film/V_{OLE} in all tests. The 2 L-plant impregnations were performed at 1 and 24 h. Results showed similar loading rates of impregnated compounds when working at different scales, showing the good scaling up of the process (Figure 1). Regarding impregnation time, the most suitable conditions to achieve the higher antioxidant activity were shown at 1 h of impregnation. The identification of the main compounds impregnated was determined by analyzing the polymer surface by Imaging Desorption Electrospray Ionization Mass Spectrometry (DESI-MS), showing a better dispersion of luteolin-7-glucoside on the polymer surface, but a higher impregnation of oleuropein.

Keywords: food packaging, polypropylene, olive leaf extract, circular economy, antioxidant properties, supercritical impregnation.

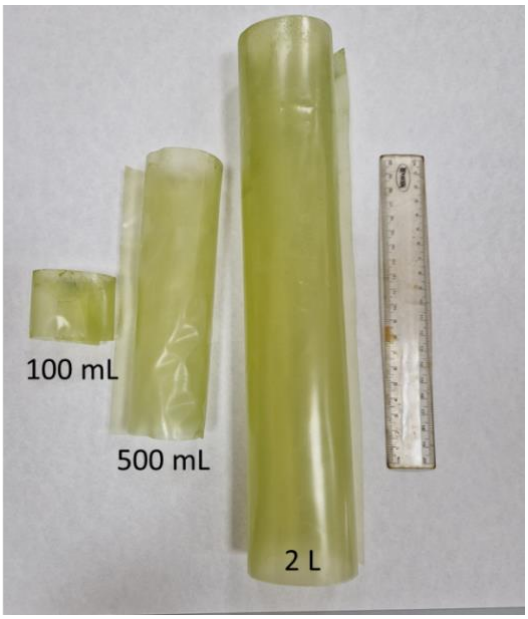


Figure 1: Films impregnated with olive leaf extract at the different scales

References:

1. Cejudo Bastante, C. Casas Cardoso, L., Mantell Serrano, C., Martínez de la Ossa, E.J. (2017) Supercritical impregnation of food packaging films to provide antioxidant properties. *Journal of Supercritical Fluids,* 128, 200–207.

Inclusion of natural antioxidants from olive pruning waste in porous biomaterials using supercritical technology

I. García-Casas*, D. Valor, H. Elayoubi, L.León, C. Pereyra and A. Montes.

Department of Chemical Engineering and Food Technology, Faculty of Sciences, University of Cádiz, International Excellence Agrifood Campus (CeiA3) 11510 Puerto Real (Cádiz), Spain.

Abstract:
In the field of biomedical applications, the development of polymeric materials has made significant advances. Among them, the copolymer poly (lactic-co-glycolic acid) (PLGA) has been widely investigated in tissue engineering and drug delivery systems due to its biodegradable, biocompatible, and safe properties. On the other hand, chitosan has gained popularity thanks to its biodegradability and ability to interact with the human body. Chitosan is a polysaccharide obtained from chitin found in natural sources.
The combination of PLGA and chitosan to incorporate the antioxidants from olive wastes opens up new possibilities in the development of bioactive compound delivery systems for pharmaceutical applications and promotescircular economy. In this context, experiments have been conducted to select the most suitable PLGA/chitosan mixture to include natural antioxidants extracted from olive wastes using supercritical fluid technology.
With the aim of evaluating the characteristics of this combination, several specific objectives were established. These included selecting the appropriate ratio of PLGA/chitosan polymers, optimizing the procedure and operating conditions, characterizing the impregnated tablets, and analyzing possible structural modifications.
It was also observed that the formation of pores and its interconectivity in the PLGA/chitosan mixture is influenced by the proportions of the polymers, and the importance of determining an optimal range to achieve proper formation of these structures was identified.
In summary, properly adjusting the extraction and impregnation parameters, considering the properties of the polymers and extract components, and finding the optimal PLGA/chitosan combination are essential aspects to obtain satisfactory results in terms of polyphenol content, antioxidant activity, and scaffold formation in the context of this research. The formation of scaffolds in the PLGA/chitosan mixture is influenced by the proportions of both polymers, and it is crucial to determine an optimal range to achieve the proper formation of these three-dimensional structures. Furthermore, the impregnation of olive extract causes changes in the color of the pellets, and the amount of impregnated chlorophyll varies depending on pressure and temperature variables. The morphology and pore connectivity are also affected by the polymer ratio and impregnation conditions. These results are essential for understanding and optimizing the structure and properties of the foams in the current study.

Keywords: scaffolds, supercritical CO_2, porous biomaterials, PLGA, chitosan, olive extracts, circular-economy, biomedical applications.

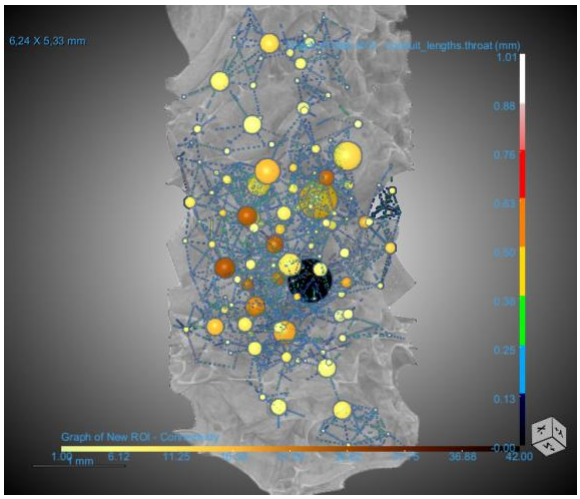


Figure 1: Figure illustrating a 3D structure and pores conectivity of PLGA-Chitosan scaffold created by DragonFly software using X-Ray Tomography images of 90-10% PLGA/Chitonsan polymer.

Hydrothermal treatment to optimize supercritical CO_2 polycaprolactone foaming processes for tissue engineering scaffolds

B. García-Jarana[1,*], D. Valor López[1], J. M. Abelleira[1], J. Sánchez-Oneto[1], J. R. Portela[1], E. J. Martínez de la Ossa[1]

[1] Department of Chemical Engineering and Food Technology, Faculty of Science, University of Cadiz, International Excellence Agrifood Campus (CeiA3), Av. Saharaui s/n, 11510 Puerto Real, Spain

Abstract:

Biodegradable materials increasingly replace biostable materials for biomedical applications, such as tissue engineering. These biomaterials offer excellent biocompatibility. Supercritical CO_2 foaming has become increasingly popular in polymer processing since it produces successfully functional scaffolds and the drawbacks of traditional process with volatile organic solvents are solved (the difficulty of removing all the solvent, the high temperatures required and the morphological characteristics in the polymers produced are not adequate).

This process is based on the unique physical properties of supercritical carbon dioxide to create a porous structure in the polymer for the tissue engineering with tuneable properties by adjusting the main foaming parameters (temperature, pressure, CO_2 contact time and depressurization gradients). However, the pore formation mechanisms follows a complex modelling, so it is difficult to obtain precise and predictable control of the pore sizes and distributions in the produced scaffolds, which causes certain limitations in the supercritical process. Therefore, the use of various types of pore forming substances (bicarbonates, polyethylene oxide, sodium chloride, sucrose, etc.) have been studied in $scCO_2$ foaming process to obtain a well-defined porosity and a good pore size distribution. Nevertheless, an extra stage is needed to remove the porogen.

Therefore, a hydrothermal treatment could favour these porous structures without the incorporation of solid porogens with its subsequent removal. This process involves water at high pressure and temperature. Presently, there are no studies on the effect of hydrothermal treatment on the fibrous structure of PCL. Therefore, in this study it is analysed the effect of performing a hydrothermal treatment before or after the supercritical CO_2 foaming process on the changes in the pore size, distribution and interconnected porous networks in the PCL produced. In addition, the effect of heat treatment on mechanical properties of PCL scaffolds obtained is studied. As can be seen in Figure 1, a hydrothermal treatment at 100 ºC, 27 bar and 10 minutes before the supercritical CO_2 foaming process produces a better distribution and interconnected porous networks compared with supercritical CO_2 foaming without treatment.

Keywords: polycaprolactone, supercritical CO_2 foaming, hydrothermal treatmens, scaffolds.

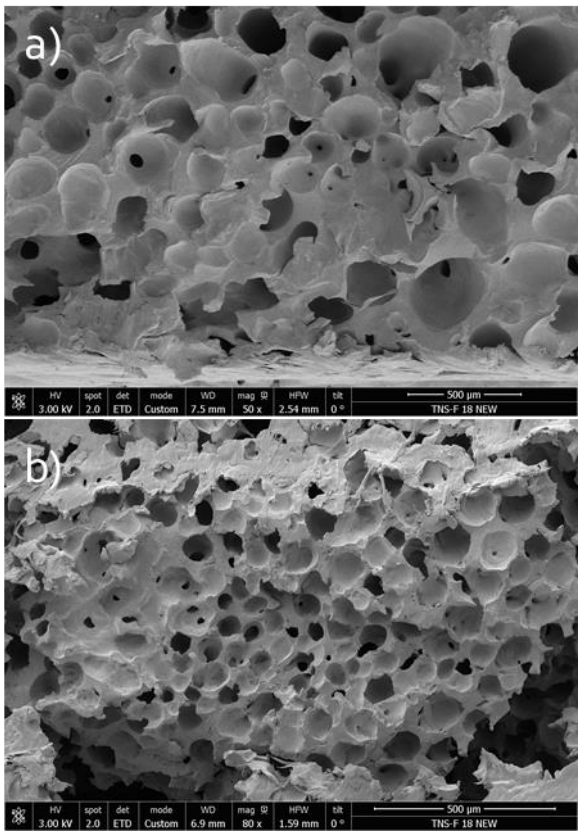


Figure 1: SEM images of PLC scaffolds produced by $scCO_2$ foaming without (a) and with (b) hydrothermal treatment .

References:

1. Alegret, N., Dominguez-Alfaro, A., Mecerreyes, D. (2019) 3D Scaffolds Based on Conductive Polymers for Biomedical Applications. *Biomacromolecules*, 20, 73-89.
2. Zhang, K., Wang, Y., Jiang, J., Wang, X.. Hou, J., Sun, S., Li, Q. (2019). Fabrication of highly interconnected porous poly(ε-caprolactone) scaffolds with supercritical CO2 foaming and polymer leaching. Journal of Materials Science, 54, 5112–5126.

Antiviral activity of silk fabric functionalized with SnO_2 nanoparticles

A. Baranowska-Korczyc [1*], D. Kowalczyk [1], K. Sobczak [2], M. Krzyżowska [3], M. Cieślak [1]

[1] Łukasiewicz Research Network - Lodz Institute of Technology, Lodz, Poland
[2] University of Warsaw Biological and Chemical Research Centre, Warsaw, Poland
[3] Military Institute of Hygiene and Epidemiology, Warsaw, Poland

Abstract:
Since the outbreak of the coronavirus disease of COVID-19, the world's attention has intensified on designing surfaces for inhibiting the spread of viral pathogens. Protective textiles, such as masks or clothes, functionalized with antimicrobial agents play a crucial role in mitigating or avoiding the spread of microorganisms. [1,2]
In this study, the antimicrobial activity of silk fabric functionalized with SnO_2 nanoparticles (SnO_2NPs) was evaluated. SnO_2NPs were synthesized by sodium stannate hydrolysis at a temperature above 60 °C. TEM analysis shows a single crystal state of cubic SnO_2 crystals characterized by a mean diameter of 3 nm, with no evidence of any impurity phase (Fig. 1a). The crystals tend to aggregate and form polycrystalline agglomerates of several nanometres. Silk fabric was functionalized with SnO_2NPs (Fig. 1b) using polydopamine as a linker. The influence of the functionalization on silk fabric structure was studied using IR and Raman spectroscopies, which revealed that dominant the β-sheet structure and high stability of silk fibroin were retained. The water contact angle and thermal properties were also evaluated before and after the functionalization.
The functionalized silk fabric was evaluated for human coronavirus 229e (VR-740, ATCC), according to the ISO Standard 18184:2019 and showed good antiviral activity. MTT test revealed nontoxic properties for the fabric before and after the functionalization.

The presented functionalized silk fabric with SnO_2NPs has a useful antiviral effect for protective textile structures including face mask designing. The functionalization does not affect fabric breathing resistance and meets the requirements of EN 149:2001 + A1:2009 standard on breathability resistance.

Keywords: silk, SnO_2, antiviral properties, COVID-19, protective textiles

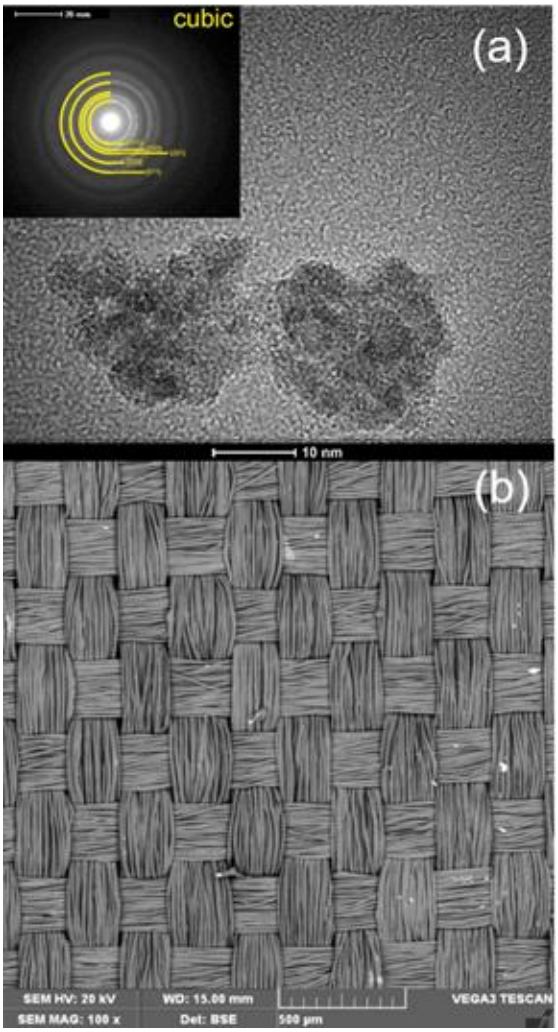


Figure 1: (a) TEM image and electron diffraction pattern (inset) of SnO_2NPs. (b) SEM image of silk fabric functionalized with SnO_2NPs.

References:

1. J. Fu *et al.* ACSNano 2023, DOI: 10.1021/acsnano.2c08894
2. M. Cieślak *et al.* Materials 2022, 15:1-16.

Acknowledgments
The research was carried out within the National Centre for Research and Development project number DOB-SZAFIR/02/B/004/02/2021.

Assumptions for obtaining thermoactive wood-based composites for furniture and interior design

A. Jeżo [1,*], G. Maksymiuk[2], M. Wronka[3], G. Kowaluk [1]

[1] Department of Technology and Entrepreneurship in Wood Industry, Institute of Wood Sciences and Furniture, Warsaw University of Life Sciences – SGGW, Warsaw, Poland
[2] Faculty of Wood Technology, Warsaw University of Life Sciences-SGGW, Warsaw, Poland
[3] Department of Human Nutrition, Warsaw University of Life Sciences-SGGW, Warsaw, Poland

Abstract:
Wood undergoes transformation to enhance properties, addressing issues like moisture sensitivity, low dimensional stability, hardness, wear resistance, susceptibility to bio-degradation, and UV radiation for composite production. An example of such modifications is wood thickening [1], which allows obtaining products with increased density and hardness. Thermal modification may reduce its hygroscopicity, increase durability, and resistance to fungi [2]. Numerous wood modification chemical systems have been extensively discussed, involving various chemicals like anhydrides, acid chlorides, isocyanates, formaldehyde, and other. [3].
One of another crucial factors influencing the performance of wood-based panels are thermal properties, including thermal conductivity. Comparing thermal conductivity of wood [4] and wood-derived composites we see that, after solid wood, plywood has the highest values of thermal conductivity followed by HDF, MDF, particle board, OSB [5] and WPC [6].
As reported by *MarketResearch.biz*, wood-based panel market size is expected to be worth around USD 334.5 Bn by 2032, growing at a CAGR of 6.4% during the forecast period (Fig.1.).

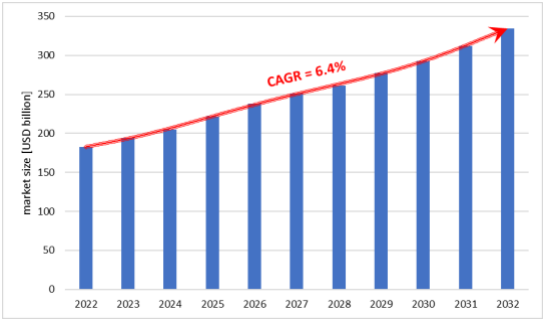


Fig. 1. Wood-based panel global market size 2023-2032.

This study aims to assess how the proportion of thermally active phase change materials in furniture affects its fundamental mechanical and physical parameters, including thermal characteristics. Phase change materials (PCM) are considered a potential solution for reducing energy consumption in buildings. Some efforts have been made to utilize phase change materials for solar energy collection. [7,8]. As [9] confirmed, positioning the PCM microcapsules above the heating tubes provides an optimum improvement in thermal performance. However, since there are no similar reports regarding attempts to use phase change materials in wood-based composite technology, the goal of the project is to fill this lack of knowledge.

Keywords: thermal activity, PCM, wood-composites, wood modification, thermal conductivity

References:

1. Grześkiewicz, M.; Krzosek, S.; Burawska, I.; Borysiuk, P.; Mańkowski, P. Influence of Thermo-Mechanical Densification (TMD) on the Properties of Structural Sawn Timber (Pinus Sylvestris L.). *Forests* **2023**, *14*, doi:10.3390/f14020231.
2. Dzurenda, L.; Orlowski, K.; Grzeskiewicz, M. Effect of Thermal Modification of Oak Wood on Sawdust Granularity. *Drv. Ind.* **2010**, *61*, 89–94.
3. Rowell, R.M. Chemical Modification of Wood: A Short Review. *Wood Mater. Sci. Eng.* **2006**, *1*, 29–33, doi:10.1080/17480270600670923.
4. Vay, O.; Busquets-Ferrer, M.; Emsenhuber, G.; Huber, C.; Gindl-Altmutter, W.; Hansmann, C. Thermal Conductivity of Untreated and Chemically Treated Poplar Bark and Wood. *Holzforschung* **2021**, *75*, 1125–1135, doi:10.1515/hf-2020-0268.
5. Sonderegger, W.; Niemz, P. Wärmeleitfähigkeit Und Wasserdampfdiffusion von Holzwerkstoffen. *Eur. J. Wood Wood Prod.* **2009**, *67*, 313–321, doi:10.1007/s00107-008-0304-y.
6. Khan, M.A.; Idriss Ali, K.M.; Shafiur Rahman, M. Swelling and Thermal

Conductivity of Wood and Wood-Plastic Composite. *Polym. - Plast. Technol. Eng.* **1997**, *36*, 179–187, doi:10.1080/03602559708000613.
7. Kenisarin, M.; Mahkamov, K. Solar Energy Storage Using Phase Change Materials. *Renew. Sustain. Energy Rev.* **2007**, *11*, 1913–1965, doi:10.1016/j.rser.2006.05.005.
8. Michael Floros, Kayden L.C. Kaller, Kosheela Devi, S.S.N. Lipid Derived Diamide Phase Change Materials for High Temperature Thermal Energy Storage. *Sol. Energy* **2016**, *139*, 23–28, doi:10.1016/j.solener.2016.09.032.
9. Babaharra, O.; Choukairy, K.; Faraji, H.; Hamdaoui, S. Improved Heating Floor Thermal Performance by Adding PCM Microcapsules Enhanced by Single and Hybrid Nanoparticles. *Heat Transf.* **2023**, *52*, 3817–3838, doi:10.1002/htj.22853.

Selected Challenges when Preparing and Characterizing Thermoactive Wood-based Composites for Furniture and Interior Equipment

A. Wronka [1,*], A. Jeżo [1], G. Kowaluk [1]
[1] Department of Technology and Entrepreneurship in Wood Industry, Institute of Wood Sciences and Furniture, Warsaw University of Life Sciences – SGGW, Warsaw, Poland

Abstract:
Energy demand in residential buildings, public buildings and offices is one of the highest, non-industrial activities of societies. This also applies to thermal energy (heating and cooling rooms). Recent studies have shown that over 40% of energy is used in these buildings produced all over the world. In light of this research, it seems necessary to find new solutions in order to maintain the temperature in rooms as constant as possible and control temperature fluctuations. It would be ideal if it was possible to stabilize the temperature in rooms without the need to introduce additional devices or technological solutions, just using the so-far existing furnishings, in a passive way. These new solutions should also include environmentally friendly strategies. One example of the way towards this target is the utilization of floor water heating systems [1].
The solution to this complicated task can be the incorporation of the structure of wood-based composites the materials, that can be characterized as thermoactive. The phase-change materials can be an example of that component [2].
The issues that have to be solved during the production of the composites are mainly based on the method of incorporation of the thermally active ingredient into the particles or fibres when preparing the composite. Also, the proper selection of the binder, which can fix together lignocellulosic materials and thermoactive additive, may play a crucial role. The pressing technique, which is dependent mainly on the type of the binder, will influence the production efficiency and can be limited by the thermally active material added.
During the testing of the produced composites, it is a fundamental task to confirm the positive thermal effect of modification, without losing the remaining requested mechanical and physical properties of the composites.
Successful implementation of the project will allow to establishment of basic technological guidelines for the production of thermally active wood-based boards for furniture and interior equipment, meeting the requirements of applicable standards, and at the same time showing high thermal functionality. Furniture made of newly designed materials could in the future increase thermal comfort in apartments, offices and public spaces, favouring optimization of energy used in the mentioned rooms. It is worth adding that the findings of the Student Furniture Scientific Group of SGGW in Warsaw show, that in typical living rooms with furniture for storage and for work, in hotel rooms, dormitories, offices, etc. the surface of the furniture boards used is what least equal to or most often larger than the wall surface. This confirms the significant potential for high-efficiency thermal insulation of the proposed solution - thermally active furniture. If the thermally active materials are successfully applied in fiberboards or particleboards, a natural development of the solution will attempt to produce wood-based composite materials for floor coverings, which should further enhance the thermal effect activity of wood-based materials for interior furnishings.

Keywords: wood-based composite, particleboard, fibreboard, furniture, floor, mechanical properties, physical properties, thermal properties, hot pressing, cold pressing.

References:

1. Khasikov, S., Thurston, U. (2021), Comparison of Energy Efficient Air-Conditioning Systems, *IOP Conference Series: Materials Science and Engineering*, Volume 1079, Chapter 3, DOI 10.1088/1757-899X/1079/4/042068.
2. Kitagawa, H., Asawa, T., Kubota, T., Trihamdani, A. R., Mori, H. (2022), Thermal storage effect of radiant floor cooling system using phase change materials in the hot and humid climate of Indonesia, Building and Environment, Volume 207, Part B, 108442, https://doi.org/10.1016/j.buildenv.2021.108442.

Polymers / Composites 2024 Session III. A: Energy and Environmental Applications

3D printed Schwarz primitive lattice based interpenetrating phase composites for improved energy absorption

Wen Feng Lu [1, 2], Xiao Guo [1, 2]

[1] Department of Mechanical Engineering, National University of Singapore, 117575, Singapore
[2] Centre for Additive Manufacturing, National University of Singapore, 117581, Singapore

Abstract:
Lightweight cellular solids are often associated with localized deformation under external load that would lead to their catastrophic failure. Cellular solids are thus often infilled with a soft secondary material, constituting interpenetrating phase composites (IPC). Owing to highly interconnected porous architectures and controllable smooth surfaces, the triply periodic minimal surface structures (TPMS) based on interpenetrating phase composites are investigated in this work. To achieve superior specific energy absorption (SEA) enhancements in the composites, an optimised Schwarz primitive lattice (P-lattice) structure is proposed by redefining the shell opening diameter with a shape parameter. Further, the influences of fabrication defects, along [100], [110], and [111] lattice directions, on the mechanical responses of the P-lattices and IPCs are studied. Compression results reveal that the modified P-lattices outperform the original P-lattices with superior compressive strength and SEA. The P-lattices also display the lowest strength and SEA along [100] as compared to that of [110] and [111]. It was found in the studies that the compressive strength and SEA of modified P-lattice along [111] were 123.66% and 64.63% higher than its [100], respectively. As for the IPCs, up to a 52% increase, from the linear addition of the two-component phases has been achieved for SEA. The IPCs also exhibit a superior specific energy absorption of 49.6 J/g, a 1109% improvement from that of the pure lattice structure, which is attributed to the high strength and large plateau strain of the composites. The results show that the internal energy of both lattice and epoxy in composites is 136% and 21%, respectively, higher than that of single structures due to the interaction effects.

Keywords: triply periodic minimal surface, interpenetrating phase composites, micro-selective laser melting, energy absorption

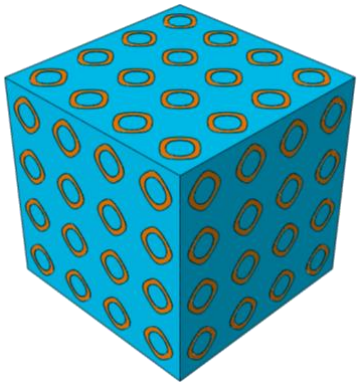


Figure 1: Figure illustrating the interpenetrating phase composites (IPCs) based on 3D printed triply periodic minimal surface structures.

References:

1. Dalaq AS, Abueidda DW, Abu Al-Rub RK.(2016) Mechanical properties of 3D printed interpenetrating phase composites with novel architectured 3D solid-sheet reinforcements. Composites Part A: Applied Science and Manufacturing;84:266-80.
2. Zhang L, Feih S, Daynes S, Chang S, Wang MY, Wei J, et al.(2018) Energy absorption characteristics of metallic triply periodic minimal surface sheet structures under compressive loading. Additive Manufacturing;23:505-15.
3. Guo X, Ding J, Li X, Qu S, Song X, Fuh JYH, et al.(2022) Enhancement in the mechanical behaviour of a Schwarz Primitive periodic minimal surface lattice structure design. International Journal of Mechanical Sciences;216.

Solvent Delamination of Multilayer Composite Waste – Challenges and Experiences

G. Denafas [1,2,*], I. Pitak [1], V. Makarevičius [1], A. Baltušnikas [1], R. Kriukienė [1], A. R. Zubas[2], A. Šleiniūtė [2], T. Mumladze[2,3]

[1] Laboratory of Materials Research and Testing, Lithuanian Energy Institute, Kaunas, Lithuania
[2] Department of Environmental Technology, Faculty of Chemical Technology, Kaunas University of Technology, Kaunas, Lithuania
[3] Department of Chemical and Environmental Technologies, Faculty of Technological Engineering, A. Tsereteli State University, Kutaisi, Georgia

Abstract:
For various purposes provided multilayer composites (MLC) include inorganic and polymer layers with different chemical structures. To MLC belong a number of electronic components, like printed circuit boards (PCB), photolvoltaic modules (PhM) or electronic cards, as well as multilayer flexible packages (MFP).
When these materials have fulfilled their functions, their recycling becomes complicated due to the aforementioned multilayer structure. Solvent delamination is one of the likely methods of preparation for recycling.
After reviewing the research results published in the last decade, it can be seen that noticeable results have been achieved in solvent delamination of PCB and MFP. These studies are continued by the joint research group of Kaunas University of Technology and the Lithuanian Energy Institute within the framework of two projects SIMULIARITY and AMIGOS, supported by the Lithuanian Research Council. Along with PCB and MFP delamination capabilities, PhM delamination capabilities are also being investigated.
The most important factors determining the efficiency of the delamination process are the solubility and oxidation resistance of the polymers performing the adhesive function, temperature, the effect of ultrasound and the particle size of the material to be delaminated.
The biggest challenges are the mechanical crushing of PCB and PhM before delamination resulting in various granulometric fractions, the encapsulation of valuable components (including metals) in the polymer layer and the constantly changing nature of the layer components used in terms of chemical and mechanical properties. In this way, the previously used solvents are no longer suitable for delamination of newer PCB. In the case of PhM delamination, we are dealing with layers of insoluble polymers, which are separated from the glass only under conditions of higher temperatures, and other methods will be needed to solve the problem of decapsulation of silicon wafers, most likely using polymer pyrolysis or gasification.

Keywords: waste multilayer composites, printed circuit boards, resins, solar panels, encapsulating polymers, multilayer flexible packages, polymer films, adhesives, delamination.

Figure 1: By dimethylsulfoxide delaminated PCB consisting of several layers of glass fabric and copper wafers bonded with epoxy resin.

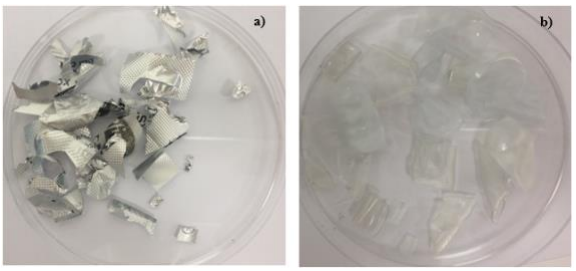


Figure 2: By organic solvents mixture delaminated blister consisting of layers of Al (a) and PVC (b).

References:

1. Tatariants, M., et all. (2017). Characterization of waste printed circuit boards recycled using a dissolution approach and ultrasonic treatment at low temperatures. *RSC Adv.*, 7(60), 37729–37738. The Royal Society of Chemistry.
2. Mumladze, T., et all. (2018). Sustainable approach to recycling of multilayer flexible packaging using switchable hydrophilicity solvents. *Green Chemistry*, *20*(15).

Metal Foam in Lightweight Heat-Exchangers: Innovation and Recycling Imperatives

Julius Eik Grimmenstein, TU Bergakademie Freiberg

Abstract

In line with the transport and energy transition, fields of application for high-performance electronics will continue to expand. Increasing performance requirements for these components are unavoidable, which of course also affects the requirements for components within various power modules. The maximum available power of electronic components, for example, is significantly linked to their cooling capacity. In order to increase the performance of power modules within the mobility sector (aviation, rail, automotive) while maintaining or reducing their weight, the use of metallized/metallic foams is currently being tested using innovative manufacturing processes.

The aim is to achieve a significant increase in performance while maintaining the same weight. In combination with variable parameters within the foam structures, other functions can also be integrated. In addition, the use of alternative manufacturing processes should significantly reduce production costs.

When developing these heat exchangers, however, particular attention should be paid to recyclability at an early stage, as recycling plays an enormously important role, especially in lightweight construction, as a result of the very complex component and material combinations used in lightweight construction. Recycling will be a necessity in the future, especially with regard to metallized polymer foams and in lightweight construction in general, due to legal requirements.

Electromagnetic properties of polymer composites based on 2000HH/2000HM-ferites and ferroelectric matrices

V.G. Kostishin, R.I. Shakirzyanov, I.M. Isaev, A.Yu. Mironovich, B.M. Skibo, M. Jaloliddinzoda

National Research Technological University "MISiS", Moscow, Russia

Abstract:
Polycrystalline, monocrystalline and amorphous magnetic materials have almost completely exhausted themselves and can no longer fully satisfy the needs of developers. Composite magnetic materials can be a good alternative. From the huge variety of magnetic composites, magnetic polymer composites (MPCs) are currently being developed at a rapid pace. One of the possible practical applications of MPCs is their use in the form of radio-absorbing materials [1].
In this work, MPCs based on fillers from powders and granules of Ni-Zn- and Mn-Zn-ferrites of spinels (ferrites of grades 2000HH and 2000HM, respectively) and a matrix of polyvinylidene fluoride (grade F2MV) were obtained and studied. The filler concentration varied from 20% to 80% by weight. Ferrite powder and ferrite granules were obtained using standard ceramic technology. The MPCs themselves were obtained by thermal pressing at temperatures of 110 °C – 190 °C. The experimental samples had the form of rings and were studied in the coaxial line path using a Rohde and Schwartz spectrum analyzer.
The following electromagnetic characteristics of the objects of study were obtained and studied: spectra of complex dielectric constant, spectra of complex magnetic permeability of objects of study and reflectance on a metal plate

Keywords: magnetic polymer composites, Ni-Zn-ferrites-spinels 2000HH, Mn-Zn-ferrites-spinels 2000HM, radio-absorbing materials, matrix, filler, magnetic permeability, dielectric constant, electrical resistivity, frequency range, attenuation of electromagnetic waves

Figure 1 shows the reflectance spectra on a metal plate MPC F2MV/2000NM-ferrite with different filler contents.

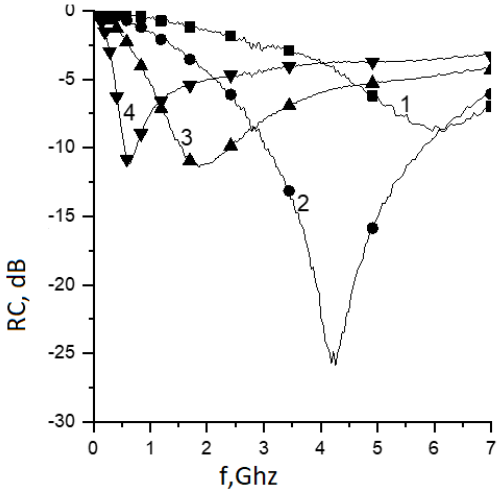


Figure 1: Reflectance spectra on a metal plate of the obtained F2MV/2000NM-ferrite MPCs concentration – 20% (1), 40% (2), 60% (3), 80% (4)

As can be seen from the presented figure, the resulting composites have good radio-absorbing characteristics. Thus, at 40% mass filler, reflection losses exceed 25 dB at maximum.
The possibilities of practical application of the obtained composites as radio-absorbing and radio-shielding materials in the construction of anechoic chambers, when conducting electromagnetic compatibility tests, etc. are discussed. A comparison is made of the radio absorption properties of the F2MV/2000NN and F2MV/2000NM composites.

References:

1. Kostishin V.G., Shakirzyanov R.I., Isaev I.M., Salogub D.V. Study of radar absorbing characteristics of polymer composites with ferrite fillers. *Industrial laboratory. Diagnostics of materials*. 2022;88(6):31-45. (In Russ.) https://doi.org/10.26896/1028-6861-2022-88-6-31-45

Tailoring the Dielectric Properties of Binder-ST Composites: RTF Experiments vs. OOF2 Modeling

Nina Kuzmić [1,2*], David Fabijan[1], Srečo Davor Škapin[1], Mikko Nelo[3], Heli Jantunen[3], Matjaž Spreitzer[1]

[1] Advanced materials department, Jožef Stefan Institute, Ljubljana, Slovenia

[2] Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

[3] Microelectronics Research Unit, University of Oulu, Oulu, Finland

Abstract:

There has been a progressing interest in particulate composites as these multi-phase systems often yield an advantageous blend of properties of the individual materials. Dielectric ceramic materials are commonly used in various electronic devices, but their large-scale production requires high energy consumption, making the need for a more eco-friendly approach increasingly evident. To address this issue, Room Temperature Fabrication (RTF) is a promising solution that involves using water-soluble inorganic compounds such as Li_2MoO_4 (LMO) to prepare functional materials. These inorganic salts can be cured at room temperature, resulting in pure ceramic or ceramic composites. One possible form is an "upside-down" composite, where a high loading of functional ceramic filler and a small amount of binder in the form of a solid and saturated aqueous solution are combined.[1]

We investigated a composite system of $SrTiO_3$ (ST) and lithium molybdate (LMO).[2] Densification occurs as the (LMO) binder deposits on the surface of (ST) filler particles during pressing and drying. Additionally, we varied the LMO content, which allowed us to convert the upside-down composite to traditional 0-3 composites.[3]

We replaced LMO with alternative binders, sodium-, barium- and magnesium-based salts, resulting in sufficient binding (relative density ~ 87 %), and relative permittivity (65-130) and dielectric losses (0.002-0.05) at 1 MHz and 5 GHz. The binder-ST composites were characterized with microstructural, FTIR, and XRD analysis.

We also investigated the influence of residual porosity on the dielectric properties through rules of mixture (ROM) and OOF2 simulations. OOF2 is a powerful tool that can simulate polarization and energy fields through the microstructure[4] and explain cracking in the composites and the effect of conducting additives and coating. RTF entails almost infinite possibilities of combining different materials for various applications.

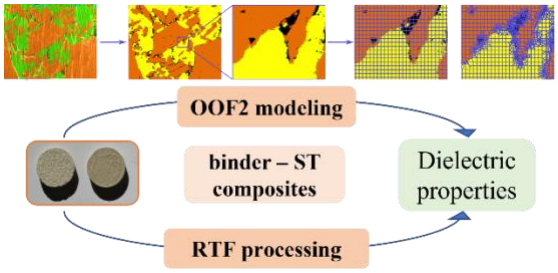


Figure 1: Figure illustrates the RTF process complemented with OOF2 modeling to improve the dielectric performance of such binder-ST ceramics experimentally.

References:

1. M. Nelo, J. Peräntie, T. Siponkoski, J. Juuti, and H. Jantunen, "Upside-down composites: Electroceramics without sintering," *Appl. Mater. Today*, vol. 15, pp. 83–86, 2019, https://doi.org/10.1016/j.apmt.2018.12.021.
2. N. Kuzmić, S. D. Škapin, M. Nelo, H. Jantunen, and M. Spreitzer, "Dielectric Properties of Upside-Down SrTiO3/Li2MoO4 Composites Fabricated at Room Temperature," *Front. Mater.*, vol. 8, p. 121, 2021, doi: 10.3389/fmats.2021.669421.
3. N. Kuzmić, S. D. Škapin, M. Nelo, H. Jantunen, and M. Spreitzer, "Room temperature fabrication and post-impregnation of LMO-ST composites: Engineering and modeling of dielectric properties," *Open Ceram.*, vol. 16, p. 100495, 2023, https://doi.org/10.1016/j.oceram.2023.100495.
4. S. A. Langer, A. C. E. Reid, S. I. Haan, R. E. Garcia, R. C. Lua, and V. R. Coffman, "The OOF2 manual," *NIST, US*, 2008.

Na-ion battery using a composite electrolyte

Yumei Wang,[1] Xiaoyu Xu,[2] Li Lu[1,2]
[1] National University of Singapore Chongqing Research Institute, Chongqing 401123
[2] National University of Singapore, Singapore 117575

Abstract:
Solid electrolyte is one type of ionic conductor that uses solid materials to conduct ions. There are many types of solid electrolytes such as inorganic and polymer electrolytes. The advantage of solid electrolyte is its capability to hinder the risk of possible thermal run-away and possibility to enhance energy density.[1] This work reports development of solid-state organic/inorganic composite electrolyte for Na-ion battery. Solid polymer electrolyte is composed of polymer matrice incorporated with inorganic particles. The ion conduction in solid polymers relies on the sodium ions migration between ion coordination sites. There are two possible kinds of sodium ion transport in host polymers, happening in amorphous and crystalline phases respectively. The first mechanism is the most commonly accepted conduction mechanism of sodium ions in SPEs, which depends on the motion of segmental chains of host polymers. To reduce space charge between the electrode and the electrolyte, ferroelectric thin layer was used. The Na-ion battery using the ferroelectric-tailored electrolyte reveals great improvement of charge/discharge cyclability and increased safety.[2] Fig. 1 compares cycleability of the batteries using solid electrolytes vs that using liquid electrolyte.[3]

Keywords: Solid-state electrolyte, composite, ionic conductivity, Na-ion battery.

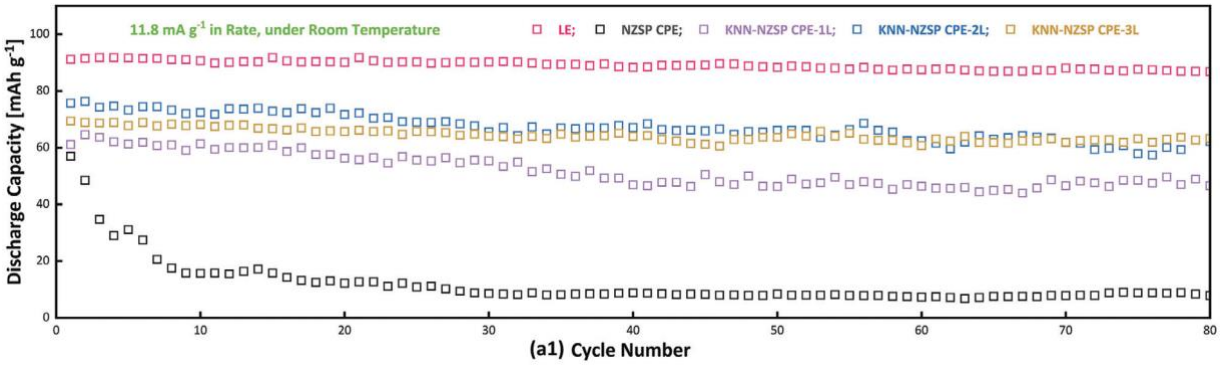


Fig. 1. Charge/discharge cycleability of battery cells using: LE liquid electrolyte, NZSP CPE composite electrolyte, KNN-NZSP CPE-1 one-layer KNN modified composite electrolyte, KNN-NZSP CPE-2 two-layer KNN modified composite electrolyte, and KNN-NZSP CPE-3 three-layer KNN modified composite electrolyte.[3]

References:

1. Xu, X. Wang, Y. Yi, Q. Wang, X. Camacho, R.P. Kungl, H. Eichel, R. Lu, L. Zhang, H. (2023), Ion Conduction in Composite Polymer Electrolytes: Potential Electrolytes for Sodium-Ion Batteries, ChemSusChem, 16, e202202152.
2. Wang, Y. Wang, Z. Sun, J. Zheng, F. Kotobuki, M. Wu, T. Zeng, K. Lu, L. (2020), Flexible, stable, fast-ion-conducting composite electrolyte composed of nanostructured Na-super-ion-conductor framework and continuous Poly (ethylene oxide) for all-solid-state Na battery, J. Power Sources, 454, 227949.
3. Wang, Y. Wang, Z. Zheng, F. Sun, J. Oh, J.A. Wu, T. Chen, C. Huang, Q. Kotobuki, M. Zeng, K. Lu, L. (2022), Ferroelectric Engineered Electrode-Composite Polymer Electrolyte Interfaces for All-Solid-State Sodium Metal Battery, Adv. Sci. 2022, 9, 2105849.

Radio absorption properties of magnetic polymer composites based on Li-Mn-Zn-spinel ferrites in the range of 0.1 – 7.0 GHz

V.G. Kostishin, R.I. Shakirzyanov, I.M. Isaev, A.Yu. Mironovich, B.M. Skibo, M. Jaloliddinzoda

National Research Technological University "MISiS", Moscow, Russia

Abstract:
Today, polycrystalline, monocrystalline and amorphous magnetic materials have almost completely exhausted themselves and no longer fully satisfy the needs of developers. Composite magnetic materials can be a good alternative. From the huge variety of magnetic composites, magnetic polymer composites (MPCs) are currently being developed at a rapid pace. One of the possible practical applications of MPCs is their use in the form of radio-absorbing materials [1].
In this work, MPCs based on a filler of Li-Mn-Zn-ferrite-spinel powder and matrices of PS-525 polystyrene and F-2M polymer were obtained and studied. The MPCs were mixed composites. Volume concentration of filler varied from 9% vol to 60% vol. Ferrite powder was obtained using standard ceramic technology. The MPCs themselves were obtained by thermal pressing at temperatures of 110 °C – 190 °C. Experimental samples were obtained in the form of rings and studied in the coaxial line path using a Rohde and Schwartz spectrum analyzer.
The spectra of the complex dielectric constant, the spectra of the complex magnetic permeability of the objects of study and the reflection coefficient on a metal plate were obtained and studied. Figure 1 shows the reflectance spectra on a metal plate MPC F2M/Li-Mn-Zn-ferrite with different filler contents.

Keywords: polymer composites, radio absorption, polystyrene material, Li-Mn-Zn-ferrite-spinel.

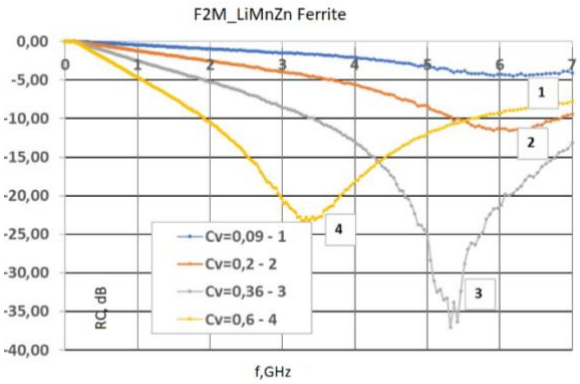


Figure 1: Reflectance spectra on a metal plate of the obtained F2M/Li-Mn-Zn ferrite MPCs

As can be seen from the presented figure, the resulting composites have good radio-absorbing characteristics. Already starting from 20% filler, reflection losses exceed a maximum of 10 dB.
The possibilities of practical application of the obtained composites as radio-absorbing and radio-shielding materials in the construction of anechoic chambers, when conducting electromagnetic compatibility tests, etc. are discussed.

References:

1. Kostishin V.G., Shakirzyanov R.I., Isaev I.M., Salogub D.V. Study of radar absorbing characteristics of polymer composites with ferrite fillers. *Industrial laboratory. Diagnostics of materials*. 2022;88(6):31-45. (In Russ.) https://doi.org/10.26896/1028-6861-2022-88-6-31-45

Multifuctional Parylene C membranes for microelectronic devices integration

J.V. Pinto [1*],B.J. Coelho[1,2], D. Carvalho[1], J. Coelho[1,2]. J.P. Neto[1], J. Martins[1], A. Roviso[1], R. Martins[1], , L.N. Boane[1], M. Cortinhal[1], H. Águas[1], M. Mendes[1], R.Igreja[1], P. Barquinha[1]

[1] *CENIMAT|i3N, Department of Materials Science, School of Science and Technology, NOVA University Lisbon and CEMOP/UNINOVA, Caparica, Portugal*
[2] Departamento de Física de la Materia Condensada, Facultad de Fisica, Av. de la Reina Mercedes, S/N, 41012 Sevilla, Spain

Abstract:
Poly(chloro-para-xylylene), or Parylene C, is a flexible dielectric polymer belonging to the poly(p-xylylene) family. It is widely used due to its unique set of properties, such as chemical inertness, transparency, flexibility, conformability, and dielectric properties. Self-supported ultrathin and robust membranes can also be attained being an excellent substrate for flexible and ultra-thin skin-like electronics applications, as in conformable membranes for detecting brain activity [ref] or sensors [1]. Within this work we present a set of different routes for exploiting the use of Parylene-C in device fabrication, taking advantage of its compatability with standard microelectronics processing methodologies. Different hybrid devices fabricated containing metal or inorganic layers in conjunction with Parylene-C in its multiples roles as organic substrate, as a dielectric and as encapsulation layer. (Figure 1). Furthermore, the facile etching mechanism of Parylene under O_2 Reactive Ion Etching leads to an increase of the surface roughness. By combining RIE with Langmuir-Blodgett methodology using self-assembled monolayers of 1.6 um polystyrene microspheres as a soft mask, produces patterned honeycomb arrays that can be applied to microstructured electrodes achieving heights ranging from hundreds of nanometres to few microns. Different sets of devices have already being obtained from TFTs with subthreshold slopes of 0.26 V/dec and low gate leak currents, digital microfluidic insulating layers [1], conformable and transparent ECoG electrodes based on AgNWs [2], supercapacitors [3] among others. We will present an overview of the possibilities that this polymer can bring to standard microelectronic processes to enable conformable, biocompatible and skin-like electronics.

Keywords: Parylene-C, microeletronic devices, TFTs, Supercacitors, conformable electronic; micro and nanostructuried electrodes.

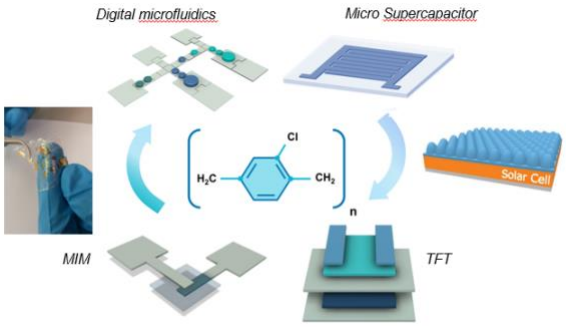


Figure 1: Overview of possible devices produced with Parylene-C membranes as substrate, dielectric and encapsulation.

References:

1. Coelho BJ, Pinto JV, Martins J, Rovisco A, Barquinha P, Fortunato E, Baptista PV, Martins R, Igreja R.(2023) Parylene C as a Multipurpose Material for Electronics and Microfluidics; *Polymers*. 15(10):2277.
2. Neto, J. P., Costa, A., Vaz Pinto, J., Marques-Smith, A., Costa, J. C., Martins, R., Fortunato, E., Kampff, A. R., & Barquinha, P. (2021). Transparent and Flexible Electrocorticography Electrode Arrays Based on Silver Nanowire Networks for Neural Recordings. *ACS Applied Nano Materials*, *4*(6), 5737–5747.
3. Correia, R., Deuermeier, J., Correia, M. R., Vaz Pinto, J., Coelho, J., Fortunato, E., & Martins, R. (2022). Biocompatible Parylene-C Laser-Induced Graphene Electrodes for Microsupercapacitor Applications. *ACS Applied Materials & Interfaces*, *14*(41), 46427–46438.

Structural simulation and alternative fabrication of a rear suspension fork link using composite materials for electrical vehicle applications.

M. Lasheras-Zubiate [1*], J:L Fernández [1], E. Teiletxea[1], G. Argandoña[1], I. Landa[1], R. Herrero[1], R. Mazquiarán[1]
[1] NAITEC, Fundación I+D Automoción y Mecatrónica, Pamplona (Navarra), Spain
*corresponding autor

Abstract:
Lightweighting plays a pivotal role in the automotive sector, especially in the context of electric vehicles. Firstly, reduced vehicle weight enhances energy efficiency, allowing EVs to cover longer distances on a single charge. Secondly, it contributes to improved acceleration and overall performance, making electric cars more appealing to consumers. Moreover, lighter EVs require smaller batteries, reducing production costs and environmental impact. Ultimately, lightweighting remains a fundamental strategy in advancing the sustainability and performance of electric vehicles. Alternative materials such as composite, as well as new fabrication technologies such as 3D printing of Continuous Fibre Reinforced Composite (CFRC), have emerged as promising alternatives in the field of manufacturing, offering numerous advantages compared to other conventional techniques. This innovative technique enables the production of highly customised and complex composite parts efficiently and accurately.
Structural simulation plays a crucial role in ensuring that lightweight design strategies in the automotive sector are successful. It helps engineers make informed decisions about materials, design choices, and manufacturing processes, ensuring that lightweight components meet safety, performance, and cost requirements. This synergy between structural simulation and lightweight design is integral to the development of more fuel-efficient, environmentally friendly, and safe vehicles in the automotive industry. Structural simulation allows to analyze how lightweight materials, such as advanced composites, will perform in vehicle components. Simulating stress, deformation, and other factors it is possible to predict if these lightweight materials meet safety and performance requirements.
The redesign and manufacturing process was executed employing advanced technologies for a fork-link, a mechanically welded component crafted from stamped steel elements derived from cut welded steel tubes. This component serves as a crucial element within the rear suspension system, responsible for the transmission of forces in three primary directions, including axial and two transverse vectors. The selection of this component was driven by its notable potential for weight reduction.
A vehicle dynamics model centered on the rear axle and a structural analysis of the original design were carried out and, based on the results obtained, the manufacturing processes, materials and mechanical properties that the new composite parts had to comply with were selected. Automatic generative algorithms (using the tool APEX Design Generative - MSC Hexagon) were used for the design, redesign and optimization of the selected material variants and manufacturing processes.
Various manufacturing technologies were employed to fabricate the components designed, resulting in weight reductions ranging from 20% to 60%. The extent of reduction depended on the specific manufacturing process and the materials chosen. Mechanical characterization of the test specimens yielded values that are well-suited for their intended application in the electric vehicle design. LCA calculations have been carried out to determine the environmental impact of the components designed and fabricated.

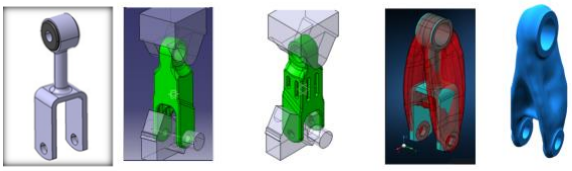


Figure 1 Initial part and different designs optimized for the materials simulated.

References:

1. Andrey V. Azarov, Fedor K. Antonov, Mikhail V. Golubev, Aleksey R. Khaziev, Sergey A. Ushanov, Composites Part B: Engineering; Volume 169, 15 July 2019, Pages 157-163.
2. Xin Wang, Man Jiang, Zuowan Zhou, Jihua Gou, David Hu; Composites Part B: Engineering Volume 110, 1 February 2017, Pages 442-458.

Addressing fire risk in electric vehicles battery boxes using inorganic polymer-based fiber-reinforced composites

A. Natali Murri [1,*], Elettra Papa [1], Elena Landi [1], Claudio Mingazzini [2], Valentina Medri [1]

[1] CNR-ISSMC, Institute of Science, Technology and Sustainability for Ceramics, Faenza (RA), Italy
[2] ENEA-TEMAF, Laboratory of Materials Technologies, Faenza (RA), Italy

Abstract:
The increasing need for secure materials in the realm of electric vehicles (EVs), especially within the construction of battery enclosures, has experienced notable growth in recent years. This growth can be attributed largely to safety concerns associated with potential fire accidents. Concurrently, the drive to diminish reliance on critical raw materials for EV components has propelled substantial research endeavors towards formulating more sustainable, fire-resistant structural materials, in adherence to the principles of a circular economy.

To strike an effective balance between the mechanical performance requirements for battery enclosures—both pre and post simulated fire accidents—and the utilization of environmentally friendly materials and technologies (including waste raw materials), innovative composite materials have been developed within the framework of "FENICE - Fire rEsistant eNvironmental frIendly CompositEs" project.

These materials are based on continuous or random chopped carbon fiber and water-based inorganic polymeric matrices. The inorganic matrices originate from aqueous blends of aluminosilicate clay powders and amorphous silica, undergoing chemical activation at room temperature through alkaline solutions of potassium silicates and hydroxides (geopolymerization process). Incorporating refractory micro-powders of oxidic ceramics further enhances the material's functionality and improves its thermal stability. The end product is a slurry exhibiting rheological properties in its initial state that align seamlessly with vacuum impregnation and lamination processes commonly employed in the production of traditional composites (FRPs).

Additionally, operating a simple post-curing step at 250° C, the material can boast exceptional resistance properties at high temperatures (>650° C) and is entirely fire-resistant (Fig. 1). Moreover, coupling the obtained laminates with thin aluminum foils on the outer surfaces, a further enhancement of the thermal properties and protection against oxidation can be pursued, as demonstrated by preliminary conecalorimeter tests.

Keywords: Electric Vehicles (EVs), Fire-resistant structural materials, Composite materials, Circular economy, Carbon fiber

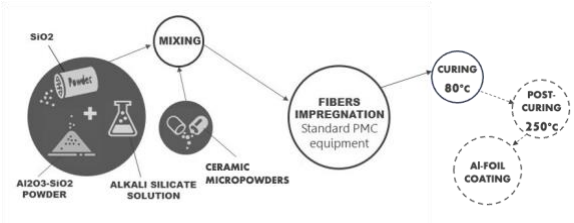


Figure 1: Figure illustrating the production process of inorganic-polymer based Cf-laminates using a sustainable process

References:

1. Medri, V.; Natali Murri, A.; Papa, E.; Mingazzini, C.; Scafè, M.; Landi, E. Ultra-High-Temperature Ceramic-Doped Inorganic Polymers for Thermo-Structural Fiber-Reinforced Composites. *Materials* 2023, *16*, 6649. https://doi.org/10.3390/ma16206649

Acknowledgements: EIT RawMaterials GmbH is acknowledged for supporting and funding this research within the project KAVA9 FENICE-Fire rEsistant eNvironmental frIendly CompositEs (Project Agreement n.o. 21099

Strong and tough double-network hydrogels with excellent adsorption performance for diclofenac: behaviors and mechanisms

Lin Wang [1], Gert-Jan Euverink [1], Francesco Picchioni [1, *],
[1] Faculty of Science and Engineering, University of Groningen, Groningen, The Netherlands

Abstract:
The development of hydrogel adsorbents with both good mechanical strength and adsorption performance is a big challenge in water purification[1]. The trade-off between swelling properties and adsorption capacities of hydrogels is a major roadblock[2]. Here, the double network strategy was adopted to induce chemically and physically cross-linking within hydrogels, and applied for sodium diclofenac removal. The incorporation of chemically and physically cross-linked domains in the hydrogel adsorbents resulted in intrinsically tough and compressible properties in their fully swollen state. which is of great practical value in wastewater treatment. Meanwhile, double network hydrogels showed good adsorption performance for sodium diclofenac removal, with the maximum Langmuir monolayer adsorption capacity of 1012 (±30) mg/g under neutral conditions, which was higher than most of reported hydrogel adsorbents. Thermodynamic studies implied the adsorption process was spontaneous and exothermic. FT-IR and XPS revealed that the adsorption mechanism was predominantly determined by ion exchanges. During regeneration, the double network hydrogel maintained good mechanical properties and reusability. In conclusion, It is shown that the double network hydrogel with rigid-flexible structure, environmental adaptability, good adsorption capacity and good reusability, has long-term application potential in the removal of refractory organic drugs in wastewater.

Keywords: hydrogel, high mechanical strength, sodium diclofenac, water treatment, adsorption, reusability

References:

1. Li, D., Zhan, W., Zuo, W., Li, L., Zhang, J., Cai, G., & Tian, Y. (2022). Elastic, tough and switchable swelling hydrogels with high entanglements and low crosslinks for water remediation, *Chemical Engineering Journal.*, 450, 138417.
2. Feng, Z., Feng, C., Chen, N., Lu, W., & Wang, S. (2022). Preparation of composite hydrogel with high mechanical strength and reusability for removal of Cu (II) and Pb (II) from water, *Separation and Purification Technology*., 300, 121894.

3Bs Materials 2024 Session III. B: Biomaterials / Biomimetics Materials / Biobased Materials applications

3D-printed poly(lactic acid) structures coated in hydroxyapatite and loaded with a drug delivery system for the reconstruction of cranial defects

A. D'Andrea[1], R. Donate[2], M. Monzón[2], I. Cacciotti[1]
[1] Department of Engineering, INSTM RU, University of Rome Niccolò Cusano, Via Don Carlo Gnocchi 3, 00166, Rome, Italy.
[2] Mechanical Engineering Department, Universidad de Las Palmas de Gran Canaria, Edificio de Fabricación Integrada, 35017, Las Palmas de Gran Canaria, Spain.

Abstract:
Any implant aimed at promoting bone regeneration, needed after traumatic brain injury (1) or a resection surgery intended for preserving the overall functionality of the bone, must take into account both the need for stimulation of new bone cellular growth and the avoidance of inflammation or infection on the site of implantation (2). This research project involves the design and tailoring of 3D-printed bio-polymeric devices for bone reconstruction purposes with additional osteointegrative and antinflammatory features for overcoming the above-mentioned issues.
Namely, poly-lactic acid (PLA) 3D-printed structures were coated with a layer of hydroxyapatite (HAp), in order to provide bioactivity and osteo-integrative properties to the implant.
The first experiments allowed determining the proper printing conditions and parameters, the thermal properties of the 3D-printed structures and their morphology.
Two different coating methods were then tested and compared: sol-gel deposition from precursor sources in solution, and powdered HAp added to the surface of the structure through pressure and heating processes.
Afterwards, ε-polycaprolactone (PCL) microparticles, both hollow and drug-loaded, were engineered in order to work as Drug Delivery Systems (DDSs) of an anti-inflammatory drug in the site of implantation. They were later embedded into the 3D-printed HAp-coated structures developed.
The two kinds of coated structures, including the DDS, were analysed through different techniques (e.g. SEM, MTT, release kinetics tests, CCK-8) to assess their physical and biological features.
Figure 1 shows a micrograph of one of the systems tested.

Keywords: tissue engineering, bone regeneration, cranial implants, hydroxyapatite, drug delivery systems, biomedical applications.

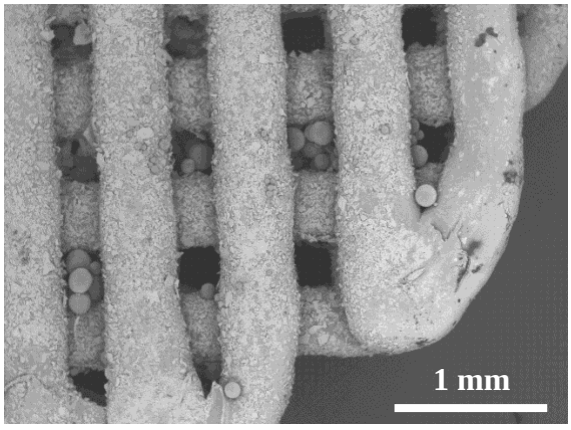


Figure 1: SEM micrograph showing the efficacy of the powdered hydroxyapatite coating with addition of the drug delivery system based on drug-loaded polycaprolactone microspheres.

References:

1. Capizzi, A., Woo, J., & Verduzco-Gutierrez, M. (2020). Traumatic Brain Injury: An Overview of Epidemiology, Pathophysiology, and Medical Management. *Medical Clinics of North America*, *104*(2), 213–238.
2. Zanotti, B., Zingaretti, N., Verlicchi, A., Robiony, M., Alfieri, A., & Parodi, P. C. (2016). Cranioplasty: Review of materials. *Journal of Craniofacial Surgery*, *27*(8), 2061–2072.

Encapsulation of ectoine in lipid nanoparticles for the treatment of inflammatory bowel disease

M. Abajo[1], V. Saez-Martinez [1]
[1] R&D Departmet, i+Med S. Coop, Vitoria-Gasteiz, Spain

Abstract:
Inflammatory bowel disease (IBD) is a severe chronic inflammatory disorder of the digestive tract that negatively affects quality of life and requires long-term dependence on effective medications. Thus, in order to facilitate the treatment of this pathology and improve the quality of life of patients, we seek to develop new systems capable of stabilizing the function of the intestinal mucosal barrier. Furthermore, mucoadhesive dosage forms have received substantial attention, as well, as new delivery systems to improve drug bioavailability by prolonging residence time and achieving sustained drug release profiles.

Ectoine molecule becomes of great interest for the treatment of IBD due to its characteristic anti-inflammatory properties and the promising results obtained in several studies carried out in animals[1]. In this regard, in several studies the encapsulation in liposomes of active ingredients similar in nature to ectoine have been carried out before. For this reason, given that ectoine seems to be a promising active ingredient in the treatment of IBD and that the encapsulation of similar active ingredients in liposomes is effective, a system for encapsulating ectoine in liposomes is proposed to cover the aforementioned objectives.

With the purpose of increasing the effectiveness of ectoine in IBD and avoiding possible adverse effects, an ectoine encapsulation system based on liposomes has been designed. In addition, mucoadhesive characteristics are also provided to this system through a coating with chitosan to prolong the residence time of ectoine and obtain a sustained release profile, in addition to the antifungal, antimicrobial and immunogenic properties of chitosan, among others[2].

Once the optimized formulation is obtained, the following characteristics are achieved, among others: an encapsulation efficiency and drug load of 77.5%, a particle size of 437nm, an ectoine sustained release profile for 7h and a Z potential of 40.3 mV, which indicates that they are nanoparticles with good stability.

Keywords: ectoin, encapsulation, liposomes, mucoadhesive, coating, chitosan, controlled release, IBD, biomedical applications.

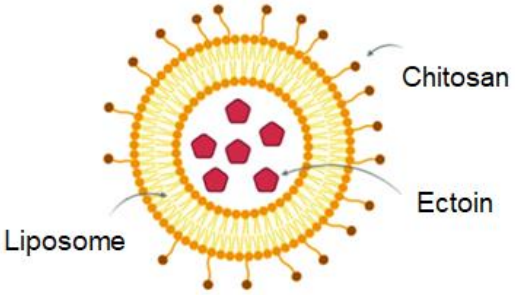


Figure 1: Figure illustrating the fundamental of the encapsulation of ectoin inside the hydrophilic nucleus of the liposomes.

References:

1. Abdel-Aziz, H., Wadie, W., Abdallah, D. M., Lentzen, G., & Khayyal, M. T. (2013). Novel effects of ectoine, a bacteria-derived natural tetrahydropyrimidine, in experimental colitis. Phytomedicine, 20(7), 585–591. https://doi.org/10.1016/j.phymed.2013.01.009
2. Filipović-Grcić J, Skalko-Basnet N, Jalsenjak I. Mucoadhesive chitosan-coated liposomes: characteristics and stability. J Microencapsul. 2001 Jan-Feb;18(1):3-12. doi: 10.1080/026520401750038557. PMID: 11201339.

Lymphatic Network Engineering and Regeneration in Vitro and in Vivo for the Lymphedema Treatment

Qixu Zhang*, Yewen Wu, Martha Fowler, Edward Chang, Mark Schaverien, Peirong Yu**

Department of Plastic Surgery, The University of Texas MD Anderson Cancer Center, Houston, TX 77030, USA.
qzhang5@mdanderson.org

Abstract

Lymphedema has been shown to be one of the most significant survivorship issues following the treatment of breast cancer. Lymphovenous bypass and vascularized lymph node transfers have provided the closest chance at a cure for lymph flow disorders. However, the availability of qualitative autologous flaps and donor site morbidity significantly limit its application. Engineered lymphatic network may offer a clinically alternative to autologous flaps. This study aimed to engineer lymphatic vessels with decellularized adipose tissue matrix (hDAM) to improve the lymphedema symptom after transplantation.

hDAM was processed and characterized by proteomic analysis (LC-MS/MS) and scanning electron microscope. hASC and HDLEC viability and adhesion on hDAM were tested by immunostaining. pre-vascularized hDAM with hASCs and HDLECs were then analyzed by 2-photon imaging system in vitro and in vivo.

hDAM maintained natural extracellular matrix structure with 3D nanofibrous features and matrisome proteins. hDAM provides a niche for hASCs and HDLECs proliferation. Extraction of hDAM induced hASCs differentiation. hDAM caused little foreign body response. Coculture of hASCs and HDLECs on hDAM successfully formed LYVE-1 positive dense lymphatic vessels. Re-cellularized constructs regenerated rich lymphatic vessel network at 1-3 months post-op.

Pre-vascularized hDAM-cell constructs showed great promise for lymphatic vessels tissue engineering and regeneration. This platform may provide a novel strategy for secondary lymphedema treatment after transplantation and guarantee further investigation.

Delivering Parasite-Derived Immunotherapeutics from Hyaluronic Acid Hydrogels Acting as Soft Tissue Supports.

Ward, V.[1,2]*, O'Dwyer, J.[1] , Lalor, R.[3] , Dalton, J.P[3], Duffy, G.P [1,2,4]

[1] Anatomy and Regenerative Medicine Institute (REMEDI), College of Medicine, Univ. of Galway
[2] SFI Advanced Materials and BioEngineering Research Centre (AMBER), Trinity College Dublin & University of Galway
[3] Center for One Health (COH) and Ryan Institute, School of Natural Science, University of Galway
[4] CÚRAM, SFI Research Centre for Medical Devices, University of Galway & RCSI, Galway, Ireland

Abstract

Hydrogel biomaterials are being investigated for their use in a range of complex diseases by providing mechanical support in soft tissue. Hyaluronic acid (HA) hydrogels have shown promise as tissue scaffolds and as injectable viscosupplements. HA hydrogels can be delivered in a minimally invasive way and can have mechanical tuneability. As with most biomaterials however, HA hydrogels can cause an undesirable immune response. Immunomodulatory strategies are being developed to limit this foreign body response. Immunomodulatory peptides, derived from parasites, are being investigated to help overcome the body's immune response to biomaterials. An immunomodulating peptide Sm16-K66 has been extracted from the parasite Schistosome mansoni[1]. Sustained delivery of this peptide could potentially mitigate an immune reaction to implanted hydrogels. This research will investigate the mechanical characteristics of HA-Tyramine modified (HA-TA) hydrogels and their ability to deliver Sm16-K66 as a therapeutic.

HA-TA hydrogels were formed with a range of polymer (2-3% w/v) and enzyme crosslinking (7.5–60 µL/mL) concentrations using a resin-printed mixer. Rheometry, nanoindentation and mechanical compression tests were preformed and formulations were altered to match biological tissue properties. Swelling and degradation properties were profiled. Release studies were performed with Sm16-K66 loaded HA-TA hydrogels to establish their release profile.

Hydrogels were formed using the custom-designed mixer at a range of HA-TA and crosslinker concentrations (A). Increasing the concentration of crosslinkers or HA-TA significantly increased the Youngs modulus of the hydrogels (B). Increasing hydrogel stiffness significantly reduced the swelling capacity (C). Hydrogels with a higher crosslinker concentration were more resistant to hyaluronidase degradation (D).

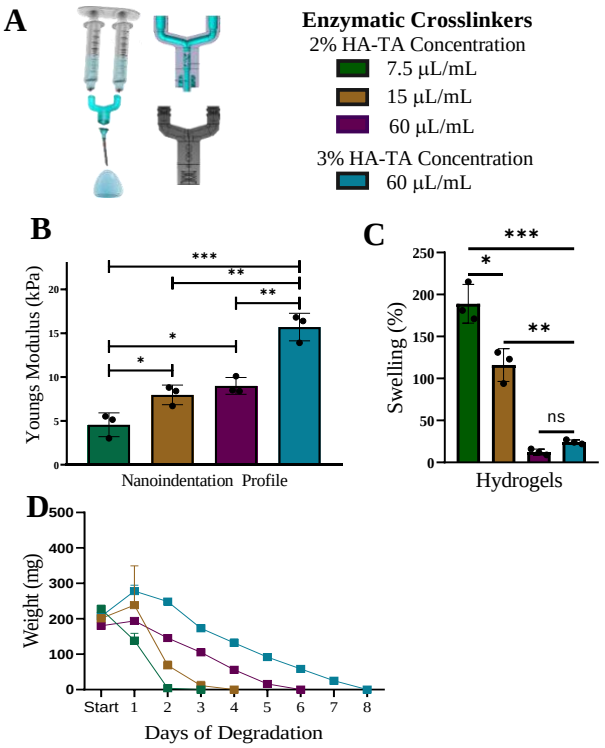


Figure 1: (A) Custom-designed mixer. (B) Youngs modulus recorded across HA-TA hydrogels by nanoindentation. (C) Swelling of HA-TA hydrogels in PBS at 37°C. (D) Degradation of HA-TA hydrogels in 10 U/mL hyaluronidase.

The custom-designed mixer ensured that hydrogels were consistently formed. Mechanical tuning of hydrogels altered their swelling and degradation, subsequently affecting their release profile. This study establishes HA-TA hydrogels as drug delivery platforms that can provide mechanical support to soft tissue.

Keywords: hydrogels, hyaluronic acid, mechanical characterisation, drug delivery, parasite-derived therapeutics.

References:

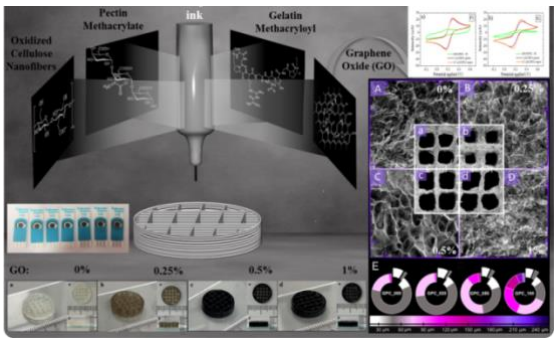
1. Shielsid J.*et al.*,J. PLoSNegl Trop Dis,14(7):1-25 2020

A novel approach in bone regeneration and detection of ALP and RUNX2 osteogenic biomarkers

M. Ionita[1,*]
[1]Faculty of Medical Engineering, University of Science and Technology Politehnica of Bucharest, Gheorghe Polizu 1-7, 011061, Bucharest, ROMANIA
*mariana.ionita@polimi.it

Abstract:
The current work targets fabrication of bone substitutes with much improved regenerative efficiency than current treatment options used in the restoration of non-healing bone defects and the reliable electrochemical biosensor for the detection of two osteogenic biomarkers, alkaline phosphatase (ALP) and Runt-related transcription factor 2 (RUNX2). The combination of cells and a biomaterial scaffold is conventionally the groundwork upon which tissue engineering is built. Based on that approach several, 3D scaffolds potentially attractive for bone repair based on biopolymers (pectin, chitosan, or gelatin), synthetic poly(vinyl alcohol) and graphene derivatives were proposed and investigated under the complex condition envisaged by real-life bone repair application. Our studies demonstrated that graphene derivatives act as a supporter of osteogenesis due to cell friendly chemistry and cell-detectable micromechanical stimuli distributed across the matrix. The addition of GO to hydrogel inks also enhanced the compressive modulus, the printability and scaffold fidelity compared to the pure polymeric system. The advent of improved fabrication technologies such as 3D printing has enabled the engineering of commercial screen printed carbon electrodes (SCPEs) with electrochemically reduced graphene oxide (RGO) to serve as the basis of a future electrochemical platform at un unprecedented resolution and reproducibility for osteogenic biomarkers detection. The SCPE-RGO platform modification and functionalization was characterized by SEM, Raman spectroscopy, and contact angle measurements and by CV and EIS for electrchmical response. The SCPE-RGO platform obtained by 3D printing has a higher sensitivity towards the detection of RUNX2 (up to 1 nM) compared to the ALP biomarker. However, further investigations are necessary in order to improve the sensitivity of the graphene-based platform for both osteogenic biomarkers and to increase the potential of this system to be fabricated at industrial scale.

Figure 1. 3D printing approach for the fabrication of scaffolds potentially attractive for bone regeneration and fabrication of reliable electrochemical platform based on SCPE-RGO



for the detection of two osteogenic biomarkers, alkaline phosphatase (ALP) and Runt-related transcription factor 2 (RUNX2).

The authors acknowledge the financial support from the Ministry of Research, Innovation and Digitization, Executive Agency for Higher Education, Research, Development and Innovation, project number PCE 103/2022 (REOSTEOKIT)

Keywords: bone regeneration, multiple myeloma, scaffold biomaterials, 3D printing, ASOs, DNA cages, molecular modelling.

Hybrid silylated hydrogels for biomecules encapsulation: design, stability and controlled release

C. Tourne-Peteilh,[1] G. Subra,[2] and A. Mehdi[1]

[1] ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
[2] IBMM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

Abstract:
The delivery of therapeutic bio-macromolecules (i.e. peptides, proteins, nucleic acids and lipids) remains a challenge due to the peculiar instability of these fragile and the wide range of biomedical applications in concern, from vaccination, chronic disease treatment, tissue engineering, to cancer therapy.

A new family of biocompatible hybrid hydrogels, have emerged recently that can cross-link with stable chemical bonds, namely siloxane, Si–O–Si. Inorganic sol–gel polymerization occurs in soft conditions and aqueous media, allowing the inclusion of water-soluble bioorganic molecules. More than, the sol–gel proceeded chemo selectively towards amino acid side chains. This is a key advantage for biomolecules encapsulation during the loading process, as it avoids unwanted side reactions involving the biomolecule of interest.

In this context, different silylated hydrogels, have been evaluated as hybrid matrices able to trap, stabilize and release model drugs. Different forms could be achieved such as microgels, by O/W/O double emulsion [1] or microfluidics [2] approaches, as well as films or monoliths. The inner structure and composition of the network are easily tunable to reach complex drug encapsulation [1] (i.e. lipophilic and hydrophilic), or to sustain release of biomolecules (proteins) over weeks.[3] Fine tuning the sol gel conditions allows to adjust the hybrid material network mechanical properties, as well as functionalizing the silylated polymer backbone with other silylated species.

For example, we were able to adapt the mechanical properties of the hybrid hydro- or xerogels, as a function of a desired protein delivery rate, from hours to several weeks. The release mechanisms were driven by several factors including the penetration of aqueous medium inside the hybrid materials resulting in the swelling, the protein diffusion, and the erosion of the material.[3]

Beyond this proof of concept, the perspectives of designing tailored hybrid hydrogels for encapsulating biomolecules are as wide as the range of available silylated (bio) polymers and other hybrid biomolecules that may constitute the network. Besides the hybrid polymer nature, the crosslinking density, the hydrophilic/hydrophobic balance and even the isoelectric point of the gel could be chosen according to the biomolecule to be delivered and the desired timeframe for delivery.

Keywords: Hybrid materials, sol-gel, encapsulation, biomolecules, controlled release.

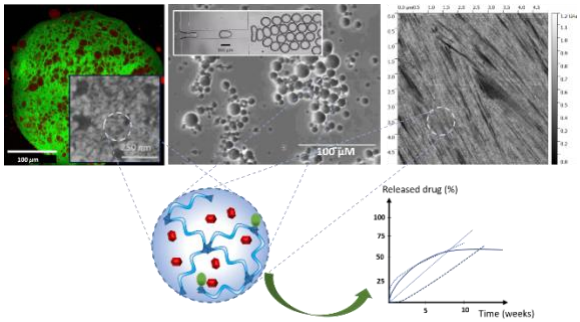


Figure 1: Exemples of hybrid hydrogels for biomolecules microencapsulation and their structure-function properties for drug sustained release goals.

References:

1. Zayed, M., Tourne-Peteilh, C., Ramonda, M., Rethore, G., Weiss, P., Martinez, J., Subra, G., Mehdi, A., Devoisselle J.-M. and Legrand, P. (2017) Microgels of silylated HPMC as a multimodal system for drug co-encapsulation, *International Journal of Pharmaceutics*, 532, 790–801.
2. Tourne-Peteilh, C., Robin, B., Lions, M., Martinez, J., Mehdi, A., Subra, G., and Devoisselle, J.-M. (2019) Combining sol-gel and microfluidics process for the synthesis of protein-containing hybrid microgels, *Chem. Commun*., 2019, 87, 13019–13186.
3. Tourne-Peteilh, C., Barège, M., Lions, M., Martinez, J, Devoisselle, J.-M., Aubert-Pouessel, A., Subra, G. and Mehdi, A. (2021) Encapsulation of BSA in hybrid PEG hydrogels: stability and controlled Release, *RSC Adv*., 11, 30887–30897.

Core-shell hydrogels as in vitro tumor models

I. Parodi[1,2,*], M.M.Fato[1,2], S. Scaglione[2,3]
[1] DIBRIS, University of Genoa, Genoa, Italy
[2] IEIIT, CNR, Genoa, Italy
[3] React4Life, Genoa, Italy

Abstract:
The development of reliable in vitro cancer models for basic research and drug testing applications is often limited by the inability to resemble the proper biomechanical features and cells diversity of the tumor microenvironment (TME) [1]. Hydrogel-based in-vitro models can reproduce tunable mechanical and biochemical features that are crucial for cancer cells biology, such as the cells proliferation, migration, their interaction with ECM and the diffusion of specific nutrients/drugs [2] [3].
In this perspective, core-shell structures with tunable stiffness can be employed as in vitro tools to resemble the heterogeneous in vivo tumor microenvironment. In fact, the production of these hydrogels allows both to create a gradient of stiffness and to realize compartimentalized zones aiming to host more than one phenotypes: tumor cells in the central part and stromal or a mix of stromal and tumor cells in the external one. In particular, alginate was chosen to encapsulate the cells for its well-known biocompatibility [4].
The biofabrication process has involved a double crosslinking step: a first one for the core part and a second one for the outer part. Specifically, the gelation of the alginate-based hydrogels took place through the diffusion of calcium ions – crosslinking chemical agent – from a $CaCl_2$-laden agar mold at physiological temperature. Uniaxial compression mechanical tests were performed after 24h swelling to extrapolate the stiffness values of the hydrogels. Mechanical tests proved that the stiffness of these gels are in the range of 40-60 kPa and thus suitable for a 3D culture of breast cancer cells.
Then core-shell hydrogels were produced, by including human breast cancer cells (MDA-MB-231) in the central part of the scaffold. Two conditions were considered: stiff core with soft shell and soft core with stiff shell. The proliferation capability of the tumor cells was maintained for the entire duration of the culture (7 days) in both the conditions, despite the presence of two matrices that might hinder the diffusion of the nutrients within the constructs, with a more considerable tendency to form aggragates in the stiff core gels.
Moreover, throughout the entire duration of the 3D culture, tumor cells remained confined within the internal part of the hydrogel, with no tendency to migrate in the shell.
Upcomings investigations will consider longer culture time (up to 14 days) to analyse the proliferation and the migration potential of cancer as well as the presence of nutrients (e.g. glucose) gradients. Furthermore, core-shell hydrogels will be employed in next studies to embed TME-stromal cells in the external part in order to have a more realistic in-vitro cancer model.

Keywords: hydrogels, tumor microenvironment, biofabrication, disease modelling

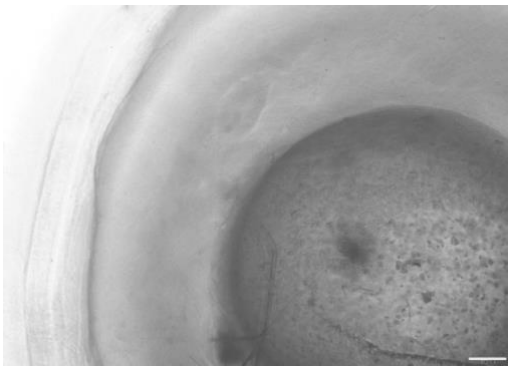


Figure 1: Example of a core-shell hydrogel with breast cancer cells (MDA-MB-231) embedded in the core part, observed at day 0. Scale bar: 100 µm

References:

1. Tse, H. M., Gardner, G., Dominguez-Bendala, J., & Fraker, C. A. (2021), The Importance of Proper Oxygenation in 3D Culture. *Frontiers in Bioengineering and Biotechnology* (Vol. 9). Frontiers Media S.A.
2. Giraldo, N. A. et al. (2019), The clinical role of the TME in solid cancer. *British Journal of Cancer* (Vol. 120, Issue 1, pp. 45–53). Nature Publishing Group.
3. Deng, B., Zhao, Z., Kong, W. et al. (2022), Biological role of matrix stiffness in tumor growth and treatment. *J Transl Med 20* (Vol. 540).
4. Sahoo, D.R., Biswal, T. (2021), Alginate and its application to tissue engineering. *SN Applied Sciences* (Vol. 3)

Cell desiccation: a cheaper and more efficient alternative for storage and transport

L.V. Barrios Silva[1], N.S. Sharifulden[1], N. Mandakhbayar[2], S.J. Shin[2], J.H. Park[2], D.J. Player[3], H.W. Kim[2], D. Vllasaliu[4], D.Y.S. Chau[1*]

[1] Eastman Dental Institute, Division of Biomaterials and Tissue Engineering, University College London, London, United Kingdom.

[2]Institute of Tissue regeneration Engineering (ITREN), Dankook University, Cheonan, South Korea.

[3] Centre for 3D Models of Health and Disease, Division of Surgery and Interventional Science, University College London, London, United Kingdom.

[4]Institute of Pharmaceutical Science, King's College London, London, United Kingdom.

Abstract:

The use of cells in fundamental scientific research and clinical therapy requires an efficient cell storage, transport, and delivery protocol. However, conventional storage and transport methods such as liquid nitrogen present logistical and financial limitations in addition to the use of cytotoxic compounds (i.e. DMSO). The proposed alternative in this study involves the development of a protective protocol to allow the storage, transport and delivery of cells in a low-, or zero-water environment. This approach would be more efficient, cheaper, logistically viable, and allow enhanced accessibility of cell-based research and therapies in remote or challenging environments such as space, developing regions, and conflict zones. This study employed systematic experimentation to identify the optimal protocol- involving protective mediums, drying protocol, additional supplements, and rehydration protocol- to ensure the survival and functionality of cells upon rehydration.

Methods: Following initial biocompatibility testing, thermo-physical and morphological profiling (i.e. DSC, TGA, FTIR, rheology) of the candidate biomaterials (e.g., gelatin, alginate, nanofibrillar cellulose), their water retention profiles, *in vitro* diffusion/permeability profiles (i.e. Franz cells), angiogenic properties using the chicken chorioallantoic membrane (CAM) assay, as well as their *in vivo* biocompatibility and tissue response by means of a subcutaneous implantation in SD wild-type rats (6 weeks old, male) were determined. Response surface analysis and fractional factorial design were also employed to identify the optimal biomaterials, supplementation, rehydration modalities and water removal techniques to induce the low water environments while maximising survival and functionality recovery of C2C12 myoblasts following rehydration.

Results: This study documents the physical, mechanical and biocompatible characteristics among the sampled biomaterial candidates. Differences in diffusion profiles were apparent and based upon the biomaterial type- highlighting the importance of matrix formulations and supplementation during the process of desiccation. Cell death, metabolic activity and functional markers of myoblasts, post rehydration, were dependent on parameters such as environmental temperature while drying, water removal method and duration, and matrix formulation (i.e. biomaterial dilution and exogenous protectant supplementation). The CAM assay and *in vivo* subcutaneous models showed that the response to rehydrated materials were comparable to controls highlighting their potential use and associated protocol for *in vivo* delivery of cell as a therapeutic application.

Conclusions: Overall, a Design of Experiment approach is a powerful tool to acquire knowledge and determine the optimal working parameters for any process such as cell desiccation. What is more, the positive *in vivo* tissue response and optimal vessel formation seen in the CAM assay results point towards good integration capabilities of the rehydrated materials and cells, and thus suggesting a feasible approach of safely using this technology in the future for the storage and delivery of cells and/or cell-based technologies and therapeutics.

Elevating Wound Healing: Unveiling the Impact of Wireless Electrical Stimulation on Cell Differentiation and Observed Improved Cell Attachment and Expansion

L. Gazvoda[1,2], M. Zabčić[1,2], M. Spreitzer[1], M. Vukomanović[1]

[1] Advanced materials Department, Jožef Stefan Institute, Ljubljana, Slovenia
[2] Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

Abstract:
Electrical stimulation has been reported to have a major effect on wound healing in mammalian cells, which appears to be beneficial for cell proliferation, migration, or differentiation, simulating natural process of healing. Using biocompatible, biodegradable and piezoelectric poly-L-lactic acid polymer (PLLA), direct electrical stimulation can be delivered to attached cells, when films are properoly prepared (oriented and crystalline polymer chains[1]). Mentioned piezoelectric properties can be activated by mechanical deformation using medically accepted ultrasound (US) therapy (MHz), that can penetrate deep into the tissue, allowing also *in vivo* applications.
Some of cell responses to electrical stimulation, such as cell viability, cell morphology, actin filament formation, changes in proliferation, immune response, was verified on keratinocytes (representative cell line for wound healing assays). We imparted (piezo)electric stimulation by solid PLLA films, prepared by tensile stretching or films with surface nano-topography (improved piezoelectric properties), prepared by template-assisted method. The observed results (Fig. 1a) indicate on cell differentiation as a response to electric stimulation (bright red arrow), since no growth was observed from day 2 to day 3 only for piezoelectric films, compared to non-piezoelectric PLLA (normal growth). It is known that proliferation and differentiation compete with each other, therefore only one occur. Through microscopic observation (Fig. 1b), improved cell attachment is observed and more cell filopodia, again only for piezoelectric PLLA, indicating on improved cell-cell and cell-material connections, and cell expansion on solid films, indicating on possible migration, as in nanotextured sample there are limitations to movement due to surface topography (island formation).
We believe that we have prepared a proactive piezoelectric material which can be implemented in the body (exploiting biocompatible and biodegradable properties), able to direct electrically stimulate adhered cells, activating piezoelectric properties by body movement or externally on-demand by US therapy.

Keywords: piezoelectric polymer, poly-L-lactic acid, ultrasound stimulation, electric stimulation, keratinocyte proliferation

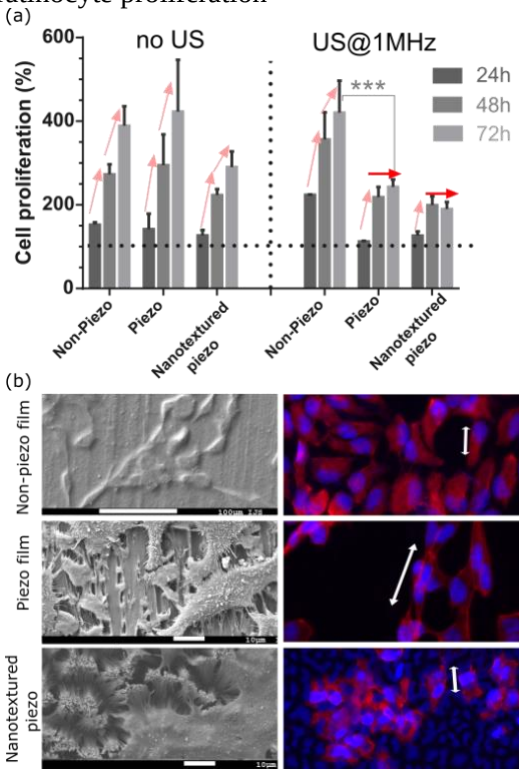


Figure 1: Figure illustrating first (a) the observed proliferation of HaCaT cells attached on non-piezoelectric, piezoelectric and nanotextured piezoelectric PLLA film under US stimulation; and (b) microscopic SEM and fluorescence images (DAPI-nuclei and Rhodamine phalloidin-actin filaments staining) of mentioned US stimulated samples for morphology and shape observation respectively.

References:

1. Gazvoda, L., Spreitzer, M., Vukomanović, M. (2020), Towards hydrophilic piezoelectric poly-L-lactide films: optimal processing, post-heat treatment and alkaline etching, Polymer Journal, 52, 299-311.

Posters Abstracts

Development of Models to Predict the Properties of Materials Produced of Polymeric Yarns

T. Rolich [1] , I. Salopek Čubrić [2], G. Čubrić [3*]
[1] Department of Fundamental Natural and Engineering sciences, University of Zagreb Faculty of Textile Technology, Zagreb, Croatia
[2] Department of Textile Design and Management, University of Zagreb Faculty of Textile Technology, Zagreb, Croatia
[3]Department of Clothing Technology, University of Zagreb Faculty of Textile Technology, Zagreb, Croatia

Abstract:
The constant developments and improvements in the field of material science are in line with the demands of modern society that bring up the quality of the product, its comfort and sustainability in the first plan. Scientists reported a high demand for increased properties of polymeric materials, particularly those that provide an effective barrier to the fluid flow, transfer of heat, air, vapour, gases, and radiation of various origins. Also, the issue of polymer sustainability is highly raised and efforts towards better solutions are given. Still, there is a lack of developed models that may be used to predict the properties of polymeric materials, both aged and non-aged. For the experiment referring to the development of models for polymeric materials, a set of 40 polymeric materials was produced. For the production are used polyester and polyamide yarns. The materials were produced as knitted fabrics consisting of 100% polyester yarn (PES), 100% polyamide yarn (PA6, PA6.6.), as well as with addition of elastane yarns along with polyester and polymide. All produced materials were tested for 11 physical-mechanical properties. So, polymeric materials were tested for thickness (d), force at break in the direction of wales (Fp1), force at break in the direction of courses (Fp2), elongation at break in the direction of wales (εB1), elongation at break in the direction of wales (εB2), bursting force (Fb), porosity (CF), heat resistance (Rct), water vapour permeability (W), overall moisture management capacity (OMMC), and drying time (VS). The testing results were used to develop models that will be able to predict 4 output (dependent) variables based on 8 input (independent) variables of polymeric materials. Two regression models were developed. The first is a linear model and the second is a linear model upgraded with square members of input variables.

Keywords: polymer, yarn, material, model, property, polyester, polyamide.

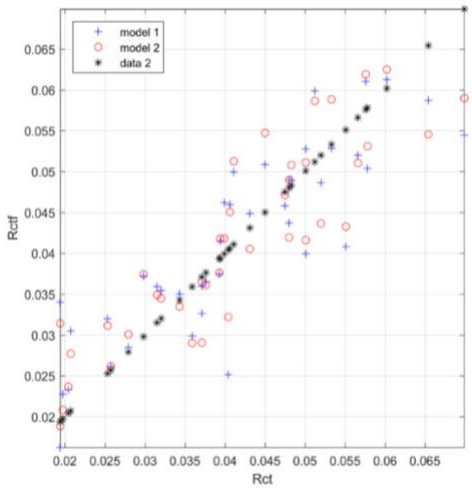


Figure 1: Figure illustrating the original data obtained from the first and second models for output variable a heat resistance of polymeric materials.

References:

1. Helmi, M., Tashkandi, S., Wang, L. (2022) Design of sports-abaya and its thermal comfort evaluation, *Text. Res. J.*, 92, 59-69.
2. Fan, J., Tsang, H.W.K. (2008) Effect of Clothing Thermal Properties on the Thermal Comfort Sensation During Active Sports, *Text. Res. J.*, 78, 111-118.
3. Salopek Čubrić, I., Čubrić, G., Katić Križmančić, I., Kovačević, M. (2022) Evaluation of Changes in Polymer Material Properties Due to Aging in Different Environments, *Polymers*, 14, 1682.
4. Salopek Čubrić, I., Čubrić, G., Potočić Matković, V. M. (2021) Behavior of Polymer Materials Exposed to Aging in the Swimming Pool: Focus on Properties That Assure Comfort and Durability, *Polymers*, 13, 2414.

Funding: This research was funded by Croatian Science Foundation, grant number IP-2020-02-5041 “Textile Materials for Enhanced Comfort in Sports”—TEMPO.

On The Measurement of the With of the Distribution of Retardation Times in Polypropylene

J. André [1*], J. Cruz Pinto [2]
[1] UTC - Engineering and Technology, UDI-Research Unit for Inland Development, Guarda Polytechnic Institute, Guarda Portugal
[2] CICECO/Department of Chemistry, University of Aveiro, Aveiro Portugal

Abstract:
Previous models for the interpretation of the creep behaviour of polymers are of course valuable, but mainly empirical or semi-empirical, and do not directly take into account the physical (molecular) underlying mechanisms, namely the detailed conformational and other transitions responsible for the material's non-linear viscoelastic behaviour [1, 2].

Keywords: polypropylene, PP, retardation times, creep, minimum retardation time.

Creep Theoretical Model

It is not difficult to understand and visualize the dynamic (compliance and/or relaxation) behaviour of any viscoelastic material as resulting from a range of motions/transitions at the molecular scale: gauche/trans conformational transitions or other motions in macromolecular ones. Actually, in polymers, single-segment gauche/trans transitions are not possible without the simultaneous participation of a small set of neighbouring segments, but the gauche/trans transitions could be taken as a simple and good paradigm for the microscopic modelling of macromolecular materials' responses to a wide range of physical excitations, of which creep is the example studied here.

We adopted a truly dynamic molecular modelling approach to general compliance and relaxation behaviour, whereby actual elementary, molecular scale, process-relevant frequencies are derived by adequate (as simple as possible) kinetic formulation.

Given the wide variety of contributing structural elements that are involved in the entire range of cooperative motions, the logical step to take is to consider an adequate distribution of cluster sizes and corresponding retardation times. A long time ago, Feltham [3] had already shown that a log-normal distribution would be a physically reasonable approximation to the retardation spectra of a wide range of viscoelastic materials. As a matter of fact, however, the analysis of the present and other experimental data [4], showed that there is a minimum retardation time, corresponding to the smallest contributing clusters (n = 1) in the least constrained local environment within the structure. So, the overall (real) creep compliance may be formulated [4, 5, 6] as

$$D(t) = D_0 + (D_\infty - D_0)\frac{erf\left[b\ln\left(\frac{\tau^*}{\tau_1}\right)\right] + erf\left[b\ln\left(\frac{t}{\tau^*}\right)\right]}{erf\left[b\ln\left(\frac{\tau^*}{\tau_1}\right)\right] + 1}$$

The effects of temperature and applied stress on the optimised values of b, τ_1, τ^*, D_0 and D_∞ (actual values and physical significance) that best fit the experimental creep strain values are discussed. Figure 1 shows the results of fitting previous equation to the experimental creep compliance curves obtained for PP at 40 ºC.

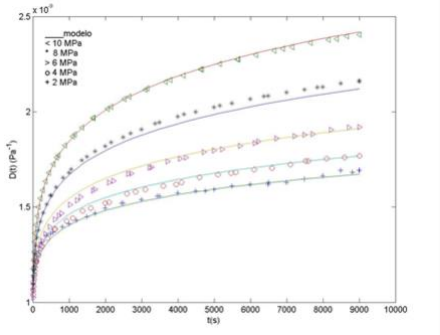


Figure 1. Model Fitting of the Creep Compliance of PP at 40 ºC.

References:

1. Kromm, F.X; Lorriot, T; Coutand, B; Harry, R; Quenisset, J.M. (2003) *Polym. Test*., 22, 463
2. Sen, A, Bhattacharya, M, Stelson, K.A, Voller, V.R. Mater. (2002) Sci. & Eng. A 338, 60.
3. P.Feltham, (1955) *British Journal of Applied Physics*, Vol. 6, 26.
4. Cruz Pinto, J.J.C; André, J.R.S., (2004) *Advanced Materials Forum II*, 759.
5. André, J.R.S, (2004) Ph D Thesis; University of Aveiro.
6. Cruz Pinto, J.J.C, André, J.R.S., Analytical Molecular Dynamics of Amorphous Condensed Matter: Thermal and Non-Linear Response Behavior, *Springer Nature*, In press

Synchrotron radiation-based FTIR Microspectroscopy and TEM investigations on the Core-Shell structure PEGylated polymeric particles

D.Makharadze [1], LJ.del Valle [1,2] , Tem. Kantaria [3], Teng.Kantaria [3], R.Katsarava [3], J.Puiggali [1,2 *]

[1] Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, Barcelona, Spain
[2] Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain
[3] Institute of Chemistry and Molecular Engineering, Agricultural University of Georgia, Tbilisi, Georgia

Abstract:
Surface modification of drug-loaded particles with polyethylene glycol (PEG) chains is a powerful tool that enhances the stability[1] and circulation time of cargo and avoids particle clearance by the immune system[2] due to the PEG stealth effect. In this study, we used a new approach to synthesize a biodegradable poly(ester amide) and a PEGylating surfactant. These were employed to fabricate particles with a core-shell structure. NP-protein interactions and self-assembling were subsequently studied by synchrotron radiation-based FTIR microspectroscopy (FTIRM) and transmission electron microscopy (TEM) techniques. The core-shell structure was identified using IR absorption bands of characteristic chemical groups. Specifically, the stretching absorption band of the secondary amino group (3300 cm^{-1}) allowed us to identify the poly(ester amide) core, while, the band at 1105 cm^{-1} (C-O-C vibration) was useful to demonstrate the shell structure based on PEG chains. By integration of absorption bands, a 2D intensity map of the particle was built to show a core-shell structure, which was further supported by TEM images

Keywords: PEG chains, Stealth effect, polymeric particles, core-shell structure, synchrotron radiation-based FTIR microspectroscopy.

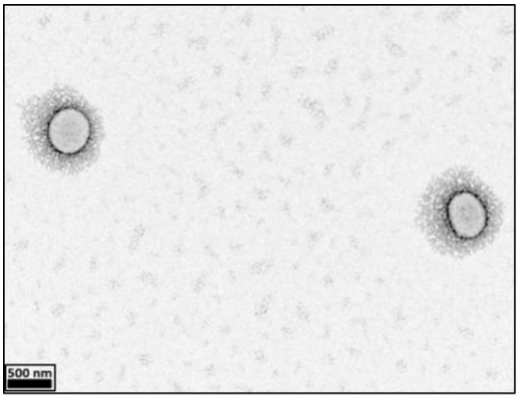


Figure 1: illustrating the core-shell structure of nanoparticles, showing the high coverage density of PEG chains around the nanoparticle core

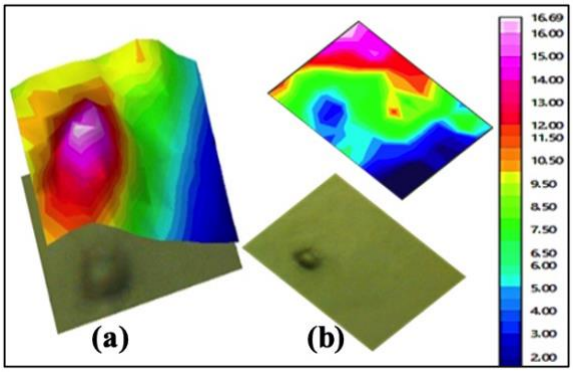


Figure 2: (a) showing the relative intensity of the secondary NH stretching absorption band**,** (b) showing the relative intensity of the C-O-C anti-symmetric stretching band

References:

1. Partikel K, Korte R, Stein NC, Mulac D, Herrmann FC, Humpf HU, Langer K. (2019) Effect of nanoparticle size and PEGylation on the protein corona of PLGA nanoparticles, Eur J Pharm Biopharm, 141, 70-80.
2. Tobío, María & Sánchez, A & Vila, Ana & Soriano, Isabel & Evora, Carmen & Vila-Jato, JL & Alonso, Maria. (2000) The role of PEG on the stability in digestive fluids and in vivo fate of PEG-PLA nanoparticles following oral administration, Colloids and surfaces. B, Biointerfaces, 18, 315-323.

Photocatalytic carbon dioxide reduction using titanium dioxide modified with metal salts

I. Pełech [1,*], K. Sobczuk [1], K. Ćmielewska [1], P. Staciwa [1], D. Sibera [1,2], E. Kusiak-Nejman [1], A.W. Morawski [1], U. Narkiewicz [1]

[1] Department Department of Inorganic Chemical Technology and Environment Engineering, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology in Szczecin, Pulaskiego 10, 70-322 Szczecin, Poland. *ipelech@zut.edu.pl*

[2] Department of Construction and Road Engineering, Faculty of Civil and Environmental Engineering,West Pomeranian University of Technology in Szczecin, Piastow 50a, 70-311 Szczecin, Poland.

Abstract:

Combustion of fossil fuels results in emission of carbon dioxide, the major anthropogenic factor related to climate change, affecting the healthy functioning of the biosphere. One of the methods to reduce CO_2 concentration is CCU (carbon capture and utilization), which allows for decreasing the CO_2 concentration and also converting its into useful products. To the conversion of carbon dioxide into methane, hydrogen or other gases the photocatalysis process can be successfully applied.

As a potocatalyst titanium dioxide is the most commonly used, however, its wide bandgap energy, which can be only activated under UV-light and fast charge carrier recombination restricts its applications. In order to reducing the bandgap energy of TiO_2 and e.g. enhancements of hydrogen production, doping with metal ions is studied.

In this work, TiO_2 photocatalysts modified with 1 wt. % of metals were prepared by a sol-gel method. At first, 20 ml of titanium precursor was mixed with 5 ml of ethyl alcohol. Next, proper amount of metal salt was dissolved in 50ml of ultrapure water and the whole was added drop by drop into a flask containing precursor and alcohol under magnetic stirring. Ammonia water was applied to adjust pH value equal 10. All the reagents were magnetically stirred for 24 hours and then left for the aging process taking 24 hours. The obtained gels were dried at 100˚C for 24 h. Next the obtained samples were calcined at 400˚C for 1 h in a high temperature furnace under argon atmosphere.

The photocatalytic processes were conducted in the gas-phase reactor. A lamp, placed in the reactor, was cooled using a thermostat equipped with a pump with a controlled temperature of 18 °C. The reactor was placed in a thermostatic chamber to maintain a stable temperature (20 °C) and exclude any light sources. 10 cm^3 of distilled water and glass fiber with the tested photocatalyst were placed in the reactor. Before experiment, the reactor was purified with pure CO_2. The gas samples for analysis were collected every 1 h and the gas phase composition was analyzed using a gas chromatography method using a Master GC chromatograph equipped with TCD and FID detectors. The amount of hydrogen, carbon monoxide, and carbon dioxide in the gas phase was calculated based on the calibration curve.

It was found that the highest amount of gaseous products were obtained using copper-modified titanium dioxide.

Keywords: photocatalyst, titanium dioxide, carbon dioxide, metals.

Acknowledgements:

The research leading to these results received funding from the Norway Grants 2014–2021 via the National Centre for Research and Development under the grant number NOR/POLNORCCS/PhotoRed/0007/2019-00.

Synthesis of Graphene/Polymer Nanocomposites based for additive manufacturing technologies

Sophio Mikaberidze[a] , Mamuka Maisuradze[a] , Natia Jalagonia[b]

[a]Georgian Technical University, Kostava 77, Tbilisi, Georgia
[b]Ilia Vekua Sukhumi Institute of Physics and technology, 7Mindeli str., Tbilisi, Georgia

Abstract

Since the beginning of the new millennium, the concept of "3D" has firmly entered our daily life. 3D printing technologies open up new possibilities for us in creativity, science, technology and everyday life. A 3D printer, or three-dimensional printing machine, is a unique modern tool with which the smallest ones, starting from parts with nanoparticles, can print macro and objects of a huge volume. In 3D printing technology, a digital model of the structure of an object is initially created in a computer, which interacts with a printer and, as a result of an appropriate command, begins to form a layer-by-layer product. The advantages of 3D printing over conventional printing are high speed, simplicity and relatively low cost [1-2].

A 3D printer is actively used in various industries: construction, medicine (for example, for the manufacture of various organs, new generation prostheses), furniture manufacturing (for example, furniture)., Reconstruction of modeling models and creating accurate analogies), toy manufacturing (for example, Various figurines and board games, inscriptions and decorations), the food industry (for example, the food industry)., the production of complex shaped candies), the production of clothes and shoes (for example, carbohydrates)., the creation of new, unusual models), etc. [3].

In this work UV curable PDMS synthesis method was investigated. Synthesized polymers are vitreous liquids. Structure and composition of reaction products were established by FT-IR and NMR methods. In the ^{1}H-NMR spectra of polymers we observed signals characteristic for methyl protons of ≡Si-CH_3 with chemical shifts of δ≈0.12 ppm and 0.55 ppm. Also we observed triplet signals characteristic for – urea fragment with chemical shift of δ≈6.1 ppm. Graphene structures containing (0.5-0.8 wt%) liquid UV curable PDMS was obtained for SLA printer. Lab homogenizator was used for good dispersion of filler into polymer matrix. It is established, that Graphene/polymer nanocomposites mechanical properties improve by increasing of filler content.

This work was supported by Shota Rustaveli National Science Foundation of Georgia (SRNSFG) (Grant number PHDF-22-575).

References

1. C. W. Hull, U.S. Patent 4575330, (1986);
2. J. W. Stansbury, M. J. Idacavage. New 3D printable polymeric materials for fused filament fabrication (FFF)Dent. Mater. 32, 54, (2016);
3. E. MacDonald, R. Wicker, Science. Multiprocess 3D printing for increasing component functionality, 353, aaf2093, (2016);

Polyhydroxybutyrate-co-hydroxyvaleriate composites with rapeseed microfibers throughout it life cycle

M. Žiganova, A. Ābele, I. Bochkov, T. Ivanova, R. Merijs-Meri, J. Zicāns
Faculty of Natural Sciences and Technology, Riga Technical University, Riga, Latvia

Abstract:
Bio-based polymer composites are important key elements for development of sustainable future materials. Development of bio-based polymer composites is in the line of EU Green Deal policy. To achieve the United Nations sustainable Development goals it is neccessary to design new composite materials with possibly high content of renewable feedstocks being competitive with existing fossil based composite materials used for dedicated applications.
Polyhydroxybutyrate-co-hydroxyvaleriate (PHBV) is convenient matrix material for achieving these sustainability goals because the polymer may be commercially synthesized by various microbial cell cultures. Modification of PHBV with rapeseed straw (RS) is convenient because this allows valorization of this low-cost agricultural residue.
In spite of certain efforts in development of PHBV composites modified with various biomass residues (e.g. peach palm particles [1], wheat straw, brewers spent grains, olive mills [2] etc), there is lack of summarized scientifically grouned information on the property change of such composites throughout it life cycle starting from preparation of such composites and ending with it biodegradation.
Consequently, the current research is focused on the development of PHBV composites with renewable feedstock microfibers, obtained from locally abundant low-cost agricultural residue biomass – rapeseed straw (RS). To increase interaction with PHBV matrix, the obtained RS microfibers were treated with N-methylmorpholine N-oxide (NMMO), as a green alternative solvent in comparison to sodium hydroxide, typically used to improve properties of natural fibers. The content of RS in the PHBV composites has been changed from 0 to 10 wt.%. Triethyl citrate (TEC) has been used as plasticizer to reduce brittleness of the developed composites. The concentration of TEC was 20%, determined to be optimal according to our previous research [3]. PHBV/TEC/RS composites have been obtained by melt compounding approach.
During the research the change of certain physical properties of the developed PHBV/TEC/RS composites has been investigated as a function of accelerated ageing exposure time and biodegradation time.
Main results of the research demonstrate that
-NMMO and alkali treatment of RS allows to obtain plasticized PHBV composites with improved biodegradability, increased stiffness but decreased strength and elongation,
-accelerated weathering, leads to increment of stiffness, but reduction of tensile strength and elongation at break of the investigated PHBV biocomposites because of increased crystallinity of the biopolymer matrix, especially in the presence of RS,
-all the developed PHBV composites demonstrate faster biodegradation in comparison to neat PHBV matrix,
-surface treatment of RS microfibers delayed biodegradation of the developed PHBV composites

Keywords: bio-based polymers, sustainable composites, weathering, biodegradation, properties.

Figure 1: Figure illustrating the degradation of the PHBV composite with 2 wt.% of RS after 90 days in soil media.

References:

1. M. A. Berthet *et al.*, "Exploring the potentialities of using lignocellulosic fibres derived from three food by-products as constituents of biocomposites for food packaging," *Ind. Crops Prod.*, vol. 69, pp. 110–122, 2015.
2. K. C. Batista, D. A. K. Silva, L. A. F. Coelho, S. H. Pezzin, and A. P. T. Pezzin, "Soil Biodegradation of PHBV/Peach Palm Particles Biocomposites," *J. Polym. Environ.*, vol. 18, no. 3, pp. 346–354, 2010.
3. M. Žiganova et al., "Visco-Elastic and Thermal Properties of Microbiologically Synthesized Polyhydroxyalkanoate Plasticized with Triethyl Citrate," Polymers (Basel)., vol. 15, no. 13, 2023.

Pectic polysaccharides extracted from melissa and lavender solid by-products of essential oil industry

A. Slavov [1,*], G. Marovska [1]
[1] Department Organic chemistry and inorganic chemistry, University of Food Technologies, Plovdiv, Bulgaria

Abstract:
Pectic polysaccharides are complex cell wall polymers found in most of the higher plants, having wide application in the food industry as a viscosity modifier and jellifying agent. Industrially pectins are primarily extracted from fruit juice by-products : citrus peels and apple pomace by dilute acid extraction. Sugar beet and sunflower head residues consist of 10 to 20% pectin and could be regarded as potential raw materials. Other pectin sources include cocoa husks, with about 9% pectic polysaccharides, beet and potato pulp, and soy hull, with pectin contents about 26-28%. There are some reports for isolation and characterization of pectic polsyaccharides from essential rose oil industry [1] but in general these pectin sources are underinvestigated.
The lavender (*Lavandula angustifolia*) is widely utilized plant by the essential oil industry. Bulgaria (one of the major producer of lavender essential oil), France, UK, China, Ukraine, Spain, and Morocco are the biggest worldwide producers. The melissa (*Melissa Officinalis*), known also as lemon balm or common balm, is a well-known medicinal plant used by mankind for more than 2000 years. The lower quantity of essential oil in the lavender (0.8–1.3% / fresh plant) and melissa (0.014% in the fresh plant) results in huge amounts of by-products. These residues commonly were discarded directly in the nearby locations. Hence, the aim of the present study was to investigate the possibility of melissa and lavender essential oil industry by-products as raw material for extraction of pectic polysaccharides. The extracted pectic polysaccharides (by dilute acid extraction – a common method for industrial manufacturing of pectin; and by sequential fractional extraction) were characterized for their physico-chemical properties and monosaccharides composition. The pectic polysaccharides obtained from melissa by-products were subjected to rheological studies, having in mind that the major application of pectins in the food industry is for preparation of gel type systems.

Keywords: pectic polysaccharides, melissa (*Melissa officinalis*), lavender (*Lavandula angustifolia*), essential oil industry by-products, valorization.

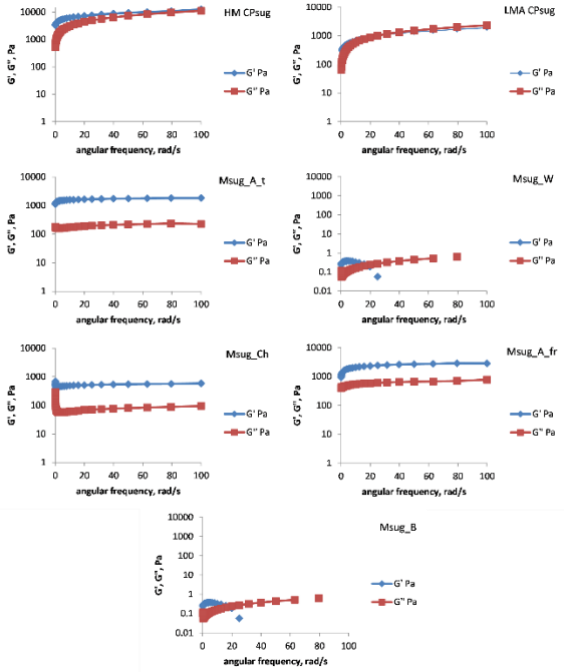


Figure 1: Frequency sweep test of high sucrose gels: melissa polysaccharide and sucrose concentration: 1.25% and 60.0% (w/w), respectively; pH – 3.5 (50 mmol/L citrate buffer). HM CPsug: HM citrus pectin; LMA CPsug: LMA citrus pectin; Msug_A_t: acid-extractable polysaccharide; Msug_W: water-soluble polysaccharide; Msug_Ch: chelate-soluble polysaccharide; Msug_A_fr: fractional extraction acid-extractable polysaccharide; Msug_B: alkali-extractable polysaccharide. Thin lines – G', thick lines – G''.

References:

1. Slavov, A., Denev, P., Panchev, I., Shikov, V., Nenov, N., Yantcheva, N., Vasileva, I. (2017) Combined recovery of polysaccharides and polyphenols from *Rosa damascena* wastes, *Ind. Crops Prod.* 100, 85–94; http://dx.doi.org/10.1016/j.indcrop.2017.02.017.

Acknowledgments:

This work was supported by the bilateral project КП-06- Austria/4 funded by the National Science Fund (Ministry of Education and Science) of Bulgaria.

Supercritical Solvent Impregnation of poly-lactic acid food films with olive leaf extract for fresh fish preservation

M. Tirado, C. Cejudo*, F. Sánchez, A. M. Roldán, L. Casas, C. Mantell
Chemical Engineering and Food Technology Department, Science Faculty, Wine and Agrifood Research Institute (IVAGRO), University of Cadiz, Puerto Real, 11519, Spain

Abstract:
Minimally processed fresh seafood is a basic product in supermarkets. However, due to their perishable nature, the marketing of prepared convenience fish limits their shelf life. One of the critical points in the production process of any food is the selection of the most appropriate packaging method that guarantees adequate preservation until it reaches the consumer, maintaining its quality and increasing its shelf life. In this sense, there is a trend in the search for the so-called active packaging. There are different types of active packaging, one of the most promising alternatives being the addition of an active substance to the polymeric packaging. These compounds could have different functional properties, including minimizing oxidation and microbiological degradation of fresh foods during storage, thanks to their antioxidant and antimicrobial properties. The result is a significant increase in the shelf life of packaged foods. The supercritical solvent impregnation is an effective tool for developing active packaging that intervenes in preserving fresh food (1). Among the bioactive components, those from natural sources have raised great interest, due to their contribution to the circular economy. The residues and by-products of the olive sector contain many antioxidant and antimicrobial compounds that can be potentially reused as bioactive ingredients. This study analyzed the effectiveness of a polylactic acid film (PLA) impregnated with an olive leaf extract (OLE) for the preservation of fresh hake fillets. The color, weight variation, pH, volatile basic nitrogen (TVB-N), trimethylamine content (TMA-N), and microbial growth have been analyzed to control the freshness of the fish. The impregnated films were more efficient in the maintenance of moisture and the retarding of microbial growth after 12 days of storage, not showing differences in the pH, TVB-N and TMA-N content. The color changes were noticeable at the end of the experiment, decreasing the *a** component and increasing the *b** one due to the migration of compounds from the extract, as well as modifying the aroma of the fish.

Keywords: polylactic acid, circular economy, supercritical solvent impregnation, fish, food packaging

Figure 1: Hake fillets packaged with impregnated PLA (above) and non-impregnated PLA (below).

References:

1. Cejudo Bastante, C. Casas Cardoso, L., Fernández-Ponce, M.T., Mantell Serrano, C., Martínez de la Ossa, E.J. (2019) Supercritical impregnation of olive leaf extract to obtain bioactive films effective in cherry tomato preservation. *Food Packaging and Shelf Life*, 21, 100338

Sustainaible Gum Arabic Adhesives intended for Corn Seed Coating

S. Fuster-Esteso [1,2], R. Torres-Vera [2], J. Martínez-Ruiz [2], J.M. Martín-Martínez [1]
[1] Adhesion and Adhesives Laboratory. University of Alicante. 03080 Alicante (Spain)
[2] Symborg S.L. A Corteva Agriscience Business. Polígono Cabezo Cortado. Avenida Jesús Martínez Cortado, 51. 30100 Espinardo, Murcia (Spain).

Abstract:
In the development of sustainable adhesives, natural polymers are good candidates, due to their lack of toxicity and biodegradability. Particularly, the natural gums have a high potential in biotechnology and agriculture.
The growing interest of the industry to achieve materials with low or zero carbon footprint facilitates the development of natural-based adhesives for seed coating.
Seed coating consists in covering with un adhesive for producing an external coating intended to alleviating biotic and abiotic stresses, thereby improving crop growth and yield.
Gum Arabic is a natural gum obtained from different species of acacia trees that grow mainly in arid and semi-arid areas of Africa and Asia. It is a multifunctional branched hydrocolloid based on arabin-galactan protein of calcium, magnesium, and potassium salts.
Waterborne gum Arabic-based adhesives with and without 3 wt.% lactic acid (LcA) were prepared by physical mixing. They were characterized by surface tension, Brookfield viscosity, gel permeation chromatography, infra-red spectroscopy, and thermal gravimetric analysis. The adhesion of the gum Arabic-based adhesives was measured by T-peel and single lap shear tests of cotton stripes/adhesive joints.

Table 1. Physico-chemical properties of gum Arabic-based adhesives.

Adhesive	pH	Brookfield viscosity (mPa.s)	ϒ (mN/m)
GA	4.1	122	62
GA/LcA	3.5	118	63

Table 2. Adhesion properties of gum Arabic-based adhesives.

Adhesive	T-peel strength (N/m)	Shear strength (MPa)
GA	241 ± 58	18 ± 3
GA/LcA	200 ± 21	19 ± 3

The addition of LcA decrease pH and Brookfield viscosity, do not affect surface tension and changed the structure of the gum Arabic (M_n=8265 Da, M_w= 21545), resulting in higher number of chains with lower molecular weights (M_n=15985 Da, M_w= 21630). Furthermore, the addition of LAc slightly decreased the adhesion of the gum Arabic adhesives, but the overall adhesion capacity remained acceptable
Whereas the gum Arabic adhesive shows microbial growth after 63 days of preparation, the addition of LcA increases their durability up to eighteen months at least (Figure 1).

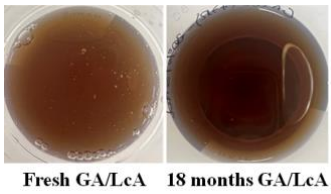


Figure 1. GA/LcA adhesive before and after 18 months of their preparation.

The coated with adhesives corn seed were monitored by scanning electron microscopy. The addition of lactic acid increases the penetration capacity of the adhesive into the corn seeds, as well as an increase in the cohesion of the outer crust of the corn seeds (Figure 2). On the other hand, the addition of gum Arabic-based adhesives reduces the surface roughness of the corn seed surface (Figure 3).

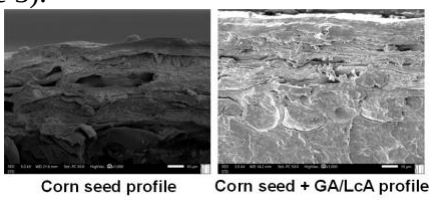


Figure 2: SEM micrographs of the corn seed profile without and with adhesive.

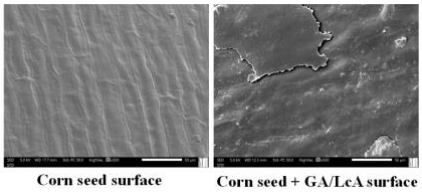


Figure 3: SEM micrographs of the corn seed surface without and with adhesive.

Keywords: Gum Arabic, Seed Coating, Lactic Acid, corn seed, durability, Scannin electron micrographs.

Phosphorus-Nitrogen synergic bio-based flame retardant from chitosan and phytic acid for plastic matrices applications

M. Expósito[1], L. Agostinis[1]
[1] AIMPLAS- Instituto tecnológico del plástico, Valencia, España

Abstract:
Polymers are highly flammable and have a significant impact on fire protection and safety systems. For this reason, it is necessary to use flame retardant additives that enhance the fire behavior.

The following study focuses on the development of flame retardants (FRs) containing phosphorus (P) and nitrogen (N)[1], generating a synergistic effect between them. To achieve this, bio-based materials such as chitosan and phytic acid are employed.

Chitosan (CS) is the second most abundant polysaccharide in the world, it is biocompatible, non-toxic, and biodegradable. Phosphorus on other side is a main alternative to halogens for organic flame retardants, nevertheless its production is based on Phosphate Rock which is in the Raw critical material list published by the Commission European[2]. Phytic acid (PA) presents 28% in mass of P and could be a sustainable alternative for phosphorous production in Europe. The interaction between CS and PA leads to the formation of a Polyelectrolyte Complex (PEC)[3] which present application as a bio-based intumescent system thank to synergic mechanism for P and N in combustion process.[4]

In this work a polyelectrolyte (PEC) has been prepared using CS and PA. the preparation of the material has been optimized and scaled up to study its inclusion in matrix. Moreover, its synergism with other commercial FR has been studied. In particular an optimal ratio with ammonium polyphosphate (APP) has been identified.

Different plastic materials have been prepared and test by cone calorimetry analysis, identifying an optimization up to 54% by HHR and THR point of view.

Keywords: fire protection, flame retardants, bio-based materials, chitosan, phytic acid, polyelectrolyte complex, intumescent system.

Figure 1: Fire Analysis Trial in Cone Calorimeter of Materials Resulting According to ISO5560.

References:

1. Ding, D., Liu, Y., Lu, Y., Liao, Y., Chen, Y., Zhang, G., & Zhang, F. (2022). Highly effective and durable P-N synergistic flame retardant containing ammonium phosphate and phosphonate for cotton fabrics. Polymer Degradation and Stability, 193, 109964.
2. COM (2017)490 "Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the 2017 list of Critical Raw Materials for the EU", 13th September 2017.
3. Zhang T., Yan H., Shen L., Fang Z., Zhang X., Wang J., Zhang B., Chitosan/Phytic acid polyelectrolyte complex: A green and renewable intumescent flame-retardant system for ethylene-vinyl acetate copolymer, Ind. Eng. Chem. Res., 2014, 53 (49), pp. 19199–19207.
4. Xiao Y., Zheng Y., Wang X., Chen Z., Xu Z., Preparation of a chitosan-based flame-retardant synergist and its application in flame-retardant polypropylene, Journal of Applied Polymer Science, 2014, 131, 40845-40853

Removal of Emerging Contaminants in waters by filtration with biochars

T. Undabeytia [1*], J.M. De la Rosa [1], Á. Sánchez-Martín [1], S Nir[2] , M. Arenas-Arévalo[1], F. Behrendt[3] A. Diéguez-Alonso [4]

[1] Instituto de Recursos Naturales y Agrobiología (IRNAS-CSIC), Sevilla, Spain.

2 The R.H. Smith Faculty of Agriculture, Food & Envir. Hebrew Univ. Jerusalem, Rehovot, Israel.

3 Technische Universität Berlin, FG EVUR, Berlin, Germany

4 Otto-von-Guericke-Universität Magdeburg, Magdeburg, Germany

Abstract:

In the last decades, the presence of organic micropollutants (ECs) has been detected in both surface and groundwater. The main types of processes used in drinking water treatment plants are clarification/coagulation, filtration (surface, fluidized bed, membrane) and oxidation (generally with chlorine or ozone). Fluidized bed filtration is incorporated in the vast majority of water treatment plants. The most commonly used material is granular activated carbon (GAC), which is very effective in the removal of organic pollutants. In this study, filtration results are presented using a biochar generated from a waste such as rice husk, versus a commercial GAC.The ECs selected were 5 pharmaceuticals (PhAcs) with different state of ionization in solution. The comparison was performed by using the same amount of material but maintaining the flow rate and constructive parameters.

A filtration model was used to validate the power of the biochar produced from agrowaste vs GAC in the removal of ECs due to its lower density, resulting in longer filters, which would increase the amount of interactions between the single molecules of solute and the sorbent bed. The parameters obtained from the experimental fitting of the filtration data by using GAC were used for prediction of the removal by using filters of identical length as those used with biochar. The outcome showed that in certain pollutants, the eluted predicted amounts by using GAC were higher than the experimentally obtained with the biochar filters. Therefore, the biochar posed in general, a higher removal capacity of ECs by weight unit than the commercial GAC.

Keywords: biochar, granular activated carbon, emerging contaminants, filtration, modeling.

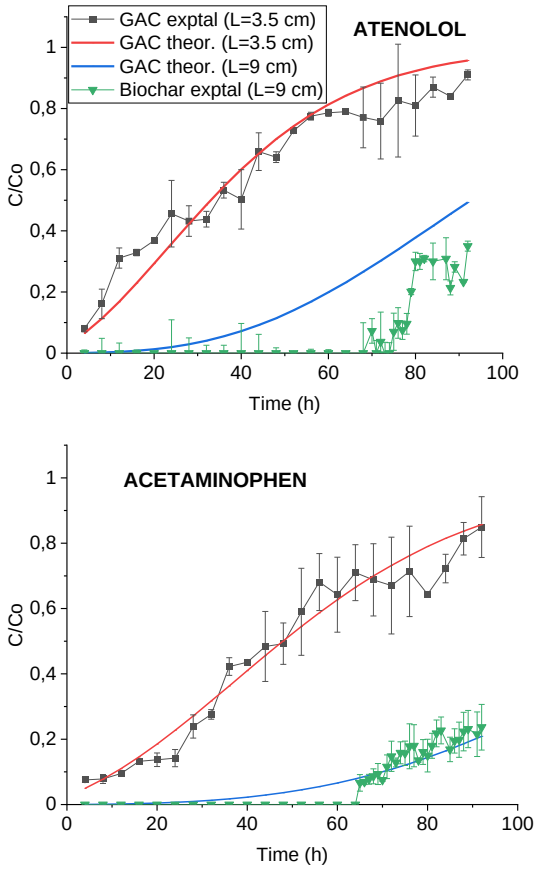


Figure 1: Eluted fractions of the PhAcs atenolol and acetaminophen, and its modeling in filtration experiments including GAC and biochar. The flow rate was 10 mL/min; the initial concentration (Co) was 1 mg/L, and the radius was 1 cm.

Acknowledgments:

This research was carried out in the frame of the grant RICERES4CHANGE (grant TED2021-130964B-I00), by the Spanish Agency of Research (MCIN/AEI/10.13039/501100011033) and the European Union (Next Generation EU/PRTR funding).

The bio-based cellulose produced by acetic acid bacteria as a potential material for sustainable packaging

C. M. Kuo [1*], S. Q. Huang[1], B. C. Shi[1], Y. R. Chang[1], Y. T. Chen[1]
[1] Department of Chemical Engineering, Chung Yuan Christian University, Taoyuan City, Taiwan

Abstract:
In response to the climate change crisis, governments around the world have formulated relevant bills and policies, hoping to regulate the use of plastic materials. Therefore, using sustainable materials to replace disposable plastics has become a way to achieve environmental protection and carbon reduction goals. Bacterial cellulose (BC) is mainly an extracellular secondary metabolite produced by acetic acid bacteria fermentation, and it is a straight-chain structural molecule composed of β-D-glucose combined with β-1,4 glycoside chains. It is currently known as the finest natural fiber, the main difference from plant fiber is that BC does not contain hemicellulose, lignin, pectin, and other cell wall components (**Figure 1**). The bio-based cellulose content is as high as 95% as a kind of high purity and high crystallinity material. Because of its unique properties such as biodegradability, good biocompatibility, high water retention, and high mechanical strength, it is widely used in food processing, health foods, textiles, conductive materials, skin care products, tissue engineering, and wound dressings to have broad application prospects. Besides, BC is also a bio-based sustainable material with promising market potential in packaging. To investigate the production and structure of BC produced by acetic acid bacteria fermentation by culture medium components and culture conditions because the structure of BC and its application are closely related. The scanning electron microscopy images, water vapor transmission rate, and tensile strength of the resulting BC materials were analyzed. Further, the weight loss, moisture content, and total plate count of the fruit to evaluate the feasibility of the resulting BC as a sustainable material applied in food preservation.

Keywords: acetic acid bacteria, bacterial cellulose, water vapor transmission rate, tensile strength, total plate count, sustainable materials, food preservation.

(a)

(b)

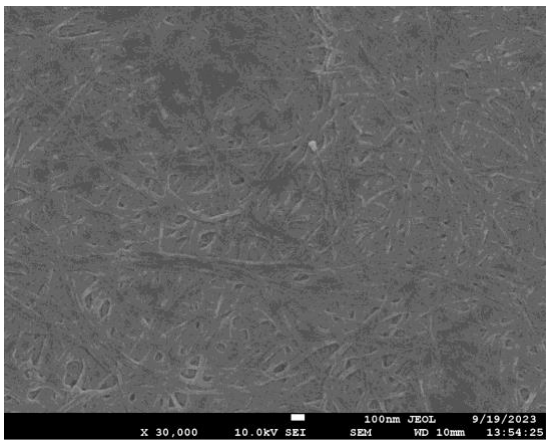


Figure 1: Bacterial cellulose produced by acetic acid bacteria and its scanning electron microscopy image (30 kx).

References:

1. Almeida, T., Silvestre, A.J.D., Vilela, C., Freire, C.S.R. (2021) Bacterial nanocellulose toward green cosmetics: recent progresses and challenges, *Int. J. Mol. Sci.*, 22, 2836.
2. Lahiri, D., Nag, M., Dutta, B., Dey, A., Sarkar, T., Pati, S., Edinur, H.A., Abdul Kari, Z., Mohd Noor, N.H., Ray, R.R. 2021. Bacterial cellulose: production, characterization, and application as antimicrobial agent. *Int. J. Mol. Sci.*, 22, 12984.

Polymeric films conjugated with silver and copper nanoparticles to enhance the antimicrobial activity

E. Hernández-Martín [1,2*], B. Merás-Saiz [1,3], M. Iriarte-Cela [1]
[1] Nanotechnology Department, Technological and Research Centre, SDLE, Móstoles, Spain
[2] Physical-Chemistry Department, Faculty of Chemical Science, University Complutense of Madrid, Madrid, Spain
[3] Biochemistry Department, Faculty of Medicine, University Autónoma of Madrid, Madrid, Spain

Abstract:
The sustained emergence of microorganisms resistant to antimicrobials and the prevalence of microbial contamination caused by them, force to the constant development of new solutions, creating a challenge for the effective therapeutic strategies. On this matter, innovative, biodegradable, non-toxic, and efficient antimicrobial materials play an increasingly important role. In this work, the development of polymeric films conjugated with different metal nanoparticles to enhance the antimicrobial activities against a wide spectrum of microorganisms has been proposed. There is considerable interest in polymer complexes with the controlled micro-nano structure, especially silver (Ag) and copper (Cu)-based complex, with a wide spectrum of antimicrobial activity and high antimicrobial efficacy. Natural polymers, such as chitosan, show antimicrobial properties, film forming, and can be used as a carrier of bioactive compounds.
Chitosan films have been prepared by the incorporation of gallic acid as antioxidant and glycerol as plasticizer to enhance mechanical properties. Then, polymeric films have been conjugated with silver nanoparticles (AgNP), copper nanoparticles (CuNP), and silver and copper mixed nanoparticles (AgCuNP). These nanoparticles have been synthetized by chemical reduction in aqueous solution and analysed by ultraviolet visible spectroscopy (UV-vis) and atomic force Microscopy (AFM). Stable polymeric films with a great and long-term antimicrobial activity were obtained (Figure 1). In order to evaluate the interactions between the components of the film forming formulations and metal nanoparticles, Fourier transform infrared (FTIR) and Raman spectroscopy analysis have been carried out. The presence of metal nanoparticles in polymeric films was confirmed by both techniques, as well as the presence of amide bonds between the primary amino groups of chitosan and the carboxylic acid of gallic acid.
Additionally, the antibacterial activity of the nanoparticles has been determined using the disk diffusion tests.
Results indicated that silver and copper nanoparticles had antimicrobial activity against bacteria, especially cupper nanoparticles, which showed the biggest inhibition halo. Copper nanoparticles also exhibited antifungal activity.

Keywords: antimicrobial activity, silver nanoparticles, copper nanoparticles, natural polymers, chitosan, gallic acid, composite film.

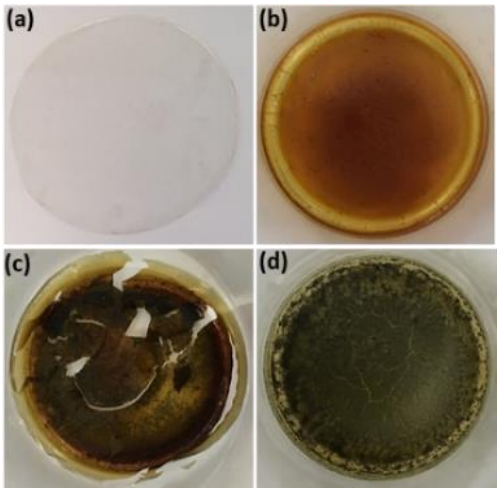


Figure 1: Polymeric films: control (a), conjugated with AgNP (b), conjugated with CuNP (c), and conjugated with AgCuNP (d).

References:

1. Zarandona, I., Puertas, A.I., Dueñas, M.T., Guerrero, P., de la Caba, K. (2020), Assessment of active chitosan films incorporated with gallic acid, *Food Hydrocolloids*, 101, 105486.
2. Lunkov, A., Shagdarova, B., Konovalova, M., Zhuikova, Y., Drozd, N., Il'ina, A., Varlamov, V. (2020), Synthesis of silver nanoparticles using gallic acid-conjugated chitosan derivatives, *Carbohydrate Polymers*, 234, 115916.
3. Usam, M., El Zowalaty, M., Shameli, K., Zainuddin, N., Salama, M. Ibrahim, N.A. (2013), Synthesis, characterization, and antimicrobial properties of copper nanoparticles, *International Journal of Medicine*, 8, 4467-4479.

Development of novel drug delivery systems based on polymeric nanofibres for the treatment of glioblastoma

Pedro V. Badía[1], Joan Moll-Carrió[1], María Fuentes-Baile[1], Rocío Díaz-Puertas[1], Miguel Saceda[1], Ma Pilar García-Morales[1], Ricardo Mallavia[1]

[1] Instituto de Investigación, Desarrollo e Innovación en Biotecnología Sanitaria de Elche (IDiBE-UMH), Universidad Miguel Hernández de Elche, Alicante, España.

Abstract:

Glioblastoma is a type of glioma with a low incidence but a high mortality rate due to its malignancy. Current treatments for glioblastoma focus on surgery followed by chemotherapy; however, systemic administration of antineoplastics damages healthy tissues and cells in the rest of the body, so their local application and controlled release is being investigated[1]. Their encapsulation in polymeric nanofibers may allow a controlled release and increase their bioavailability[2,3]. In this work, the electrospinning technique was used to synthesize poly (methyl vinyl vinyl ether-*alt*-maleic acid) (PMVEMA) nanofibers in both ester (Es) and acid (Ac) forms, as a drug delivery system for temozolomide (TMZ), carmustine (BCNU) and doxorubicin (DOX). For their morphological characterization, field emission scanning electron microscopy (FESEM) was used, observing diameters between 300 and 400 nm for PMVEMA-Ac nanofibers loaded with TMZ or DOX at a concentration of 1:20 (% w/w) with respect to the polymer and 737 nm for PMVEMA-Es loaded with BCNU at a concentration of 4:25 (% w/w). In addition, the encapsulation of TMZ in the nanofibers was confirmed by infrared spectroscopy and energy dispersive X-ray spectroscopy (EDX). On the other hand, the presence of DOX in the nanofibers was observed using the confocal microscopy technique. Finally, the antineoplastic effect of the encapsulated drugs was tested with the MTT cell viability assay in glioblastoma cell lines from patients of the Hospital General Universitario de Elche (HGUE). In this assay, a dose-dependent decrease in cell viability was observed at increasing concentrations of the encapsulated drug. Furthermore, our next step is quantifying its encapsulation efficiency by UHPLC and its subsequent release.

Keywords: PMVEMA-Ac; PMEMA-Es; polymeric nanofibers; carmustine; doxorubicin; temozolomide; antineoplastics; electrospinning; glioblastoma.

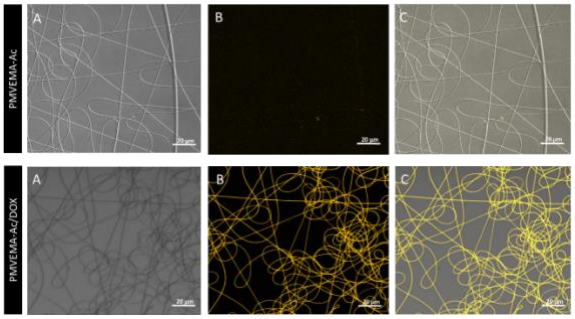


Figure 1: Photographs taken by confocal microscopy of PMVEMA and PMVEMA-Ac/DOX 1% nanofibers. A) Bright field B) Fluorescence C) Merge of A and B. λ_{exc}= 475 nm, λ_{em}= 590 nm.

References:

1. Anderson, A. R., & Segura, T. (2020). Injectable biomaterials for treatment of glioblastoma. Advanced materials interfaces, 7(20), 2001055.
2. Singh, B., Kim, K., & Park, M. H. (2021). On-demand drug delivery systems using nanofibers. Nanomaterials, 11(12), 3411.
3. Mira, A., Mateo, C. R., Mallavia, R., & Falco, A. (2017). Poly (methyl vinyl ether-alt-maleic acid) and ethyl monoester as building polymers for drug-loadable electrospun nanofibers. Scientific reports, 7(1), 17205.

Assessing Smoke Emission Characteristics of Innovative Cork-Based Composites Incorporating Recycled Plastic Materials

T. Barboni, S. Petlitckaia, P-A. Santoni
SPE CNRS UMR 6134, University of Corsica, Corté, France

Abstract:
Utilizing waste materials as both fillers and matrix components in composite material fabrication presents an economically viable and ecologically responsible approach to production. Various waste materials, including plastic, paper, and glass, can serve as fillers, enhancing the strength and overall properties of composite materials. Moreover, employing waste materials as the primary matrix component reduces the dependency on virgin resources and contributes to waste reduction in the environment.

In the scope of this investigation, a novel composite material was formulated, incorporating discarded polymer waste (such as PP or PEHD caps) and cork powder derived from previously unused cork, also known as male cork. The primary focus of this study was the assessment of the flammability characteristics exhibited by this innovative material. A comprehensive combustion test was conducted utilizing a cone calorimeter under an external heat flux of 40 kW/m^2. Gas emissions were quantified using an IRTF spectrometer, COV (Compounds of Volatile Organic) compounds were analyzed using GC/MS, and aerosols were monitored with the assistance of a He-Ne laser.

The outcomes of this investigation revealed that the primary gases emitted during the analysis were primarily composed of H_2O, CO_2, CO, CH_4, and NOx. The production of aerosols was notably prominent, while VOCs were generated in limited quantities but exhibited high toxicity. It was observed that materials containing PP were more susceptible to ignition and less resistant to combustion compared to composites based on HDPE. Furthermore, the data indicated that an increase in cork content led to heightened flammability in the samples, though the combustibility remained unaffected by cork content in the case of PP-based composites. Toxicity levels were lower in cork-based composites containing 0% to 10% cork by weight. However, toxicity increased significantly in composites containing 15% and 20% cork by weight.

Keywords: composite materials, polymer and cork wast, polypropylene and high density polyethylene, flammability, combustibility, smoke, gas emission, toxicity

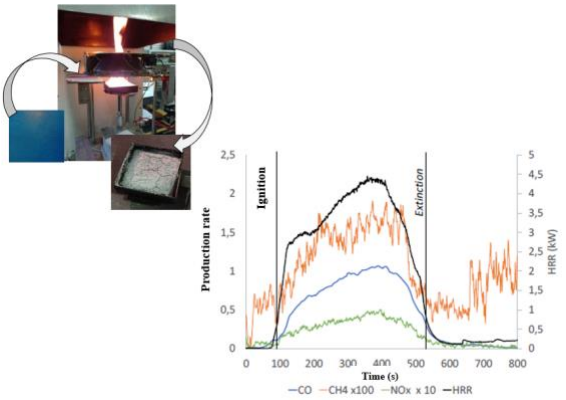


Figure 1: Figure illustrating the test performed on a cone calorimeter and the results of characterization of gas emission by IRTF.

Multiferroic ceramic composites obtained by three sintering methods

Przemysław Niemiec, Dariusz Bochenek, Grzegorz Dercz, Artur Chrobak, Grzegorz Ziółkowski
Institute of Materials Engineering, University of Silesia in Katowice, 75 Pułku Piechoty 1a, 41–500 Chorzów, Poland

Abstract:
The work presents the results of experimental research of multiferroic ceramic composites (P-F) obtained with three sintering methods, i.e., free sintering FS (pressureless), hot pressing HP, and spark plasma sintering SPS. The multiferroic composites were obtained by connecting the $Pb_{0.94}Sr_{0.06}(Zr_{0.46}Ti_{0.54})_{0.99}Cr_{0.01}O_3$ ferroelectric material (90%) and $Ni_{0.64}Zn_{0.36}Fe_2O_4$ ferrite material (10%).
The P-F composite materials at room temperature show both magnetic and electrical properties. The tests showed that all sintering methods allowed the obtaining of multiferroic composite materials with favorable functional parameters and properties. High values of permittivity are in the range from 585 to 784 (for 10 kHz, at room temperature) and from 6443 to 8336 (for 10 kHz at the ferroelectric-paraelectric phase transition temperature), while dielectric loss tangent values are in the range from 0.003 to 0.013 (for 10 kHz at room temperature). The residual polarization P_r of the composites ranges from 1.16 to 2.09 μC/cm^2, while the coercive field E_c ranges from 0.80 to 1.51 kV/mm. The M magnetization values at -268°C range from 4.57 to 5.66 Am^2/kg. The P-F$_{SPS}$ composite sample has the most significant M value drop at room temperature (18.2%), while the P-F$_{HP}$ sample retains the highest magnetization stability (7.9%). The microstructure of the composite sample obtained by the SPS method is fine-grained but has the highest porosity. In contrast, in the FS method, high temperatures favor excessive grain growth, which causes an increase in grain size inhomogeneity. The HP hot pressing method provides the most favorable microstructure of multiferroic composites, which improves the sinterability of the ceramic sinter, obtaining high density and appropriate densification of the material. It translates into the most optimal set of functional parameters of multiferroic composites.

Keywords: multiferroics; ferroelectric-ferromagnetic composites; perovskite-type materials; dielectric properties; magnetic properties.

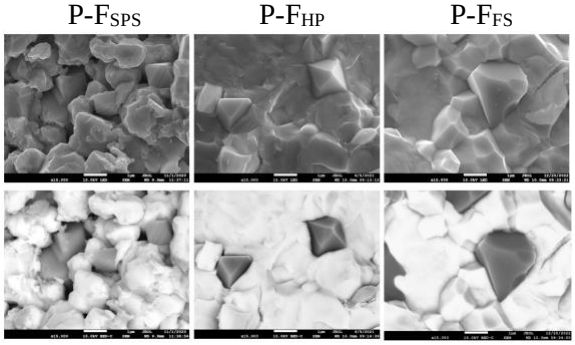


Figure 1: Microstructure of the P-F multiferroic ceramic composites (SEM-BSE images).

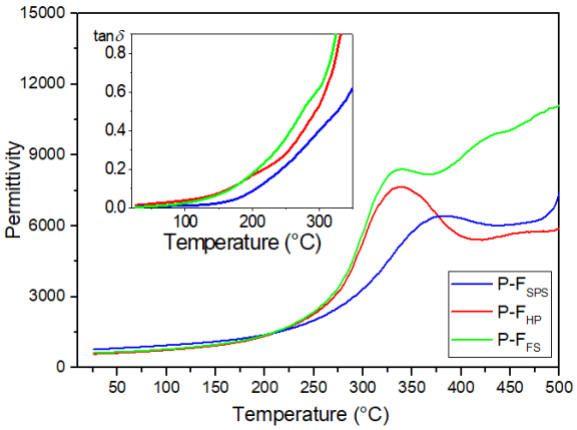


Figure 2: Temperature dependencies of dielectric properties for the P-F multiferroic composites (for 10 kHz).

References:

1. Fiebig, M., Lottermoser, T., Meier, D., Trassin, M. (2016), The evolution of multiferroics. *Nat. Rev. Mater.* 1, 16046.
2. Shanmugasundram, H.P.P.V., Jayamani, E., Soon, K.H. (2022), A comprehensive review on dielectric composites: classification of dielectric composites. *Renew. Sust. Energ. Rev.* 157, 112075.

Multiferroic composites based on $BaTiO_3$ and nickel-zinc ferrite material

Dariusz Bochenek, Przemysław Niemiec, Grzegorz Dercz, Artur Chrobak, Grzegorz Ziółkowski
Institute of Materials Engineering, University of Silesia in Katowice, 75 Pułku Piechoty 1a, 41–500 Chorzów, Poland

Abstract:
This study investigates the structural, morphological, dielectric, ferroelectric, electromechanical, magnetic, and conductivity properties of $BaTiO_3$-$Ni_{0.64}Zn_{0.36}Fe_2O_4$ (BT-F) multiferroic composites compacted via free sintering method. The influence of the ferrite content in multiferroic composites on the physical properties was investigated and discussed. Three compositions of the BT-F multiferroic composite were obtained with content 85/15 (85BT-F), 90/10 (90BT-F), and 95/05 (95BT-F).
X-ray results confirmed the presence of two main phases of the composite, with strong peaks from $BaTiO_3$ material and weaker reflections coming from nickel-zinc ferrite. The BT-F composite materials were demonstrated to exhibit multiferroism at room temperature. All composite compositions have high permittivity and low dielectric loss tangent values, and the ferroelectric properties of the ferroelectric component BT are maintained at a high level. The magnetic properties of the composite depend on the amount of the ferrite phase in the composite and are the strongest for the composition 85BT-F (magnetization in *RT* is 4.12 emu/g).
The work optimized the process conditions of the free sintering method for obtaining BT-F composite materials with improved electrical and magnetic properties. An improved set of multifunctional properties expands the possibilities of using multiferroic composites in microelectronics.

Keywords: ferroelectrics; $BaTiO_3$; multiferroics; multiferroic composites.

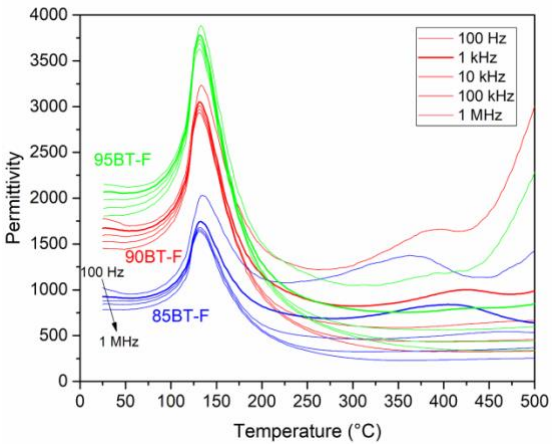


Figure 1: Temperature dependencies of permittivity for the BT-F multiferroic composites: (for 100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz).

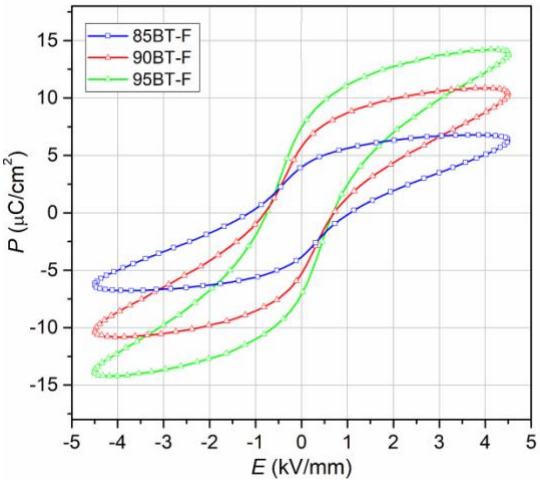


Figure 2: Hysteresis loops for BT-F multiferroic ceramic composites (at *RT*, for 5 Hz, *E*=4.5 kV/mm).

References:

1. Pachari, S., Pratihar, S.K., Nayak, B.B. (2020), Microstructure driven magnetodielectric behavior in ex-situ combustion derived $BaTiO_3$-ferrite multiferroic composites, *J. Magn. Magn. Mater.* 505, 166741.
2. Pachari, S., Pratihar, S.K., Nayak, B.B. (2019), Improved magneto-capacitance response in combustion derived $BaTiO_3$-($CoFe_2O_4$/$ZnFe_2O_4$/$Co_{0.5}Zn_{0.5}Fe_2O_4$) composites, *J. Alloys Compd.* 784, 897–905.

Optimization of parameters for producing piezoelectric BT/PVDF nanocomposites using additive manufacturing

L. Santiago-Andrades [1*], M. J. Sayagués[2], F. J. Gotor[2], R. Moriche[1]
[1] Dpto. de Física de la Materia Condensada, Universidad de Sevilla, Sevilla 41080, Spain
[2] Instituto de Ciencia de Materiales de Sevilla, CSIC, Sevilla 41092, Spain

Abstract:
Piezoelectric nanogenerators (PENGs) have emerged as an alternative to conventional batteries for powering low-energy devices. PENGs can convert mechanical energy from the environment into electrical energy. In general, these systems consist of a piezoelectric ceramic filler embedded into a polymeric matrix. On the one hand, piezoelectric ceramics, such as perovskite barium titanate (BT), exhibit a high piezoelectric response [1] but, in contrast, they are brittle and have low flexibility. On the other hand, piezoelectric polymers, such as polyvinylidene fluoride (PVDF) β phase, offer high flexibility and versatility in fabrication, as well as good electrical properties. Therefore, to obtain materials with both characteristics – high piezoelectric coefficients and high flexibility – the combination of the two phases is needed [2]. This work studies the processability of nanocomposite materials consisting of a PVDF piezoelectric polymer matrix with a homogeneously dispersed BT ceramic phase [3]. The main aim is to develop PENGs that allow the final geometry to be fabricated using additive manufacturing methods, as the incorporation of the ceramic phase into the polymeric matrix requires the optimization of the operational parameters of the manufacturing process as well as of the composite material itself. The possibility of obtaining the β phase directly from the printing process is discussed as well as limitations induced by the addition of BT. Some of the limitations are not only caused by the relatively high ceramic content but also by changes in the morphology of the geometry of the feedstock particles. This optimization process will be conducted in order to achieve flexible PENGs with high piezoelectric coefficients (Figure 1).

Keywords: barium titanate, polyvinylidene fluoride, piezoelectric, nanocomposite, additive ma- nufacturing.

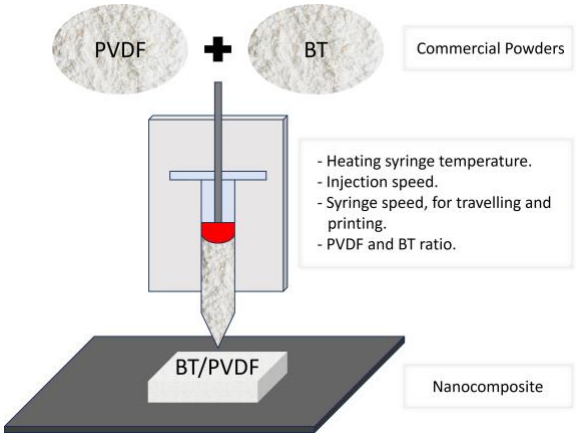


Figure 1: Scheme representing in a generic way the process to be implemented and optimized: the 3D printing of BT/PVDF nanocomposites from commercial powders. It shows part of the parameters to be adjusted.

References:

1. Qian W. et al. (2022), Ferroelectric $BaTiO_3$ based multi-effects coupled materials and devices, *Advanced Electronic Materials*, 8, 2200190.
2. Su H. et al. (2021), Enhanced energy harvesting ability of polydimethylsiloxane-$BaTiO_3$-based flexible piezoelectric nanogenerator for tactile imitation application, *Nano Energy*, 83, 105809
3. Zheng, J. et al. (2022), $BaTiO_3$/PVDF-TrFE skeleton separators with superior ion conductivity and mechanical property integrated for flexible seconds self-charging supercapacitors, *Journal of Power Sources*, 528, 231213.

Influence of the addition of BT nanoparticles on the piezoelectrical, mechanical and tribological properties of BT/PVDF nanocomposites

A. Otero [1*], M.J. Sayagués[2], F. J. Gotor[2], R. Donate[3], M. Monzón[3], R. Paz[3], F. Gutiérrez-Mora[1], R. Moriche[1]

[1] Dpto. de Física de la Materia Condensada, Universidad de Sevilla, Sevilla 41080, Spain

[2] Instituto de Ciencia de Materiales de Sevilla, CSIC, Sevilla 41092, Spain

[3]Departamento de Ingeniería Mecánica, Grupo de Investigación en Fabricación Integrada y Avanzada, Universidad de Las Palmas de Gran Canaria, Campus Universitario de Tafira s/n, 35017 Las Palmas, Spain

Abstract:

During last decades, barium titanate (BT) has been widely proposed as filler to develop piezoelectric nanogenerators (PENGs) [1, 2]. Particularly, it has been suggested as filler for polyvinylidene fluoride (PVDF)-based nanocomposites to enhance the piezoelectric response [3]. For this purpose, dispersion of the ceramic filler into the polymeric matrix is a key question, not only because the dispersion itself, but also because its incorporation as second phase strongly affects the β phase formation in the PVDF [4] as well as the mechanical and tribological behavior of the system.

The main aim of this work is to analyze how the incorporation of the BT nanoparticles modifies the mechanical and electrical properties of BT/PVDF nanocomposites. For this purpose, nanocomposites with contents up to 60 vol% were prepared by compression molding. The BT nanoparticles were dispersed by dry milling to avoid the use of organic solvents. Microstructural analysis of as-milled powder showed a well distributed dispersion with no appreciable agglomerates. It is important to point out the change of morphology induced in the powder, from a spherical to a planar form. After compression molding, the β phase of the PVDF diminished and, consequently, thermomechanical postprocessing was needed. To stablish the better processing route, piezoelectrical response was characterized. It was also demonstrated that the addition of the BT nanoparticles considerably influenced the microhardness, stiffness, and tribological response of the nanocomposites, which are conditioned not only by the BT content, but also by the interfacial strength.

Keywords: barium titanate, polyvinylidene fluoride, piezoelectric, nanocomposite, additive ma- nufacturing.

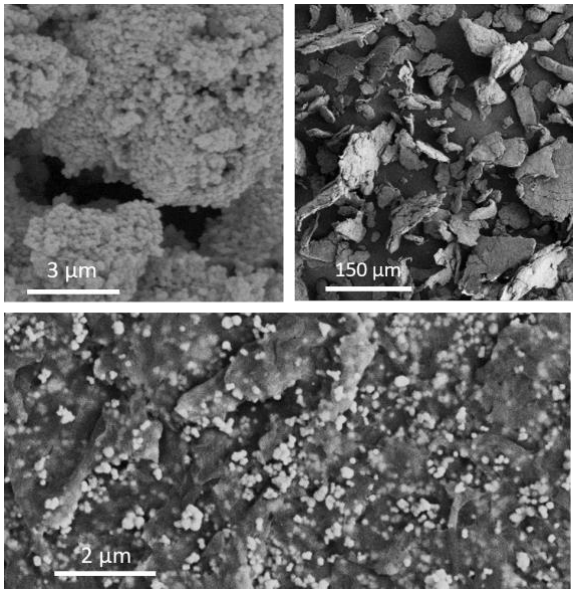


Figure 1: Microstructural features of (a) as-received PVDF, (b) as-milled BT/PVDF and (c) distribution of BT throughout.

References:

1. Yang X. et al. (2023), Dielectric and Energy Storage Properties of Coupling Agent Modification of BT PVDF Nano-composite Films, *Journal of Electronic Materials*, 52, 6968–6976.
2. Kim T. et al. (2023), Scalable, flexible $BaTiO_3$/PVDF piezocomposites prepared via supersonic spraying for use in energy harvesting and integrated energy storage devices, *Nano Energy*, 115, 108682.
3. Kubin M. et al. (2023), Piezoelectric properties of PVDF-TrFE/$BaTiO_3$ composite foams with different contents of TrFE units, *Polymer Composites*, 44, 7804–7816.
4. Bhiogade A. et al. (2023), Improved pyroelectric effect in PVDF/$BaTiO_3$ composite flexible films mediated by enhanced β – PVDF phase formation, *Journal of Polymer Research*, 30, 288.

High-temperature mechanical and electrical characterization of zirconia composites with 2D nanomaterials

F.J. Coto-Ruiz[1,2], A. de la Cruz-Blanco[1,2], R. Moriche[2], Á. Gallardo-López[2], F. Gutiérrez-Mora[2], A. Morales-Rodríguez[2], R. Poyato[1]

[1] Instituto de Ciencia de Materiales de Sevilla, ICMS, CSIC-Universidad de Sevilla, Avda. Américo Vespucio 49, Sevilla 41092, España

[2] Depto. Física de la Materia Condensada, ICMS, CSIC-Universidad de Sevilla, Apdo. 1065, Sevilla 41080, España

Abstract:

Today, solid oxide fuel cells (SOFCs) have become one of the most promising options for electric power generation. One of the fields of improvement of these cells is the optimization of the properties of the electrolyte, being one of the most used the ceramic of cubic zirconia doped with 8 mol% yttrium oxide (8YCSZ). Very recently, some studies propose the incorporation of nanomaterials, such as reduced graphene oxide (rGO) as a second phase to improve the properties of the 8YCSZ electrolyte [1, 2].

In this work, composites of 8YCSZ ceramic and rGO nanostructures have been prepared using Spark Plasma Sintering (SPS). The samples have been characterized by SEM, Raman spectroscopy and XRD.

The effect of rGO on the electrical performance of the composites was analyzed by Impedance Spectroscopy (IS) in a range of temperatures in argon atmosphere, differentiating the conductivity in the direction parallel and perpendicular to the nanosheets main *ab* plane. The experimental data were analyzed through the impedance spectra, i.e., the Z" vs Z' representation. The conductivity values were obtained by simulations using the equivalent circuit model with the Zview software.

In addition, high-temperature mechanical behavior of the composites was studied and compared to the monolithic 8YCSZ to characterize the effect of the 2D nanomaterials on the deformation mechanisms.

Keywords: composite, zirconia, 8YCSZ, rGO, SPS, electrolyte, SOFC, hydrogen economy, fuels cells, impedance spectroscopy, equivalent circuit model, high-temperature mechanical behavior.

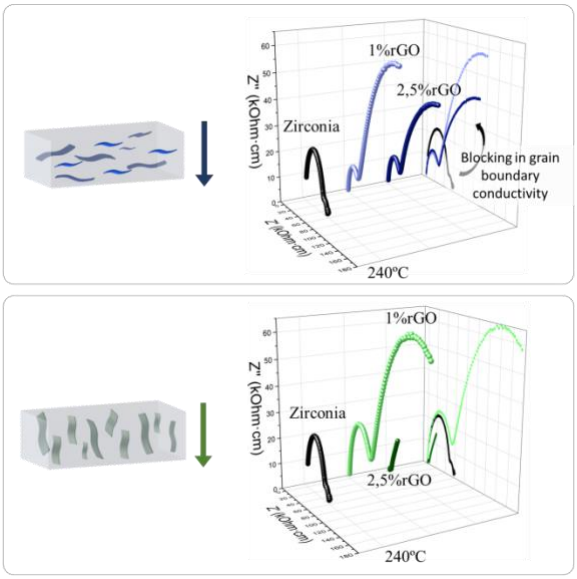


Figure 1: Impedance spectra at 240 ºC for 8YCSZ and composites with 1 and 2.5 %vol of rGO for conductivity perpendicular and parallel to the nanosheets, respectively.

References:

1. Kurapova, O. Y. et al. Structure and electrical properties of YSZ-rGO composites and YSZ ceramics, obtained from composite powder. Electrochimica Acta 320, 134573. ISSN: 0013-4686 (2019).
2. Glukharev, A. et al. YSZ-rGO composite ceramics by spark plasma sintering: The relation between thermal evolution of conductivity, microstructure and phase stability. Electrochimica Acta 367, 137533. ISSN: 0013-4686 (2021).

Photoreduction of carbon dioxide over TiO_2/Ru composites

D. Sibera[1*], I. Pełech[2], P. Staciwa[2], K. Ćmielewska[2], K. Sobczuk[2], E. Ekiert[2], E. Kusiak-Nejman[2], A. W. Morawski[2], U. Narkiewicz[2]

[1] Department of Construction and Road Engineering, Faculty of Civil and Environmental Engineeing,West Pomeranian University of Technology in Szczecin, Piastow 50a, 70-311 Szczecin, Poland.

[2] Department of Inorganic Chemical Technology and Environment Engineering, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology in Szczecin, Pulaskiego 10, 70-322 Szczecin, Poland.

* dsibera@zut.edu.pl

Abstract:

This work presents the results of photoreduction of carbon dioxide investigations obtained for TiO_2/Ru composites with addition from 0,1 wt% to 5,0 wt% of ruthenium. TiO_2 samples used to produce the composites were prepared from titanium IV isopropylate. Ruthenium used to prepare the composites came from ruthenium red. To produce the composite, at first titanium IV isopropylate was dissolved in ethanol and ruthenium red was dissolved in water. After that, the water solutions of ruthenium red was dropped into the mixture and mixed using a magnetic stirrer at ambient conditions. After 24 h, the mixture was transferred into a microwave assisted solvothermal reactor and treated at 4.0 bar for 15 min. Subsequently, the solution was transferred to a Petri dish and dried at 80 °C for 48 h. The dried materials were heated in argon atmosphere at 400 °C for 1 h. All received materials were characterized using XRD, SEM, and low-temperature nitrogen adsorption (BET) methods. The presence of nanometric ttitanium dioxide was confirmed in all the samples. The average size of the TiO_2 nanocrystallites (determined using the Scherrer equation) was between 9 nm and 11 nm.

The photoreduction of carbon dioxide was carried out in a gas phase system. The proces was performed in a bottle-shaped glass reactor equipped with a quartz cooler constantly supplied with fresh water. In the cooler a medium-pressure mercury lamp TQ 150 Z3 (Heraeus, Germany) was set. The reactor was placed in the thermostatic chamber in order to cut off any light sources and to ensure a stable temperature. Before the process, the system was rinsed with pure CO_2 for 16 h, then, it was closed and the lamp was turned on. The gas phase was constantly stirred with the pump. The composition of the gas phase was analyzed with a Master GC gas chromatograph (DANI Instruments, Italy), equipped with a 4 m Shin-carbon ST 100/120 micropacked column. The detectors were TCD and FID with the methanizer. Argon was the carrier gas. The content of individual components in the gas phase in subsequent measurements was calculated based on the calibration curve. The amount of hydrogen, carbon monoxide and methane produced during the processes was determined. Based on the results, it was found that the most effective catalyst for the photoreduction of CO_2 was the sample with the 0,5 wt% of ruthenium and that hydrogen was the main product.

Keywords: TiO_2, ruthenium, photoreduction, photocatalyst

Acknowledgements:

This research was funded by National Centre for Research and Development from Norway Grants 2014-2021, under the grant number NOR/POLNORCCS/PhotoRed/0007/2019-00.

Dynamics of a thin-walled composite structure with a piezoelectric sensor deformation

L.Zárybnická [1*], M. Marek [1], R.Kolman [1,2]

[1] Department of Technical studies, College of Polytechnics Jihlava, Tolstého 16, 586 01 Jihlava, Czech Republic

[2] The Czech Academy of Sciences, Institute of Thermomechanics, Dolejškova 1402, 182 00 Prague, Czech Republic

Abstract:

Composite materials continue to be a hot topic in additive manufacturing, with Fused Filament Fabrication technology being one of the most affordable and offering great potential for producing composites with integrated continuous fibers using Composite Fiber Coextrusion technology (1). The advantages of composites produced in this way include the production of various product shape modifications, prototype production and processing on affordable equipment (2). Another critical factor is the choice of fiber type or fiber arrangement for an industrial application (3).

Analysis of vibration problems is becoming an increasingly important factor in engineering due to the increase in size and speed of modern machines. The vibration issue becomes critical in, e.g. balancing machines, the vibration of shafts and transmission systems, the vibration of turbine blades and turbine discs, and the turbulence of rotating shafts. This can only be thoroughly described based on vibration theory (4). Only with the help of this theory can structures be designed with the best possible characteristics, which will keep the working conditions of the machine as far away as possible from critical conditions where strong vibrations may occur.

The submitted abstract aims to study the dynamics of a thin-walled composite structure with a thin-walled piezoelectric sensor deformation. The polymer matrix is a construction thermoplastic polyamide with two types of fibers incorporated - carbon and basalt. The samples produced have been tested regarding vibration determination and classical mathematical properties concerning the type of arrangement of the continuous fibers (Figure 1).

Keywords: composite, infill structure, 3D print, piezoelectric sensor deformation, carbon fiber, basalt fiber, FEM

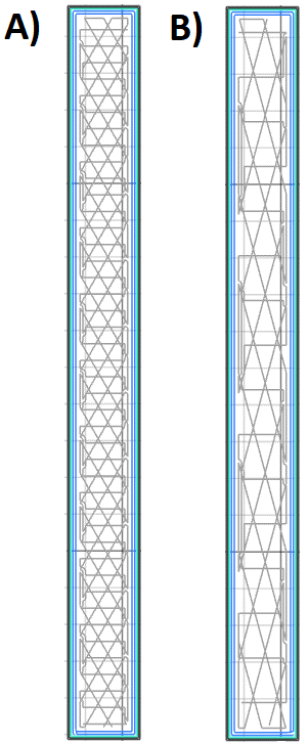


Figure 1: Structure of fiber arrangement in the composite, A - isogrid, B - anisogrid.

References:

1. Ngo, T. D., Kashani, A., Imbalzano, G., Nguyen, K. T., Hui, D. (2018). Additive manufacturing (3D printing): A review of materials, methods, applications and challenges. *Composites Part B: Engineering*, *143*, 172-196.
2. Jandyal, A., Chaturvedi, I., Wazir, I., Raina, A., Haq, M. I. U. (2022). 3D printing–A review of processes, materials and applications in industry 4.0. *Sustainable Operations and Computers*, *3*, 33-42.
3. Mahltig, B., & Kyosev, Y. (2018). Inorganic and composite fibers: production, properties, and applications.
4. De Silva, C. W. (2006). *Vibration: fundamentals and practice*. CRC press.

Laboratory Evaluation of the Use of Seashell and Bio-based Epoxy Asphalt in Porous Asphalt Mixtures

Mohammad Alharthai [1,*]
[1,*] Department of Civil Engineering, Najran University, College of Engineering, Najran 66462, Saudi Arabia, maalharthai@nu.edu.sa, +966504329945

Abstract:
Over the past few decades, due to the depletion of many good aggregate sources and increased negative environmental impact from excavation and processing of virgin aggregates, we should consider other alternatives to replace natural aggregates. This study investigates the substitution of conventional aggregate with a seashell in asphalt mixtures and evaluates the optimal substitution percentage in aggregate gradations of various nominal maximum aggregate sizes (NMASs) (i.e., 4.75, 9.5, and 12.5 mm). Laboratory experiments were performed on open-graded asphalt mixture specimens with the coarse aggregate of sizes between 2.36 and 12.5 mm being replaced by the seashell at various percentages (0, 15, 30, 45, and 100%). Three types of materials are mainly used in the experiments: asphalt binder, aggregate, and seashell. One Superpave performance-graded (PG) asphalt binder, PG 76-22, was selected for this study. It is a styrene-butadiene-styrene (SBS) modified binder. The aggregate used in this study is of granite type. The seashell was provided by a local gravel and washed shell supplier in Tampa, Florida. This study also aims to improve the durability and strength of asphalt mixture by using bio-based epoxy asphalt binder (BEAB). In the study, a BEAB formula was firstly developed using an epoxidized soybean oil (ESBO) that is considered as a renewable resource. Specimen properties relevant to the performance of open-graded asphalt mixtures in the field were tested, evaluated, and compared. Specifically, a Marshall stability test, Cantabro test, indirect tensile strength test, air void content test, and permeability test were conducted to evaluate the strength, resistance to raveling, cracking resistance, void content, and permeability of open graded asphalt mixtures. The results show that there is no significant difference in the Marshall stability and indirect tensile strength when the coarse aggregates are replaced with seashell. This study also found that the optimum percentages of seashell in open-graded asphalt mixture were 15, 30, and 45% for 12.5, 9.5, and 4.75 mm NMAS gradations, respectively.

Keywords: Porous asphalt mixture; sustainable pavement materials; Florida washed shell; aggregate gradation; Bio-based epoxy asphalt; Epoxidized soybean oil.

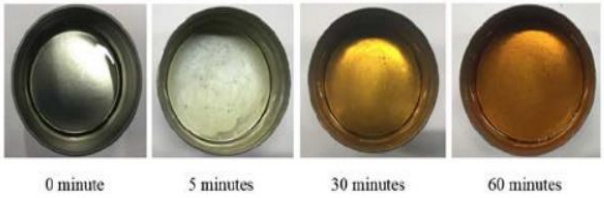


Figure 1: illustrating the curing process of Bio-based Epoxy Resin in which Epoxidized Soybean Oil was mixed with maleic anhydride and maintained at 145°C [1].

Figure 2: illustrating the shell particles of coarse aggregate sizes (12.5, 9.5, 4.75, and 2.36 mm) for use in the mixture preparation[2,3].

References:

1. Lu, Q.; Xin, C.; Alamri, M.; Alharthai, M.(2021). Development of porous asphalt mixture with bio-based epoxy asphalt. *J. Clean. Prod*. 2021, 317, 128404.
2. Alharthai, M., Lu, Q., Elnihum, A., & Elmagarhe, A. (2021). Laboratory Evaluation of the Use of Florida Washed Shell in Open-Graded Asphalt Mixture. *Materials*, 14(22), 7060.
3. Elmagarhe, A., Lu, Q., Alharthai, M., Alamri, M., & Elnihum, A. (2022). Performance of Porous Asphalt Mixtures Containing Recycled Concrete Aggregate and Fly Ash. *Materials*, 15(18), 6363.

RECOVERING AND TRANSFORMING FISHING WASTE FOR A SUSTAINABLE FUTURE

Sónia Miranda1*, Mónica Fernandes1, Renato Reis1, Tânia Simões2, João Redol2, Pedro Manuel3, Cristina Serralheiro3, Pedro Ramalhete4

1 Innovation in Polymer Engineering (PIEP), Portugal; 2Neutroplast, Portugal; 3Bitcliq, Portugal; 4 Justdive, Portugal

Abstract:
Marine pollution, particularly arising from fishing activities, poses a significant threat to global aquatic ecosystems. The improper disposal of fishing gear, such as nets and traps, contributes to the phenomenon known as 'ghost fishing,' resulting in direct harm to marine fauna and the generation of persistent waste in the aquatic environment. The unnatural presence of these substances leads to consequences such as habitat destruction, entanglement of animals, facilitation of invasive species transfer between ecosystems, and sediment deposition. These factors can have potential impacts on benthic animal life and feeding. At the forefront of environmental sustainability, the SeaRubbish2Cap project introduces an innovative approach to comprehensively tackle the issues of ocean waste recovery, with a strong emphasis on the circular economy and sustainable recycling. To address this challenge, the project is developing a user-friendly mobile application that allows fishermen to identify and mark the locations where they lose their fishing artifacts at sea. This data aids in targeted collection efforts and contributes to a better understanding of marine waste distribution. The located waste originating from fishing activities in the Peniche region's ocean floor was collected through a professional and careful process to minimize damage to the underwater environment. Additionally, practical strategies for proper waste treatment were thoroughly explored. This involved a multi-step process, including the meticulous removal of contaminants, segregation based on object characteristics, cleaning, and individual characterization of each waste item. Various techniques were employed to ensure thorough characterization, such as flow index (MFR), FTIR analysis (Fourier Transform Infrared Spectroscopy), and utilization of DSC (Differential Scanning Calorimetry).

During the waste analysis, the identification of polymers and contaminants, including shell fragments from crustaceans, guided the meticulous selection of suitable elements for the treatment process. Subsequent to the comprehensive treatment procedure, a co-rotating twin-screw extruder was employed to fabricate a compound incorporating 70 wt% of recycled marine waste with polyethylene reclaimed from Neutroplast's industrial processing. The resultant product demonstrates potential utility across various applications, effectively exemplifying the SeaRubbish2Cap project's adept response to the environmental challenge. This underscores its feasibility and success in generating valuable materials while advocating for environmental stewardship.

Keywords: Marine waste, Circular economy, Polymer compound, Waste characterization.

Figure 1: Ghost fishing - a sea turtle entangled in plastic, emphasizing the urgency of marine waste collection and recovery.

Development of feather-based materials

K. Wrześniewska-Tosik[1], T. Mik[1], E. Wesołowska[1], T. Kowalewski[1], M. Pałczyńska[1], J. Wietecha[1]
[1] ŁUKASIEWICZ Research Network - Lodz Institute of Technology, Lodz, Poland

Abstract:
Geotextiles are widely used in agriculture, livestock, or earth-retaining structures. Most of the nonwovens in use are re made of synthetic fibers such as polypropylene (PP), polyester (PET), polyamide (PA), of which PP fibres account for 60% of all fibers used in the production of nonwoven fabrics. All the above-mentioned fibers are characterized by a low susceptibility to biodegradation in natural conditions, which may result environmental problems regarding soil contamination and accumulation of microplastics. The problem of the long decomposition cycle of such materials and the concern for the protection of the natural environment have resulted in significant interest in research and application in recent years in composite nonwoven fabrics containing fibers from natural or biodegradable polymers. Poultry feathers are a by-product of the poultry industry. The outstanding properties of feathers such as: hydrophobic properties, biodegradability, good thermal and acoustic insulation combined with their low cost and availability open way towards valuable and ecological products. Here we show the possibility of exploitation the potential of feathers as source of raw material for conversion into functional end-products such as nonwovens - geotextiles manufactured by the needling method to be used for agricultural sector. The composite feather-based material combines the characteristic of biodegradability with the ability to fertilize the soil during its biodegradation.
Nonwoven were made of feathers with PLA /cotton. A method for producing nonwovens using a needle method is that the PLA/cotton are subjected to loosening and carding, after which they are arranged on a horizontal plane and then the shredded feathers in the amount of up to 40 wt. % are evenly distributed on such a single fleece. By combining individual layers, a multilayer composition is formed which is subjected to a needling with take-up 1.5 -2.5 m/min to give a multilayer nonwoven. In order to strengthen the multilayer nonwoven fabric, it is subjected to thermal consolidation using calender at different temperature depending on the type of fibres used and the kind of consolidation. Elaborated nonwoven were characterized by mechanical properties such as: thickness, strength, air permeability measurements and biodegradation in soil.
Keywords: nonwoven, geotextiles, feathers, needle punch technique.

Figure 1: Nonwoven geotextiles from PLA/Cotton combined with keratin fibres.

ACKNOWLEDGMENTS
The investigation presented in this paper was carried out as a part of research project UNLOCK " Unlocking a feather bioeconomy for keratin-based agricultural products". Grant Agreement number: 101023306 — UNLOCK — H2020-BBI-JTI-2020

References:

1. Mukhopadhyay, S. (2014) Natural and synthetic fibres for composite nonwovens, at „*Composite Nonwoven Materials: Structure, Properties and Applications*", page 20-29.
2. Global Market Insights, Inc (2020) Polypropylene (PP) nonwoven fabrics market 2020 – 2026, https://www.gminsights.com/industry-analysis/polypropylene-pp-nonwoven-fabrics-market-report
3. Hsieh, C.W. (2016) Geotextiles in agriculture and aquaculture, at "*Geotextiles From Design to Applications*", 511-530

Alimentary Protein Isolate and Chitosan Derivatives Complexes as Novel Biomaterials for Skin Repair

D. Ianev [1*], B. Vigani [1], M. Mori [2], C. Valentino [1], M. Ruggeri [1], G. Sandri [1], S. Rossi [1]
[1] Department of Drug Science, University of Pavia, Pavia, Italy
[2] 1MED SA, Agno, Switzerland

Abstract:
Polysaccharides (PL) and proteins (PR) are main biopolymers extensively employed in scaffold manufacturing for tissue regeneration, due to their qualities such as biocompatibility, biodegradability, and low toxicity[1]. The interaction between PL and PR can be exploited fot the development of PL-PR complexes as biomaterials, easily processable and capable of assuming different geometries and sizes depending on the preparation method employed[2]. These diverse complexes are typically classified as either noncovalent or covalent based on their bonding characteristics[3]. The present work aims to produce new sustainable and high-value biomaterials, consisting of complexes between alimentary proteins such as whey protein isolate (WPI, containing more than 90% proteins) and chitosan (CS) or trimethyl chitosan (TMC), to be used for the manufacturing of scaffolds for skin repair. The raw materials used are sourced from waste generated by the food industry. Various combinations of the raw materials were considered: WPI (Milei GmbH) and CS (Sigma Aldrich) or TMC (ChitoLytic), taking into account specific variables such as the molecular weight (MW) of the PR, pH values, and experimental conditions responsible for WPI denaturation, such as temperature and time. The obtained PL-PR complexes were subjected to: (i) rheological measurements to point out the presence of a positive or negative rheological synergism ($\Delta\eta/\eta$), indicating the strength of the PL-PR interaction; (ii) turbidimetric analysis at 480 nm to investigate the formation of soluble complexes or coacervates (insoluble complexes); (iii) DLS and ELS measurements to determine complexes size and ζ potential; (iv) SEM analyses on freeze-dried PL-PR complexes to observe their micro/nanostructure. Additionally, *in vitro* studies were conducted to assess the complexes cell biocompatibility, their potential in enhancing cell proliferation, and their antioxidant activity. Furthermore, changes in WPI secondary and tertiary structures during denaturation and interaction with PL were evaluated using intrinsic tryptophan fluorescence spectroscopy and by dosing free sulphydryl group content. The in depth characterization of these biomaterials indicates that the functional properties of PL-PR complexes are closely linked to biopolymer properties (such as MW, charge density, and chain conformation) and experimental conditions employed (including pH and denaturation conditions). Specifically, it was demonstrated that WPI denaturation at 70°C for 20 minutes, both before and after mixing with PL, played a crucial role in forming the PL-PR complexes. Denaturation of WPI before PL addition led to the obtainment of soluble complexes characterized by higher rheological synergism and lower absorbance values compared to coacervates formed when WPI was denaturated after PL addition. Moreover, the rheological analysis indicated that low MW CS exhibited stronger interactions with WPI compared to medium MW CS when subjected to identical denaturation conditions. ELS analysis suggested that electrostatic interactions predominantly drove TMC:WPI complex formation, while intrinsic tryptophan fluorescence spectroscopy highlighted the prevalence of hydrophobic interactions involved in CS:WPI complex formation. The innovative biomaterials obtained were utilized to produce dissolving microneedles for the treatment of abnormal scars.

Keywords: protein-polysaccharide complex, chitosan, trimethyl chitosan, whey protein isolate, biomaterial, sustainable.

References:

1. Tiwari, N., et al. (2023), Recent progress in polymeric biomaterials and their potential applications in skin regeneration and wound care management, *Journal of Drug Delivery Science and Technology*, vol. 83, p. 104319.
2. Bealer, E.J., et al. (2020), Protein–Polysaccharide Composite Materials: Fabrication and Applications, *Polymers*, vol. 12, p. 464.
3. Falsafi, S.R., et al. (2022), Protein-polysaccharide interactions for the fabrication of bioactive-loaded nanocarriers: Chemical conjugates and physical complexes, *Pharmacological Research*, vol. 178, p. 106164,

Cellulosic responsive membranes for dynamic water collection

S. D. Almeida[1], P. L. Almeida[1,2], M. H. Godinho[1], A P. C. Almeida[1,3,4*]
[1] i3N/CENIMAT, Department of Materials Science, NOVA School of Science and Technology, Caparica, Portugal
[2] Mechanical Engineering Department, Lisbon Superior Institute of Engineering, Lisbon, Portugal
[3] LAQV/Requimte, Department of Chemistry, NOVA School of Science and Technology, Caparica, Portugal
[3] iBET Instituto de Biologia Experimental e Tecnológica, Oeiras, Portugal

Abstract:
Inspiration comes from humidity-responsive plant skeletons[1, 2], spider webs[3] and Namib Desert beetle's[4] ability to respond and capture water from air. Plants produce a large variety and amount of cellulose, forming mesoand microstructures with unique characteristics and complex shapes. These structures are far beyond any current materials that can be artificially produced through technology. They are flexible, lightweight, low-cost, mostly destroyed and barely exploited. These organized structures in conjunction with liquid crystalline systems are great candidates to build-up hygromorphic water collection membranes. The evaporation of water is a ubiquitous phenomenon in the natural environment and a great source of clean energy. The energy associated with theevaporation of water from the ocean, watercourses or seaports is so subtle that is not given much attention to. This renewable source could supply enormous volumes of water. Every day, vast amounts of water evaporate poweredby heat energy from the sun.

This nature-inspired approach to produce cellulose-based meshes responsive membranes for water collection will involve specific material engineering strategies: i) to precise control the supporting flexible structure and directional movements of the cellulosic meshes; ii) chemical modification of cellulose skeleton in order to promote hydromorphic movement and consequent watercollection; and iii) control the responsiveness of the anisotropic liquid crystalline elastomers used.

These membranes are suitable to be used in countries susceptible to the occurrence of regular drought episodes and that have access to ocean or water courses from which water is constantly lost due to evaporation. These membranes can also be used inside of closed greenhouses where most of water resulting from the evapotranspiration of plants may be recovered without the consumption of energy.

Keywords: Cellulose, Bioinspired, Sensors, Moisture, Clean energy, Anisotropy.

References:

1. Almeida, A.P.C., et al., Soft Matter, 2019. 15(13): p. 2838-2847.
2. Reyssat, E. and L. Mahadevan, J R Soc Interface, 2009. 6(39): p. 951-957.
3. Zheng, Y., et al., 2010. 463(7281): p. 640-3.
4. Hamilton, W.J. and M.K. Seely, Nature, 1976. 262(5566): p. 284-285.

Acknowledgments

The authors acknowledge the Associate Laboratories for Green Chemistry – LAQV (UIDB/50006/2020 and UIDP/50006/2020), I.P. (FCT), and Institute of Nanostructures, Nanomodelling, and Nanofabrication – i3N (LA/P/0037/2020, UIDP/50025/2020 and UIDB/50025/2020) which are financed by national funds from FCT/MCTES and Fundação para a Ciência e a Tecnologia, I.P and European Cooperation in Science & Technology (COST) Action: CA21159 - Understanding interaction light - biological surfaces: possibility for new electronic materials and devices (PhoBioS). A. P. C. Almeida is grateful for the financial support from FCT, Portugal, through the research project grant (2022.01619.PTDC) attributed to her.

Development of 3D graphite scaffolds due to carbonization of biomaterial spongin at temperatures up to 2200 °C

M. Kotula [1,2,*], A. Kubiak[1,2], B. Leśniewski [1,2], M. Pajewska-Szmyt [2], H. Ehrlich [2,3]

[1] Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland
[2] Center for Advanced Technologies, Adam Mickiewicz University, 61-614 Poznan, Poland
[3] Institute of Chemical Technology and Engineering, Poznan University of Technology, Poznań, Poland

Abstract:
The idea of fabricating carbon materials with controlled microstructure and morphology, especially at large scales and from renewable natural sources is a current trend in material science. Carbonization of appropriative structural biological materials is one of the directions within extreme biomimetics [1]. One of the biological materials is spongin, the fibrous skeletal proteinaceous composite of sponges belonging to the class Demospongiae (phylum Porifera), which are cultivated worldwide [2]. The sponginous structure is formed by single fibers up to 100 μm thick and composed of nanofibers that interconnect into complex hierarchical 3D networks with high porosity (Fig.1A). Spongin can be converted to carbon at temperatures about 1200°C without loss of its form or structural integrity. Also, its specific surface area has been increased due to the appearance of nanopores, favoring its further functionalization [2]. In this study, for the first time, we carbonized spongin scaffolds (Fig. 1B, 1D) at 2200°C for 1 hour under Ar flow and obtained highly ordered graphite in the form of mechanically stable centimeters-large 3D scaffolds, which represents a groundbreaking step in extreme biomimetics. In the course of the study, a number of advanced methods and techniques were used to characterize the physicochemical and morphological properties of the obtained material. Among them, it is worth mentioning X-ray excited photoelectron spectroscopy (XPS), Raman spectroscopy, microscope imaging - optical, scanning electron microscope (SEM/EDX), and high-resolution transmission electron microscopy (HRTEM).

Keywords: biological material, spongin, carbonization, extreme biomimetics, carbon allotropes

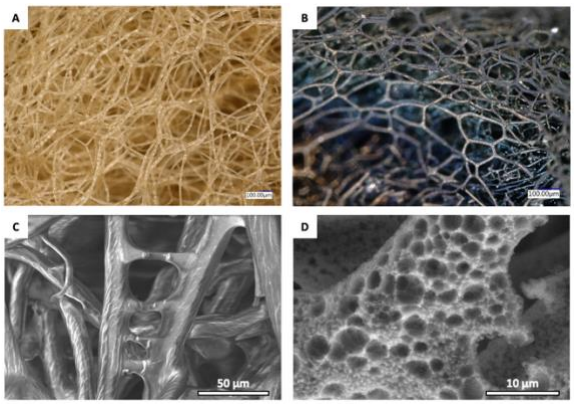


Figure 1: Digital microscopy (A,B) and SEM (C, D) images of typical 3D morphology of sponging isolated from *Hippospongia communis* demosponge prior (A, C) and after carbonization at 2200°C (B, D).

Acknowledgments:
This research was funded by the National Science Centre, Poland within the framework of the project Maestro 12 No. 2020/38/A/ST5/00151

References:

1. Petrenko, I.; Summers, A.P.; Simon, P.; et al. Extreme biomimetics: Preservation of molecular detail in centimeter-scale samples of biological meshes laid down by sponges. Sci. Adv. 2019, 5, 1–12
2. Tsurkan, D.; Simon, P.; Schimpf, C.; Motylenko, M.; Rafaja, D.; Roth, F.; Inosov, D.S.; Makarova, A.A.; Stepniak, I.; Petrenko, I.; et al. Extreme Biomimetics: Designing of the First Nanostructured 3D Spongin–Atacamite Composite and its Application. Adv. Mater. 2021, 33, 30

Marine Spongin-containing Scaffolds for Creation of functional Iron-Based 3D Composite Materials

A. Kubiak [1,2,*], M. Pajewska-Szmyt[2], M. Kotula[1,2], B. Leśniewski[1,2], H. Ehrlich [2,3]
[1] Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland
[2] Center of Advanced Technology, Adam Mickiewicz University, Poznan, Poland
[3]Institute of Chemical Technology and Engineering, University of Technology, Poznan, Poland

Abstract:
In 1968, the initial discovery of crystalline mineral phases of lepidocrocite (γ-FeOOH) forming on the proteinaceos spongin fibres of marine sponges was a groundbreaking observation[1]. This research on iron-based biominerals from marine sponges is compatible with the biomimetics field[2]. The fascinating inquiry that arises is whether the marine sponges could provide a sustainable source of distinct 3D scaffolds, that are apt for the biomineralization of iron ions on their microporous surface.
Recently, an innovative biomimetic methodology was employed to synthesize lepidocrocite on a spongin scaffold in an *in vitro* setting[3]. This research delved into the intricate interplay between iron ions and the spongin scaffold within a corrosive artificial seawater environment, ultimately leading to the pioneering creation of an iron oxide-spongin composite (Figure 1). Furthermore, an extreme biomimetic approach was harnessed to facilitate the assembly of goethite on the spongin scaffold, involving the combination of crystalline iodine and powdered iron with spongin at ambient temperature (Figure 1). Remarkably, these composites exhibited notable stability even following a sonication period of 2 hours.
Additionally, the study elucidated the underlying mechanisms that govern the formation of both iron oxides on spongin fibers. Both composites underwent analysis using instrumental techniques, such as optical microscopy, scanning electron microscopy (SEM/EDX), high-resolution transmission electron microscopy (HRTEM), FTIR, X-ray diffraction, and confocal micro X-ray fluorescence spectroscopy (CMXRF). For the first time we successfully used these 3D composites as sensors for dopamine detection.
This research investigates the overlap between science and nature, revealing new prospects for environmentally friendly materials and creative applications, including sensors, catalysts, and pollutant adsorbents.

Keywords: marine sponge; spongin; lepidocrocite; goethite, biomineralization; biomaterials; biomimetics; extreme biomimetics;

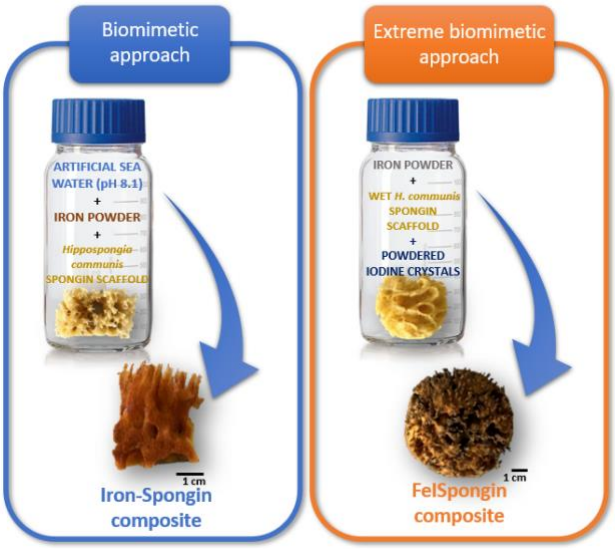


Figure 1: Schematic illustration of the preparation of Iron-Spongin- and FeISpongin-composite materials for the study.

Acknowledgments:
This research was funded by the National Science Centre, Poland within the framework of the project Maestro 12 No. 2020/38/A/ST5/00151

References:

1. Towe, K. M., Rützler, K. (1968) Lepidocrocite Iron Mineralization in Keratose Sponge Granules, *Science*, 162, 268–269.
2. Ehrlich, H., Wysokowski, M., Jesionowski, T. (2022) The philosophy of extreme biomimetics, *Sustain. Mater. Technol.*, 32, e00447.
3. Kubiak, A.; Pajewska-Szmyt, M.; Kotula, M.; Leśniewski, B.; Voronkina, A.; Rahimi, P.; et al. (2023) Spongin as a Unique 3D Template for the Development of Functional Iron-Based Composites Using Biomimetic Approach In Vitro. *Mar. Drugs*, 21, 460.

Slow crack growth resistance of zirconia-hydroxyapatite composites

A.Wojteczko[1],M. Ziąbka[1*]
[1]AGH - University of Krakow, Faculty of Materials Science and Ceramics, Department of Ceramics and Refractory Materials,
al. A. Mickiewicza 30, 30-059 Krakow, Poland
*correspondence:agdudek@agh.edu.pl

Abstract:
ZrO_2/HAp composites are used as materials in implantology due to their biocompatibility and bioactivity. However, it is important to prevent the complete decomposition of hydroxyapatite during the sintering process. To avoid this phenomenon, lower sintering temperatures (up to about 1200°C) are used. To lower the sintering temperature of the entire system, where the tetragonal ZrO_2 was the matrix, powder preparation with small crystal size was necessary. The production of stabilized zirconia powder with yttria (3 mol%) was carried out by co-precipitation using ammonia water, where zirconyl chloride and yttrium oxide dissolved in nitric acid were precursors. This resulted in zirconia gel, which was then placed in an autoclave, where crystal growth occurred (Figure 1). The filtered and washed powder was dried and mixed in two proportions: 80 wt.% ZrO_2 + 20 wt.% HAp and 60 wt.% ZrO_2 + 40 wt.% HAp in a high-energy attritor mill. The compressed samples were sintered at 1150°C. While zirconia matrix provides relatively good strength and fracture toughness, oxide ceramics can undergo subcritical cracking which is crutial parameter in the case of a long-term loading in a humid environment (such as human body). Therefore, it is important to determine slow crack growth parameters and then to estimate lifetime of materials undegoing given conditions. In this research, dynamic method with a constant stress rate was used as a method, which allowed for conducting numerous tests (for reliable statistically results) within a relatively short period of time.

Keywords: ZrO_2/HAp composites, hydroxyapatite, hydrothermal method, subcritical cracking, constant stress rate.

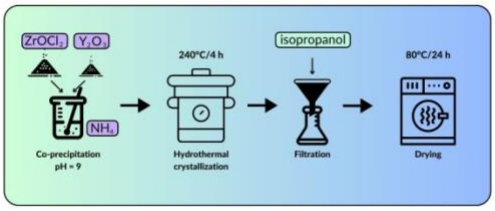


Figure 1: Scheme of the ZrO_2 powder synthesis.

Funding:
This work was supported by program "Excellence Initiative – Research University" for the AGH University of Krakow, grants ID 1449 and ID 4073 (PI - M. Ziąbka).

Optimizing Advanced Implant Surfaces: Employing Composite Coatings of Bioglasses and Antimicrobial Substances for Improved Bone Repair and Enhanced Antimicrobial Protection

Irina Ungureanu (Negut)[1,*], Carmen Ristoscu[1], Valentina Grumezescu[1], Claudiu Hapenciuc[1]
[1]National Institute for Lasers, Plasma and Radiation Physics, 409 Atomistilor Street, 077125 Magurele, Romania
negut.irina@inflpr.ro

Abstract:
To enhance the bioperformance of implant-like surfaces, composite coatings prove to be a desirable option. In this regard, we propose the application of multifunctional composite coatings incorporating bioglass, antimicrobial substances, and polymers tailored for hard tissue applications. Using matrix-assisted pulsed laser evaporation (MAPLE), we deposited a layer of polymeric material onto titanium substrates. Subsequently, MAPLE was employed to apply a second layer of bioglass + antimicrobial substances onto the initial coating. The antibacterial effectiveness of MAPLE-deposited composite coatings was assessed against standard strains of Staphylococcus aureus, Enterococcus faecalis, Escherichia coli, and Pseudomonas aeruginosa. Additionally, the biocompatibility of these coatings was evaluated using mouse osteoblast-like cells. Our study demonstrates that laser-deposited coatings exhibit both biocompatibility and resistance to microbial colonization and biofilm formation, making them promising candidates for biomedical research.

Keywords: bioglass, polymers, antimicrobial, biomedical, laser deposition

Characterization & Degradation of Polymers using Various Scaffold Designs for Use in Critical Size Bone Defects

Samantha Meyr[1,2], Eman Mirdamadi[2], Ryan Smith[1], and Martha O. Wang[1]
[1]Robert E. Fischell Institute for Biomedical Devices, University of Maryland College Park, USA;
[2]Fischell Department of Bioengineering, A. James Clark School of Engineering, University of Maryland, College Park, MD

Abstract:
Critical size bone defect (CSD) treatment options remain a significant clinical orthopedic challenge. Globally there are 150 million fractures annually, of which approximately 100,000 cases result in nonunions costing approximately $2.5 billion. Autografts, the gold standard CSD treatment, are histocompatible and provoke minimal immunogenic response; however, can cause donor site morbidity and cannot suffice for the graft size required. Current treatment options are limited in patient contour, cost, and risks associated with the procedure. Bone tissue engineering is a solution to create customizable 3D scaffolds using biomaterials to promote bone regeneration. Novel scaffolds have been shown to act as a template to the relative extracellular matrix while bone regenerates. Additive manufacturing, specifically through 3D printing, using medically relevant materials including polymers such as polycaprolactone (PCL), poly(lactic) acid (PLA), and acrylonitrile butadiene styrene (ABS) can provide these novel scaffolds for osteogenesis. To evaluate per FDA standards, we evaluated cytotoxicity using L-929 fibroblast cells, as well as the mechanical, and thermal properties of each polymer using various scaffold designs including triangular, honeycomb, and interconnected pores of overlapping squares to determine which would have the potential for optimal bone tissue regrowth.

Keywords: 3D printing, bone tissue engineering, cytotoxicity, degradation, scaffolds

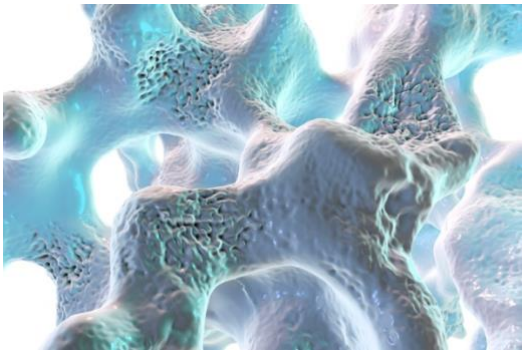


Figure 1: Figure illustrating the fundamental target question that we are attempting to solve experimentally: can we characterize different polymers and designs to determine optimal bone tissue scaffold conditions using low cost procedures such as 3D printing

References:

1. Huang, E., Zhang, N., Goodman, S. *et al.* Novel techniques and future perspective for investigating critical-size bone defects. *Bioengineering*, 9(4): 171. DOI: 10.3390/bioengineering9040171
2. Jahir-Hussain, M *et al.* The effect of pore geometry on the mechanical properties of 3D-printed bone scaffold due to compressive loading. *IOP Conf. Ser.: Mater. Sci. Eng.*, 1051. DOI: 10.1088/1757-899X/1051/1/012016
3. Lopez Reyes, R., Ghim, M., Cho, YS. *et al.* Development and assessment of modified-honeycomb-structure scaffold for bone tissue engineering. *Additive Manufacturing*, 54. DOI: 10.1016/j.addma.2022.102740
4. Mitrin, B. Mechanical properties and failure mechanisms of 3D-printed scaffolds: A preliminary study. *IOP Conf. Ser.: Mater. Sci. Eng.*, 1029. DOI: 10.1088/1757-899X/1029/1/012074

Antibacterial activity and biological response of zirconia based ceramic composites

M. Ziąbka [1*], A.Wojteczko [1]
[1] AGH - University of Krakow, Faculty of Materials Science and Ceramics, Department of Ceramics and Refractory Materials,
al. A. Mickiewicza 30, 30-059 Krakow, Poland
*correspondence:ziabka@agh.edu.pl

Abstract:
In this study, the hydrothermal method was used to synthesize materials of ZrO_2 and ZrO_2 composites that were obtained with varying proportions of bioactive hydroxyapatite (HAp), hexagonal boron nitride (hBN), bioglass (BG), and bioglass containing copper (BGCu). The primary objective of this investigation was to study the influence of incorporation of these bioactive fillers on the biological characteristics of these materials. Specifically, we assessed their antibacterial activity against both Gram-positive and Gram-negative bacteria, as well as their impact on cytotoxicity, cell viability, and the proliferation of fibroblastic and osteoblastic cells in direct contact with sintered samples.
The cytotoxicity of the materials and their effects on cell proliferation were evaluated using Toxilight tests. Additionally, we measured the levels of Reactive Oxygen Species (ROS) generated by these materials. Subsequent examinations through scanning electron microscopy (SEM) and optical microscopy were conducted following cell and bacterial culturing. Our findings indicated that all materials demonstrated a high degree of biocompatibility. However, it is noteworthy that a slight cytotoxicity was observed in the composites modified with HAp and hBN (Figure 1). Furthermore, these same composite materials exhibited notable antibacterial properties against various Gram-positive bacteria and some Gram-negative strains.

Keywords: zirconia composites, antibacterial, proliferation, cytotoxicity, viability.

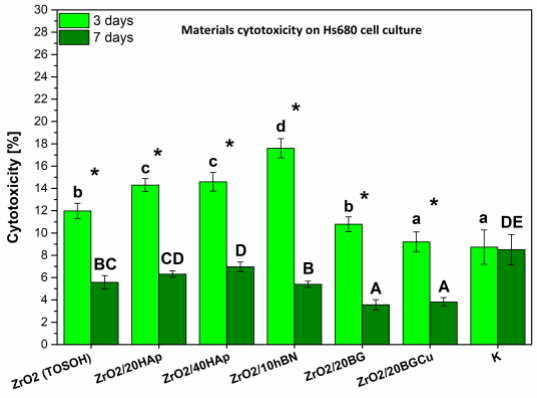


Figure 1: Materials cytotoxicity on Hs680 cell culture.

Founding:

This work was supported by program "Excellence Initiative – Research University" for the AGH University of Krakow, grants ID 1449 and ID 4073 (PI - M. Ziąbka).

Stimuli responsive imine bonds for the green synthesis of antimicrobial-chitosan conjugates

E. Simó-Ramírez[1], R. Heras-Mozos[1], C. López de Dicastillo[1], R. Gavara[1], P. Hernández-Muñoz[1]*
[1] Instituto de Agroquímica y Tecnología de Alimentos (IATA-CSIC), Paterna, Spain.
* Corresponding author: phernan@iata.csic.es

Abstract:
Green synthesis and click-unclick chemistry use effective and efficient procedures to develop materials avoiding the use of organic solvents and unnecessary energy costs. Inside click-unclick systems, the use of dynamic covalent chemistry can be useful to develop active materials with novel properties and functionalities. Several types of covalent bonds can be reversed in response to external stimuli and environmental factors. Among them, imines or Schiff bases (C=N) formed by condensation between carbonyl groups with amino groups are of considerable interest due to their hydrolysis is favoured in acidic medium [1]. This property can be useful in the field of active food packaging for sustained release of highly volatile antimicrobial agents.

In this study, naturally-occurring bioactive aldehydes have been stabilized on the surface of chitosan particles by means of reversible Schiff bases. Imine formation (Figure 1) was carried out using water as solvent without the use of heating, and with reduced reaction times, following the principles of green chemistry. Next, the reversibility of formed imine bonds and subsequent release of the anchored volatile was studied. Chitosan was selected for the condensation of antimicrobial aldehydes due to its high number of amino groups along the polymer chain. Benzaldehyde and trans-2-hexenal were chosen as natural-occurring aldehydes due to their proven antifungal activity. Both aldehydes were successfully grafted onto the amino groups of chitosan particles. The formation of imine bonds was characterized by spectroscopic techniques and quantified by elemental analysis. Different chitosan:aldehyde weight ratios were tested, achieving chitosan substitution degrees of 62 % for benzaldehyde and 54 % for trans-2-hexenal. The reversibility of the imine bond and the release of the immobilized aldehyde were studied by chromatographic and spectrophotometric techniques, showing a higher imine hydrolysis at acidic (pH 2 and 3) than at neutral (pH 7) conditions, and subsequently, a greater aldehyde release. Chitosan particles modified with benzaldehyde presented a complete reversibility of the imine bond, and dissolved at acidic pH. However, the particles modified with trans-2-hexenal showed a small degree of crosslinking preventing their dissolution at acidic pH. In this study, pH-responsive chitosan particles capable of releasing bioactive volatiles have been successfully created. Functionalized particles show considerable potential to be used as smart sustained release systems of volatile antimicrobials and hence, they could be applied on the design of active food packages to increase the shelf-life of postharvest products.

Keywords: green synthesis, imine bonds, antimicrobial-chitosan conjugates, dynamic covalent chemistry, chitosan, reversible Schiff bases, antimicrobial aldehydes, active food packaging.

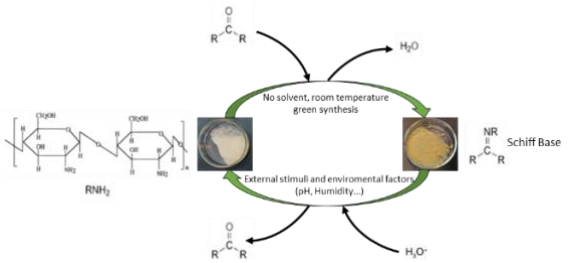


Figure 1: Figure illustrating the reversible Schiff base formation between primary amine groups of chitosan and carbonyl groups of naturally-occurring bioactive aldehydes using a synthesis procedure according to the green chemistry principles.

References:

1. Xin. Y., Yuan, J. Polymer Chemistry, 3, 3045–3055, 2013.

Novel functionalized gold nanoparticles with improved contact-based antimicrobial properties

Martina Žabčić[1,2,*], Lea Gazvoda [1,2], Matjaž Spreitzer[1], Marija Vukomanović[1]
[1] Advanced Materials Department, Jožef Stefan Institute, Jamova 39, Ljubljana 1000, Slovenia
[2] Jožef Stefan International Postgraduate School, Ljubljana 1000, Slovenia

Abstract:
Gold nanoparticles (AuNPs) are used in various applications due to their non-toxicity, stability, and the possibility of functionalization. Surface-finctionalized nanoparticles with cationic amino acids (arginine) show a strong antibacterial effect through non-specific interactions between guanidine functional groups on AuNP and phosphate groups in the bacterial envelope. Therefore, these particles with a contact-based antimicrobial mechanism exhibit great potential for biomedical purposes [1-2]. Here, we present the contact-based antimicrobial effect of new AuNP functionalized with three cationic amino acids (arginine, lysine, and histidine) on doped hydroxyapatite as a template. The characterization of prepared samples was done by X-ray diffraction (XRD), ultraviolet–visible spectroscopy (UV-Vis), electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR), while antimicrobial properties were determined by bacterial growth kinetics and serial dilutions agar plate test. Prepared nanoparticles have been tested against different strains of bacteria (*E. coli*, *P. aeruginosa*, *B.subtilis*, and *S. epidermidis*) in order to compare their antimicrobial effects on gram-positive and gram-negative bacteria. They showed inhibition of bacterial growth, or a complete bactericidal effect (Figure 1). It has been noticed that when three amino acids are present, particles exhibit better antimicrobial properties than in the case of only one. Finally, interesting information about the size and morphology of the particles using transmission electron microscopy (TEM) was obtained.

Keywords: Functionalized gold nanoparticles, cationic amino acids, hydroxyapatite, contact-based antimicrobials.

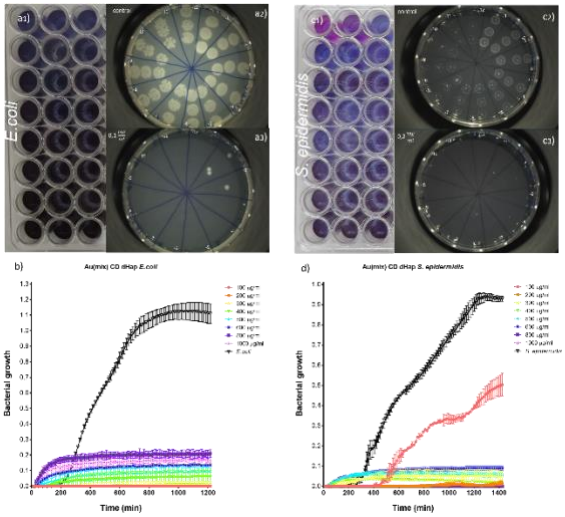


Figure 1: Figure illustrates antimicrobial activity of arginine/histidine/lysine functionalized gold nanoparticles against *E.coli* and *S.epidermidis*: serial dilutions agar test (a_{1-3}, c_{1-3}), and bacterial growth kinetics (b, c) in *E.coli*, and *S.epidermidis*, respectively.

References:

1. Vukomanovic M. *et al*. (2021) Nano-engineering stable contact-based antimicrobials: Chemistry at the interface between nano-gold and bacteria, *Colloids and Surfaces B: Biointerfaces*, 208, 112083.
2. Vukomanovic M. *et al*. (2022) Development of a ternary cyclodextrin–arginine–ciprofloxacin antimicrobial complex with enhanced stability, *Communications Biology*, 5, 1234.

Poly(alkylene citrate) (PAC) and PAC-based materials as novel promising candidates for vascular graft production

Lucie Svobodová[1]*, Filip Koper[2], Agata Flis[3], Martina Trávníčková[1], Elżbieta Pamuła[3], Lucie Bačáková[1], Wiktor Kasprzyk[2]

[1] Dept. of Biomaterials and Tissue Engineering, Institute of Physiology of the Czech Academy of Sciences, Prague, Czech Republic
[2] Dept. of Biotechnology and Physical Chemistry, Cracow University of Technology, Cracow, Poland
[3] Dept. of Biomaterials and Composites, AGH University of Science and Technology, Cracow Poland

Abstract:
We have focused on materials for blood vessel substitutes of small diameter (< 6 mm). Materials suitable for this purpose must be well-biocompatible and non-toxic, non-thrombogenic and non-immunogenic, biodegradable within the adequate time window, must have mechanical properties matching those of natural tissues, and their production should be economically viable. It seems that our newly-developed poly(alkylene citrate)-based materials (PAC) fulfill each of these conditions. We have tested two types of PAC: cPOC, i.e. cross-linked poly(1,8-octamethylene citrate) [1] and cPHC, i.e. cross-linked poly(1,6-hexamethylene citrate) [2].

Oxidative stress is one of the major cardiovascular problems, thus an antioxidative action would be an advantageous property of grafts. For this reason, we modified PACs with glutathione (GSH, antioxidative agent) in four different concentrations (0, 0.4, 0.8 and 1.6 % w/w).

The efficacy of material cross-linking and its potential alteration by GSH were studied using solid-state nuclear magnetic resonance (ssNMR). Further analysis has shown the nature of the compound formed during the synthesis of cPACs and responsible for the antioxidative activity and fluorescence as the additional property of materials that is possible to use especially during *in vivo* testing of materials.
For testing biocompatibility, i.e. the adhesion and proliferation of cells, we used cell types relevant for vascular tissue engineering i.e. human adipose-derived stem cells (ASCs), normal human dermal fibroblasts (NHDFs), human umbilical vein endothelial cells (hUVECs) and human umbilical artery smooth muscle cells (SMCs).

Keywords: poly(alkylene citrate), poly(hexamethylene citrate), poly(octamethylene citrate), glutathione, vascular grafts, biocompatibility

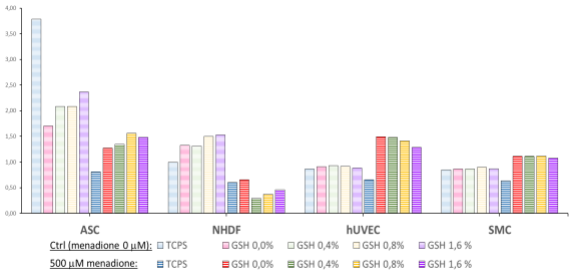


Figure 1: Figure illustrating antioxidative action of cPHC (2:3) with several concentrations of glutathione used for material preparation hence increasing the ability of especially endothelial cells (hUVEC) and smooth muscle cells (SMC) to survive in free radical enriched environment induced by 500 µM menadione (vitamin K3). Resazurin metabolic assay.

References:

1. Flis, A.; Trávníčková, M.; Koper, F.; Knap, K.; Kasprzyk, W.; Bačáková, L.; Pamuła E. (2023) Poly(octamethylene citrate) Modified with Glutathione as a Promising Material for Vascular Tissue Engineering, *Polymers*, *15*, 1322 - 1337.
2. Koper, F., Świergosz, T., Żaba, A., Flis, A., Trávníčková, M., Bačáková, L., Pamuła, E., Bogdał, D., Kasprzyk, W. P. (2021**)** Advancements in structure–property correlation studies of cross-linked citric acid-based elastomers from the perspective of medical application. *J. Mater. Chem. B***,** 9, 6425 - 6440.

Acknowledgments:
Co-funded by the European Union (grant No. CZ.02.01.01/00/22_008/0004562) and Polish National Science Centre (SONATINA, grant No. UMO-2018/28/C/ST5/00461).

The Role of Manganese in the Evolution of Calcium Phosphate Bioceramics

Bożena Tyliszczak, Dagmara Słota, Karina Niziołek, Julia Sadlik, Agnieszka Tomala, Agnieszka Sobczak-Kupiec

Cracow University of Technology, Faculty of Materials Engineering and Physics
Department of Materials Engineering, Cracow, Poland

Abstract:
In recent years, significant progress in biomaterial engineering has been focused on the modification of hydroxyapatite (HAp), the main mineral component of bone, to enhance its properties and broaden its applications. This study centers on doping HAp with manganese (Mn) to explore the effects of this modification on the material's structure, biocompatibility, and mechanical and antibacterial properties. Manganese was selected for its potential osteostimulative properties and ability to improve parameters related to cell adhesion and bone tissue growth. Research has indicated that an appropriate concentration of manganese can significantly enhance the biological and mechanical properties of hydroxyapatite, opening new avenues in bone tissue regeneration and other biomedical applications.

For a comprehensive understanding of the action mechanisms, a phase, morphological, and chemical analysis of the modified hydroxyapatite was conducted. Advanced microscopic techniques such as Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were employed to reveal subtle changes in the crystal structure and surface topography of HAp post-manganese doping. These analyses demonstrated that introducing manganese could induce changes in the size and shape of grains, which directly impacts the material's mechanical properties and resorption rate.

Conclusions from the study underscore that modification of hydroxyapatite by doping with manganese is a promising technique that can significantly improve the properties of biomaterials and expand their application in regenerative medicine and implantology. Continuing this research could lead to the development of new generations of implants that will further enhance bone healing and regeneration.

Keywords: hydroxyapatite (HAp), manganese doping, biomaterials engineering, regenerative medicine

Acknowledgments

Project “Hierarchical approaches for osteochondral tissue engineering”. This research was funded in whole by National Science Centre, Poland, grant no. UMO-2022/45/B/ST8/02557.

References:

1. Lee, H.W., Knowles, J.C., Kim, H.W. (2015). Manganese-based degradable bioactive materials for bone tissue engineering. J. Tissue Eng. 6(1).
2. Wei, J., Igarashi, T., Okumura, Y., Matsuda, S., Ohtsuki, C. (2017). Effects of manganese on the structure and mechanical properties of hydroxyapatite. JCS-Japan, 125(10), 824-828.
3. Li, J., Zhang, X., Huang, Y., Wang, J., Zhang, L., Hu, Q. (2020). Manganese-Doped Calcium Phosphate Bioceramics with Enhanced Antibacterial Activity and Cytocompatibility. ACS Biomater. Sci. Eng., 6(1), 260-270.
4. Hou, Z., Li, X., Zhao, Q., Zhang, W., Qiao, Y., Yuan, W. (2018). Fabrication and characterization of manganese-doped calcium phosphate coatings on magnesium alloy for biomedical applications. Mater. Sci. Eng. C ., 92, 646-653.Montoneri, F., Montoneri, E., Boffa, V., Sharts, O. (2011), Protein helical structure enhancement in fluorinated-phosphonate nanoporous silica glasses characterized by circular dichroism spectroscopy, *Int. J. Nanotech*., 8, 471-491.

Polymer - Ceramic Composites Enriched in Silk Fibroin For Osteochondral Applications

Agnieszka Sobczak-Kupiec, Dagmara Słota, Karina Niziołek, Dominika Trager, Bożena Tyliszczak

Cracow University of Technology, Faculty of Materials Engineering and Physics
Department of Materials Engineering, Cracow, Poland

Abstract:
A major hurdle in treating osteochondral defects is the different healing abilities of two types of tissues involved - articular cartilage and subchondral bone. Biomimetic approaches to OC-construct engineering, based on recapitulation of biological principles of tissue development and regeneration, have potential for providing new treatments and advancing fundamental studies of OC tissue repair. The overall goal of the investigation is to design a new hierarchal, gradient composite biomaterial based on biopolymer matrix contains incl. structural protein (i.e. silk fibroin) and CaPs with enhanced properties, which could be used for surgical implants.

Its aim was to determine the physicochemical properties of composite materials containing silk fiber fibroin (2%), tricalcium phosphate, PEGDA (polyethylene glycol diacrylate) and a photoinitiator (2-hydroxy-2-methylpropiophenone). Physicochemical analyzes were carried out and the swelling coefficient was determined, pH and conductometric measurements, SEM microscopic analysis and FTIR spectroscopy measurements were made. Incubation was carried out in Ringer's solution and PBS solution.

It has been shown that the composition of the produced composites affects their physicochemical properties, such as stability, sorption and conductivity in conditions determined by the solutions in which they were incubated. This constitutes a good basis for continuing research into the use of composite materials in the field of tissue engineering.

Keywords: hydroxyapatite (HAp), silk fibroin, composites,

Acknowledgments
Project "Hierarchical approaches for osteochondral tissue engineering". This research was funded in whole by National Science Centre, Poland, grant no. UMO-2022/45/B/ST8/02557.

References:

1. N. Bustamante-Hernández, J. Montiel-Company, C. Bellot-Arcís, J. Mañes-Ferrer i M. Solá-Ruíz, „Clinical Behavior of Ceramic, Hybrid and Composite Onlays. A Systematic Review and Meta-Analysis," International Journal of Environmental Research and Public Health, 2020 Lee,
2. H.W., Knowles, J.C., Kim, H.W. (2015). Manganese-based degradable bioactive materials for bone tissue engineering. J. Tissue Eng. 6(1).
3. G. Kumar i S. Mohanty, „Hydroxyapatite: A Versatile Bioceramic for Tissue Engineering Application," Journal of Inorganic and Organometallic Polymers and, 2022.
4. V. Irawan, T. Sung, A. Higuchi i T. Ikoma, „Collagen Scaffolds in Cartilage Tissue Engineering and Relevant Approaches for Future Development,"Tissue Eng Regen Med., 2018.
5. C. Wilson, R. Clegg, D. Leavesley i M. Pearcy, „Mediation of Biomaterial–Cell Interactions by Adsorbed Proteins: A Review," Tissue Engineering, 2005.
6. W. F. Daamena, J. H. Veerkampa, J. van Hestb i T. H. van Kuppevelt, „Elastin as a biomaterial for tissue engineering," Biomaterials, 2007.
7. A. R. Amini, C. Laurencin i S. Nukavarapu, „Bone Tissue Engineering: Recent Advances and Challenges," Crit Rev Biomed Eng, 2013
8. A. Nikodem i K. Ścigała, „Impact of some external factors on the values of mechanical parameters determined in tests on bone tissue," Acta of Bioengineering and Biomechanics, tom 12, nr 3, pp. 85-93, 2010.

Tissue-Engineered Tri-leaflet Valved Stents on Biodegradable Poly-ε-Caprolactone Scaffolds

M. Saeid Nia [1,2], J. A. Seiler [1,2], G. Lutter [1,2]

[1] Department of Cardiovascular Surgery, University Hospital Schleswig-Holstein (UKSH), Kiel, Germany
[2]DZHK (German Centre for Cardiovascular Research), Partner Site Hamburg/Kiel/Lübeck, Hamburg, Germany

Abstract:
Heart valve replacement is an essential medical intervention for patients with heart valvular disease. However, despite their progress, heart valve prostheses are still associated with limitations. Contrary to the available options, tissue-engineered heart valves are promising substitutions, especially in pediatric patients[1]. The latter is facilitated through engineering new and fully functional tissue by the cultivation of appropriate cells on optimized biological scaffolds. The scaffold is the main component that provides a platform for cells and growth factors and contributes to its mechanical properties and stability. Therefore, scaffolds play an important role in the enhancement of cell attachment and proliferation[2]. In this study, poly-ε-caprolactone (PCL) nanofiber scaffolds were used to generate tissue-engineered heart valves and a 3D leaflet matrix. They were seeded with human endothelial colony-forming cells (ECFCs), human induced pluripotent stem-cell-derived mesenchymal stem cells (iMSCs), and porcine MSCs (pMSCs). Fluorescence microscopy and SEM were used to analyze cell adhesion, proliferation, and distribution. Both EFCFs and MSCs cells showed good distribution and adhesion on PCL fibers, forming a closed cell cover already evident after 14 days for ECFCs and 21 days for MSCs. Besides, irrespective of the cell type used, more than 90% of valve leaflets were entirely covered with cells across nearly all leaflet areas at the end of the full three-week culturing cycle. The mechanical properties of seeded PCL scaffolds were investigated and compared with native porcine pulmonary valve leaflets under uniaxial loading. There were no significant differences between Young's modulus and mean elongation at F_{max} of unseeded and seeded PCL scaffolds in comparison to those of native leaflets. The successful colonization of a biodegradable PCL nanofiber matrix with human ECFCs and iMSCs demonstrated in this study, presented a promising candidate for the generation of tissue-engineered heart valves.

Keywords: Heart valve tissue engineering, iMSCs, ECFCs, pMSCs, PCL nanofibers, biodegradable scaffold

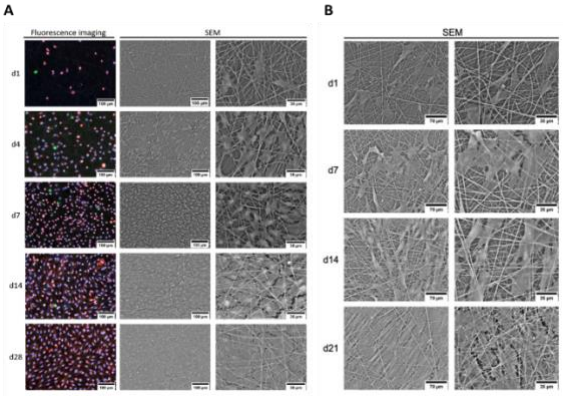


Figure 1: Representative fluorescence and scanning electron microscopy (SEM) images of the morphology of the growth of ECFCs (A) and MSCs (B) on uncoated PCL fibers for up to 28 days (A) or 21 days (B) (Figures were adopted from Lutter et al., 2022).

References:

1. Haupt, J., Lutter, G., Gorb, S.N., Simionescu, D.T., Frank, D., Seiler, J., Paur, A., Haben, I. (2018), Detergent-based decellularization strategy preserves macro- and microstructure of heart valves. Interactive CardioVascular and Thoracic Surger Interact Cardiovasc Thorac Surg, 26, 230–236.
2. Soltani Khaboushan, A., Shakibaei, M., Kajbafzadeh, A.-M., Majidi Zolbin, M. (2022), Prenatal neural tube anomalies: a decade of intrauterine stem cell transplantation using advanced tissue engineering methods. Stem Cell Rev Rep 18, 752–767.
3. Lutter, G., Puehler, T., Cyganek, L., Seiler, J., Rogler, ., Herberth, T., Knueppel, P-, Gorb, S. N., Sathananthan, J., Sellers, S., Müller, O. J., Frank, D., Haben, I. (2022), Biodegradable poly-ε-caprolactone scaffolds with ECFCs and iMSCs for tissue-engineered heart valves. Int J Mol Sci., 4, 23:527.

Silver nanoparticle as therapeutic options to fight the resistome, mobilome and virulome of multidrug resistant *Acinetobacter baumannii* circulating clones in South Romania

I. Gheorghe-Barbu[1,2], I. Czobor Barbu[1,2], V.M. Corbu[2,3], A-Ș. Dumbravă[1], D-M Găboreanu[1], G.-A Grigore[1], C.O. Vrâncianu[2], M. Surleac[4], S. Paraschiv[4], D. Oțelea[4], D. Ficai[5], A. Ficai[5], M.C. Chifiriuc[1,2,6]

[1]Department of Microbiology and Botany, Faculty of Biology, University of Bucharest, Bucharest, Romania,

[2]Research Institute of the University of Bucharest, University of Bucharest, Bucharest, Romania,

[3]Department of Genetics, Faculty of Biology, University of Bucharest, Bucharest, Romania,

[4] National Institute of Infectiosus Diseases ,,Matei Bals'', Bucharest, Romania

[5]National University of Science and Technology Politehnica Bucharest, Romania

[6]Romanian Academy of Scientist, Bucharest, Romania

Abstract:

Acinetobacter baumannii (AB) is recognized as serious opportunistic nosocomial pathogen, due to their high number of resistance determinants to antibiotics, biocides as well as virulence markers (VMs) (1).

We aim to demonstrate the potency of silver nanoparticles (AgNPsol) as therapeutic options against multidrug resistance (MDR) AB isolated four years consecutively from intra-hospital infections (IHI), hospital sewage (Hs) wastewater treatment plants (WWTPs) and surface water samples (SWs) from two geographical locations [Târgoviște (T) and Râmnicu Vâlcea (VL)] in South Romania.

AgNPsol synthesized by solvothermal method (2) were investigated for their antimicrobial and anti-biofilm activity through qualitative and quantitative methods on a total number of 183 AB strains isolated in the same temporal sequence from IHI, Hs, WWTPs and SWs from two South Romanian locations and characterized at phenotypic and genotypic level throught disc diffusion, chromogenic methods and subjected to whole genome sequencing (WGS, Illumina and MinION, Nanopore).

The comparative analysis of the MDR level to 5-7 antimicrobial agents (aminoglicosides, carbapenems, quinolones, cephalosporins, β-lactam inhibitors, tetracyclines) according to the isolation source and the geographical location in decreasing order corresponded to $WWTP_{2019}T>WWTP_{2020}T>Hs_{2020}VL>WWTP_{2021}T=SW_{2019}T=WWTP_{2020}VL=WWTP_{2021}VL>SW_{2020}T>Hs_{2019}T>$ (20/18/13/9/6/4 %). AB strains belonged to ten phylogenetic groups in different isolations sources in T and VL: **ST2**-*bla*$_{OXA-66}$; *bla*$_{OXA-23}$; *bla*$_{ADC-30}$; *bla*$_{ADC-73}$; *bla*$_{TEM-1}$ (IHI T; VL, Hs T, WWTP T; VL, SW T; VL); **ST636**-*bla*$_{OXA-66}$; *bla*$_{OXA-72}$; *bla*$_{ADC-74}$ (IHI T; VL, Hs VL, WWTP T; VL, SW T; VL); **ST1**-*bla*$_{OXA-66}$; *bla*$_{OXA-23}$; *bla*$_{OXA-72}$; *bla*$_{OXA-92}$; *bla*$_{ADC-30,74,81}$; *bla*$_{TEM-1}$ (Hs VL, WWTP T;VL,); **ST79**-*bla*$_{OXA-65}$; *bla*$_{OXA-23}$; *bla*$_{OXA-72}$; *bla*$_{ADC-5}$; *bla*$_{TEM-1}$ (WWTP T, SW T); **ST150**-*bla*$_{OXA-121}$; *bla*$_{ADC-163}$ (SW T); **ST10**-*bla*$_{OXA-68}$; *bla*$_{ADC-76}$ (SW T); **ST154**-*bla*$_{OXA-69}$; *bla*$_{ADC-160}$ (WWTP T); **ST113**-*bla*$_{OXA-64}$; *bla*$_{ADC-57}$ (WWTP T); **ST33**-*bla*$_{OXA-64}$; *bla*$_{ADC-57}$ (SW VL); **ST858**- *bla*$_{OXA-23}$; *bla*$_{OXA-51}$; *bla*$_{ADC-79}$ (WWTP VL) associated with the presence of VMs encoding for adherence, biofilm formation, immune modulation, nutrition, regulation, exotoxins and delivery systems. OXA-23 was chromosomally located while OXA-72 was linked to pMAL1 and pA105-like plasmids types. The qualitative screening of the antimicrobial activity of AgNPsol demonstrated the efficiency against the growth of all tested AB strains with different potency (56% of AB strains for arbitrary unit identification 2 and respectively 44% of the strains for arbitrary unit identification 1). The quantitative evaluation of the antimicrobial efficiency of Ag NPsol against AB strains revealed that the most susceptible were AB isolated in 2020 and 2021 from WW of the two locations (6.5 µg/mL). AB isolated showed high potential for biofilm development.

An additional step was provided towards understanding the mechanisms by which AgNPsol interfere with the AB persistence and spread.

Keywords: multidrug resistance; hight risk clones; antropically poluted water environments; silver nanoparticles, antimicrobial activity.

Funding
We acknowledge the financial support of PN-III-P1-1.1-TE-2021-1515 (TE112/2022), PN-III-P2-2.1-PED-2021-2526 (736 PED/2022), PN-III-P1-1.1-PD-2021-0540 (PD102/2022) and COFUND-AQUATIC POLLUTANTS-BIOCIDE (ERANET 243/2021) research projects awarded by The Romanian Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI).

References:

1. Lima, W.G.; Brito, J.C.M.; Cruz Nizer, W.S. Ventilator-Associated Pneumonia (VAP) Caused by Carbapenem-Resistant *Acinetobacter baumannii* in Patients with COVID-19: Two Problems, One Solution? *Med. Hypotheses* **2020**, *144*, 110139,
2. Corbu VM, Dumbravă AȘ, Marinescu L, Motelica L, Chircov C, Surdu AV, Gheorghe-Barbu I, Pecete I, Balotescu I, Popa M, Marinas IC, Ianovici N, Ciobanu D-G, Dițu LM, Ficai D, Oprea OC, Ficai A, Eugenia Șesan T and Chifiriuc MC (2023), Alternative mitigating solutions based on inorganic nanoparticles for the preservation of cultural heritage. Front. Mater. 10:1272869.

Inorganic nanoparticle-based multifunctional coatings for the preservation of Romanian cultural heritage objects

A.Ş. Dumbravă[1,2], I. Gheorghe-Barbu[1,3], V.M. Corbu[3,4], D.M. Găboreanu[1,3], I.C. Marinaș[3], I. Pecete[5], D. Ficai[6], A. Ficai[6], M.C. Chifiriuc[1,3,7] , T.E. Șesan[1,8]

[1] Department of Microbiology and Botany, Faculty of Biology, University of Bucharest, Bucharest, Romania

[2] Department of Technological Irradiation (IRASM), Horia Hulubei National Institute of Physics and Nuclear Engineering–IFIN-HH, Măgurele, Romania

[3] Research Institute of the University of Bucharest, University of Bucharest, Bucharest, Romania

[4] Department of Genetics, Faculty of Biology, University of Bucharest, Bucharest, Romania

[5] Central Reference Synevo-Medicover Laboratory, Bucharest, Romania

[6] National University of Science and Technology Politehnica Bucharest, Bucharest, Romania

[7] Academy of Romanian Scientist, Bucharest, Romania

[8] Romanian Academy of Agricultural and Forestry Sciences, Bucharest, Romania

Abstract:

The diversity and richness of human civilization depend on the preservation of cultural heritage, furthermore, the development of effective strategies to prevent the contamination of cultural heritage objects by biodeteriogenic microorganisms has become a priority (1). To increase the applicability of Cu, ZnO, and Ag nanoparticles (NPs), this study evaluated the antimicrobial efficiency of NPs when applied to silanized materials, using wood as a study material model.

Fragments with an area of 1 cm^2 of wood were selected as a study model, treated with two types of silanized materials (triethoxysilane, APTES and Silane SH) and NPs, and used to determine the antimicrobial and antibiofilm efficiency, respectively the impact on the capacity of the microbial strains (*Penicillium chrysogenum*, n=2; *Bacillus cereus* and *B. megaterium*) to secrete extracellular enzymes and organic acid involved in the degradation of cultural heritage objects.

The results showed that treated materials coating with Cu, ZnO, and Ag NPs solutions maintained the antimicrobial activity of the NPs, lowering the viability of deteriogenic microorganisms after direct contact (Figure 1 A-B). Additionally, the applied treatment prevents the adherence capacity of the strains to the material's surface, highlighting its function in avoiding microbial biofilm development (Figure 1 C). The impact of the NP solutions used to treat the wood materials varied depending on the tested strain and the extracellular products (enzymes or organic acids) secreted.

The obtained results demonstrate that the silanized materials with Cu, ZnO, Ag NPs can be used to optimize innovative strategies for cultural heritage preservation.

Keywords: cultural heritage objects, biodeterioration, enzyme/organic acid production, nanoparticles, antimicrobial activity, antibiofilm activity.

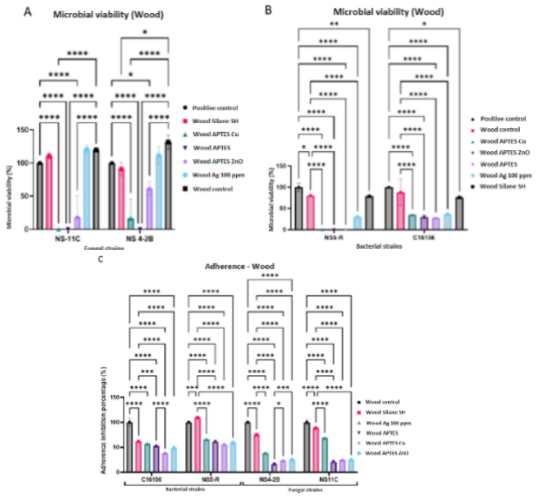


Figure 1: Viability of the microbial strains in the presence of wood materials treated with NPs (A: *P. chrysogenum* NS11-C and *P. chrysogenum* NS4-2B; B: *B . cereus* C16156 and *B. megaterium* NS5-R). C) Graphic representation of the inhibitory effect of wood materials on the adherence capacity of bacterial strains and fungal strains.

References:

1. Cappitelli, F., Cattò, C., & Villa, F. (2020). The control of cultural heritage microbial deterioration. *Microorganisms*, 8(10), 1542.

Funding

The financial support of the Research Project PN-III-P2-2.1-PED-2021-2526 (736 PED/2022) awarded by The Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI), C1.2.PFE-CDI.2021-587 (41PFE/30.12.2021) and CNFIS-FDI-0609/2023 are acknowledged.

Biomechanical and Morphological Evaluation of Cryopreserved Porcine Tissues

M. Casarin [1,*], M. Todesco [2], C.G. Fontanella[3], A. Morlacco[1], F. Dal Moro[1], L. Astolfi[4] and A.Bagno[3]
[1] Department of Surgery, Oncology and Gastroenterology, University of Padua, Padua, Italy
[2] Department of Civil, Environmental and Architectural Engineering, University of Padua, Padua, Italy
[3] Department of Industrial Engineering, University of Padua, Padua, Italy
[4] Department of Neuroscience, University of Padua, Padua, Italy

Abstract:
Cryopreservation allows supplying ready-to-use biological substitutes; after *in vivo* implantation, they have the advantage to provide proper biochemical signals to the host cells thanks to the growth factors present in the extracellular matrix (ECM), thus fostering tissue regeneration. The overall quality of these substitutes largely depends on the possibility to conveniently cryopreserve and store them to provide scaffolds ready for implantation [1]. To check possible effects of cryopreservation on the integrity of biological substitutes, different porcine tissues (i.e., pericardium, ureter, descending aorta and small intestinal submucosa SIS) were treated with a solution composed by 10% dimethyl sulfoxide (DMSO) and 10% Fetal Bovine Serum (FBS) in Dulbecco's Modified Eagle Medium (DMEM) high glucose, and then stored at -80°C for 1.5-4.5 months. Tissues morphology and mechanical behavior were assessed. Tissue samples were dehydrated, paraffin embedded and Hematoxylin and Eosin (HE), Masson's Trichrome (MT) and Alcian Blue (AB) stainings were performed to evaluate ECM maintenance. Mechanical uniaxial tensile tests were carried out by elongating dog bone-shaped specimens until rupture (v=0.2mm/s) after 10 cycles of preconditioning at increasing deformations (10%, 20%, 30%, 40%, and 50%). From the stress vs. strain curves, Ultimate Tensile Strength (UTS) and Failure Strain (FS) were calculated as maximum resistance and maximum elongation reached by each sample; the Young's modulus (E) was calculated as the slope of the curve in the linear region.
The microscopic appearance of the investigated tissues was not affected by the cryopreservation treatment, as demonstrated by HE, MT and AB stainings, with collagen and glycosaminoglycans maintenance, respectively. As to the mechanical response (Figure 1), no significant difference was found in any tissue before and after cryopreservation in terms of UTS, while in the case of FS statistical differences were detected for native porcine pericardium (NPP) and SIS along the longitudinal direction. Lastly, regarding E, a statistical difference was exhibited by SIS along the circumferential direction.
In conclusion, the cryopreservation procedure did not affect the micro/macro tissue morphology, as demonstrated by histological analyses and mechanical tests. Further studies will be performed in order to investigate possible DMSO residues in the matrix and to assess the influence of cryopreservation on cells-ECM interactions.

Keywords: Cryopreservation, biological tissues, biomechanics, biomaterials

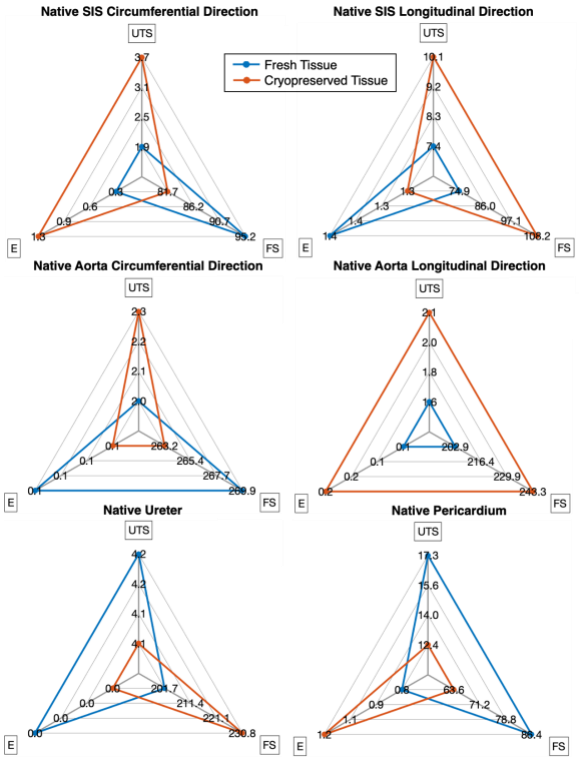


Figure 1: Mean values of biomechanical parameters of porcine tissues (UTS [MPa], FS [%] and E [MPa]).

References:

1. Arutyunyan, I., Elchaninov, A. (2022) Cryopreservation of Tissue-Engineered Scaffold-Based Constructs: from Concept to Reality, *Stem Cell Reviews and Reports,* 18:1234–1252.

Understanding cell-matrix interactions between primary neurons and breast tumor cells in a brain-like 3D microenvironment

E. Türker[1,*], J. Faber[2], M.S. Andrade Mier[1], N. Murenu[1], P. Stahlhut[3], G. Lang[3], S. Budday[2], N. Schaefer[1], P.Strissel[4, 5], R.Strick[4], C.Villmann[1]
[1]Institute of Clinical Neurobiology, University Hospital Würzburg, Germany
[2]Institute of Continuum Mechanics and Biomechanics, FAU of Erlangen-Nürnberg, Germany
[3]Department for Functional Materials in Medicine and Dentistry, University Hospital Würzburg, Germany
[4]Department of Gynecology and Obstetrics, Laboratory for Molecular Medicine, University Hospital Erlangen, Germany,
[5]Institute of Pathology, University Hospital Erlangen, FAU of Erlangen-Nürnberg, Germany

Abstract:
Cells are embedded in highly dynamic aqueousmicroenvironment containing, fibrous proteins and many other biochemical substances that facilitate cellular functions.[1] This three dimensional (3D) macromolecular environment with a distinct porosity is called the extracellular matrix (ECM) providing biophysical strength and biochemical stimuli for cell-matrix interactions, cell-cell communication, migration, proliferation and differentiation. Every tissue contains a specific composition of ECM proteins. Under disease conditions such as cancer, changes in structural and biochemical properties may alter the stiffness, signalling processes, cellular migration, and tumor progression. Triple negative breast cancer (TNBC) is one of the malignant subtypes of cancer which has a 46% incidence rate of brain metastasis.[2] The breast tumor overexpresses fibronectin, collagen and hyaluronic acids (HA) during progression. On the other side, a normal brain ECM harbours less fibrous proteins instead it has a hyaluronic acid rich environment. Therefore, we investigate the growth and proliferation behavior of tumor cells when exposed to different environments and how breast tumor cells interact with brain cells? Recent studies have shown that breast tumor cells form pseudo-synaptic contacts with neurons resembling glutamatergic synapses.[3] First, we focused on cell-matrix interactions and characterized hydrogel porosities suitable for tumor cell growth as well as consequences of hydrogel stiffness for cell proliferation (Figure 1). Based on cell-matrix interactions, we are further working on a 3D disease model to study the consequences of the implemented matrix on cell-cell interactions of breast tumor cells with neurons and astrocytes of the brain.

Keywords: extracellular matrix, 3D cell culture, breast tumor, biomaterials, scaffolds, stiffness

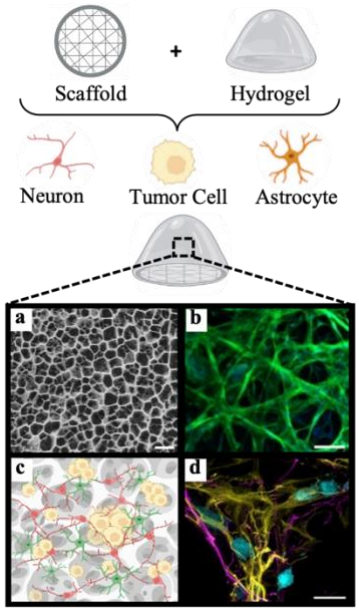


Figure 1: Schematic illustration of cellular distribution and interaction within a 3D scaffold reinforced hydrogel. a) Cryo-SEM image of a porous hydrogel, b) tumor cells behaviour on scaffold, c, d) interactions of neuronal cells with tumor cells (blue: breast tumor cells, yellow: astrocytes, magenta: neurons. Scale bar: 2µm, 20µm and 100µm)

References:

1. Frantz, C., Stewart, M. K, Weaver, M. V. (2010) The extracellular matrix at glance, *Journal of Cell Science* 123, 4195-4200.
2. Lv, Y., Ma, X., Du, Y., Feng, J. (2021) Understanding Patterns of Brain Metastasis in Triple-Negative Breast Cancer and Exploring Potential Therapeutic Targets, *Onco Target and Therapy*,14, 589-607.
3. Zeng, Q., Michael, I.P., Zhang, P., Saghafinia, S., Knott, G., Jiao, W. J., Galvan, J.A., Robinson, H.P.C., Zlobec, I., Ciriello, G., Hanahan, D. (2019) Synaptic Prixmity enables NMDAR signalling to promote brain metastasis, *Nature*, 573, 526-531.

Using Biosurfactant Molecules for hydrocarbon desorption from solid surfaces: A Molecular Dynamics Study

A. B. Salazar-Arriaga [1,], H. Dominguez [1*]
[1] Material Research Institute, Universidad Nacional Autónoma de México, Cd. México, C.P 04510, México.

Abstract:
Previous computer simulation works, using synthetic surfactants, have proved their capacity to desorb alkane molecules from solid surfaces. In the present paper, we use environmentally friendly surfactants, biosurfactants, to investigate their effectiveness in desorption of hydrocarbons from a dolomite surface. Molecular simulations are carried out for the biosurfactant, called surfactin, on a mixture of hydrocarbon molecules deposited on the solid surface forming a layer structure. Different concentrations of the surfactin were tested and it was observed that in all cases the surfactant headgroups are located within the aqueous phase while the surfactant tails are close to the hydrocarbon molecules, i.e., the desorption occurs by the surfactant tails. The results are compared with simulations of the same system, dolomite/hydrocarbons, using synthetic surfactants such as the sodium dodecyl sulfate (SDS). The analysis is given in terms of density profiles along the normal of the solid/oil/water interface, pair correlation functions and adsorption isotherms. Additionally, a mixture of both surfactants was prepared at different compositions, to find an optimal concentration to see desorption. The results indicate that the mixture presents better contaminant removal from the dolomite surface than the single surfactants. The results show how biosurfactants can be used as a different alternative to desorb contaminant from solid surfaces

Keywords: Molecular dynamics, biosurfactants, synthetic surfactants, hydrocarbon desorption, dolomite surface.

References:

1. Salazar-Arriaga, A. B., Dominguez, H. (2022), Electric Fields Applied to Surfactant Molecules for Enhancing Removal of Hydrocarbons from a Solid Surface: A Molecular Dynamics Study, *Phys. Chem. C.*, 126, 11761-11768.
2. Salazar-Arriaga, A. B., Dominguez, H. (2020), Decane structure on a graphite surface with sodium dodecyl sulfate and betaine surfactant mixtures: A molecular dynamics study, Chem. Phys., 539, 110945.

Polyvinyl caprolactam polyvinyl acetate-polyethylene glycol grafted copolymer as an excellent solubility enhancer of apigenin and its neuroprotective potential

A. Stasiłowicz-Krzemień [1*], N. Rosiak [1], J. Cielecka-Piontek [1]
[1] Department of Pharmacognosy and Biomaterials, Poznan University of Medical Sciences, Poznan, Poland

Abstract:
Apigenin, a commonly found monomeric flavonoid belonging to the flavone subclass of flavonoids, demonstrates notable biological activity. This includes antioxidant, anti-inflammatory, antibacterial, and neuroprotective effects. It is widely present in numerous herbs, vegetables, and fruits, contributing significantly to the human diet and offering potential health advantages. However, the pharmacological potential of apigenin is hindered by its intrinsic low solubility, leading to limited bioavailability.

The goal of this research was to increase the solubility and membrane permeability of apigenin by using various excipients through co-precipitation with a functional carrier in supercritical carbon dioxide, using a supercritical fluid extractor. This initiative was undertaken with the additional aim of enhancing the neuroprotective activity associated with apigenin.

Apigenin and solubility enhancers were placed in an extraction vessel and heated to 50°C. Carbon dioxide was introduced into the vessel under a pressure of 5000 PSI, and the static process was allowed for 30 minutes. 24-hour solubility was studied. Upon identification of the excipient exhibiting the highest potential for enhancing apigenin solubility, an exhaustive exploration of various amorphization parameters was conducted to achieve optimal solubility enhancement. Alterations in the crystalline behavior of apigenin were studied through X-ray powder diffraction analysis. Furthermore, apparent solubility and gastrointestinal/ blood-brain barrier membrane permeability using the PAMPA model were performed. The study extended to the evaluation of the formulated systems' potential to scavenge DPPH radicals and inhibit acetylcholinesterase and butyrylcholinesterase activities.

The co-precipitation technique with a functional carrier in supercritical carbon dioxide emerged as an effective method for amorphizing apigenin and significantly increasing its solubility and membrane permeability. The excipient demonstrating the most substantial potential for enhancing apigenin solubility was identified as polyvinyl caprolactam polyvinyl acetate-polyethylene glycol grafted copolymer (Soluplus). The notable improvement in solubility facilitated an elevation in the neuroprotective potential of apigenin.

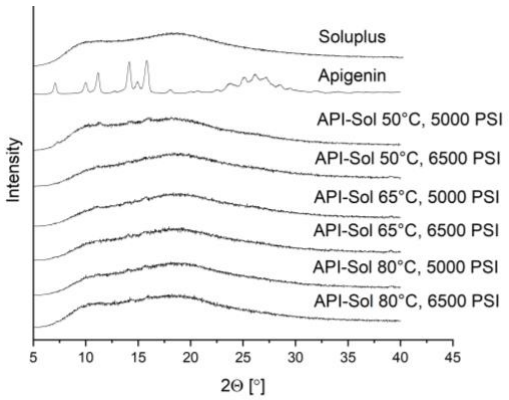


Figure 1: The experimental X-Ray powder diffraction patterns of studied samples.

Acknowledgments: This research was funded in whole by National Science Centre, Poland, the grant Preludium nr UMO-2021/41/N/NZ7/01125.

Keywords: supercritical carbon dioxide, apigenin, X-ray powder diffraction, solubility, neuroprotection

SETCOR
Conferences & Exhibitions