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Silicon Carbide For Neutron Diagnostic In Plasma

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Abstract

The exploitation of fusion technology demands the development of a new generation of plasma diagnostic, capable of operating in the reactor's harsh environments. Neutron monitors based on solid state silicon detectors are well established for neutron beams and monitoring or nuclear waste. Even if standard silicons are unable to face the condition of reactors such ITER, the aforementioned requirements are met by Silicon Carbide (SiC) detectors. A new generation of SiC has been developed at INFN-LNS, with high resistance to radiation, fast response time, stability and good energy resolution. These devices, thanks to their capability to operate in harsh environments, are really promising not only for plasma diagnostics in fusion reactors, but also for nuclear physics with high intensity beams and in laser facilities.

We will present an extended characterization of SiC, focused on the aspect of resistance to neutron irradiation from thermal energy to few GeV. In particular, a campaign of irradiation was performed at the n_TOF facility, where SiC have been exposed to an integrated neutron fluence of 10^{12} neutrons per cm^2, peaked in the MeV energy region, comparable with the values reached inside a fusion reactor.

Keywords: neutron, silicon, silicon carbide, plasma diagnostic, radiation hardness.

1. Introduction

Wide-band-gap Solid State Detectors (SSDs) have a growing interest in high neutron flux applications, such as thermonuclear fusion machines [1-2] or spallation sources [3-4]. SSDs features are good pulse height energy resolution, fast response time and compact dimensions, making them an interesting solution for measuring and monitoring the high neutron fluxes in harsh environments.

The development of large high-power tokamaks (such as ITER) requires neutron detectors to be installed closer to the plasma region and, therefore, to be able to sustain the high temperature and neutron flux of such an environment. This is driving interest in new and more neutron-resilient SSDs, such as silicon carbide detectors.

Silicon carbide is a very promising material for use as a neutron detector in these fields because of its high resistance to radiation, fast response time, high stability and good energy resolution.

A new generation of SiC has been developed and characterized at INFN-LNS [5]. The use of Silicon Carbides is not limited to the plasma diagnostic, but they represent a promising detector for nuclear physic measurements, intense beam diagnostic and laser facilities.

In this work we present the campaign to study the response of SiC to intense neutron fluence that has been carried out at the neutron Time Of Flight (n_TOF) facility at CERN [6].

2. Experimental set-up

2.1 Main performances of new SiC generation

The Silicon Carbide detector (SiC) used in these measurements are a new generation of devices developed within the SiCILIA collaboration between INFN, IMM and ST-Microelectronic. Details on the prototypes processing are given in ref [**5**]. The device that was employed has an active thickness of 100 μm and area of 5 mm^2 × 5 mm^2. The read-out was based on a charge preamplifier from the ASCOM company [**7**] (45 mV/MeV of gain, 600 μs of decay time, 1.5 keV at zero pF, and 12eV/pF of slope) and a spectroscopic amplifier ORTEC-474. The detector was biased through the preamplifier circuit by a CAEN A1821H VME module. The detector was bias with a negative voltage of 300 V, corresponding to the full depletion.

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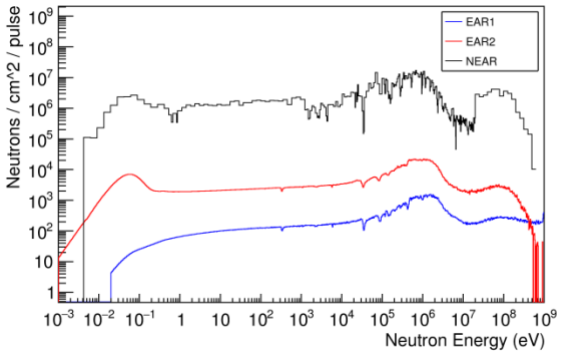
Similar prototypes were tested in the past and compared with a commercial silicon device, to evaluate their performance. The energy resolution measured with the 5485.56 keV alpha particles produced by ^{241}Am was 0.4% for the SiC and 0.22% for the commercial silicon. Moreover, radiation damage studies were conducted by using ion beams: both electrical characteristics and the spectroscopic behaviour were investigated [**8**]. It has been observed that the radiation damage produces an increase of the point defects and a consequent increase of the leakage current of the detector. Furthermore, even an increase of the ideality factor and a decrease of the doping concentration of the epitaxial layer has been observed at high irradiation fluence. From the spectroscopic point of view, SiC detectors show a small worsening of the resolution even at larger fluence (10^{13} ions/cm^2).

2.2 n_ToF facility

At the n_TOF facility [6] at CERN an intense pulsed neutron beam is produced by the spallation of 20 GeV/c protons accelerated by the Proton Synchrotron (PS) on a massive lead target, with energies from thermal to few GeV. Two experimental areas (EAR1 and EAR2) and an irradiation point (NEAR) are present, with distance of about 185, 20 and 3 meters from the neutron source respectively. Two moderators, consisting of a few centimeters of water, are present outside of the spallation target in the direction of EAR1 and EAR2, to increase the quantity of low energy neutrons that are produced. Neutron energy is determined by the time-of-flight technique, measuring the time spent from the neutrons to reach the areas. In Fig. 1 the neutrons per pulse and cm^2 in the three irradiation positions are reported, note the large difference in term of flux, given by the distance from the source. All the three curves are characterized by a wide peak around 1 MeV but, while in EAR2 and NEAR a relevant thermal component is present, in EAR1 it is almost absent because of the presence of boric



acid in its moderator.

Figure 1. Neutrons per pulse and cm^2 in EAR1 (blue) and EAR2 (red) and NEAR (black).

3. Neutron Irradiation at n_ToF facility

The device has been irradiated in both experimental areas and NEAR. Initially, the detector was placed in EAR1 with a total neutron flux of about 10^{10}/cm^2. The detector operated in air at a reverse voltage of 300 V, a ^{6}LiF sample was placed at a close distance (1 mm) in front of the detector to produce alpha and tritons by the reaction ^{6}Li(n,^{3}H)^{4}He at 2.05 and 2.73 MeV respectively. The stability and resolution of the detector was monitored online by recording the spectra of the deposited energy in each run and measuring the position and width of the triton peak.

As can be seen from Fig. 2, the 10^{10}/cm^2 neutron flux did not cause any appreciable deterioration of the detector performance. The result agrees with the results of a previous irradiation performed at Frascati Neutron Generator (FNG) facility [9].

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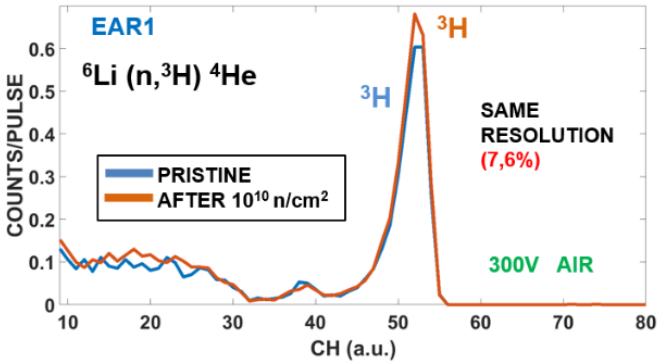

Figure 2. ^{3}H Spectrum in air and with 300V working reverse voltage in pristine condition and after 10^{10} n/cm^2.

In the second phase, the SiC detector was placed in the NEAR area. In this case, the device was not biased since the intense radiation present in NEAR would have damaged the electronics. The detector was exposed to a total fluence of 10^{12} n/cm^2, to evaluate the radiation damage, the CCE (Charge Collection Efficiency) was measured and compared with the values in pristine conditions. Even if we observe a worsening of CCE after a total flux of 10^{12} n/cm^2, as can be seen from fig. 3, the effect can be compensated by increasing the bias voltage: for bias above 400 V the total charge is collected.

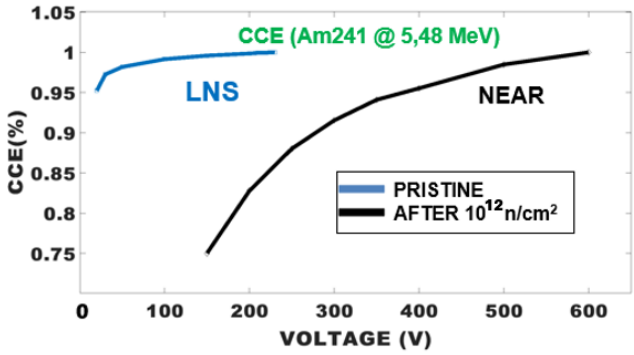

Figure 3. CCE obtained both at LNS and at CERN using alpha particles source (americium).

Finally, in the third phase the SiC detector was irradiated in the EAR2 area with a total flux of about 10^{11} n/cm^2, with a relevant thermal neutron contribution. The detector worked in vacuum and again a ^{6}LiF film was used to perform the online monitoring.

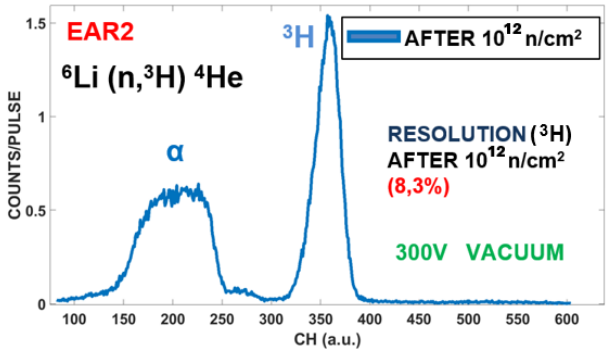

Figure 4. ^{3}H and alpha spectra in vacuum and with 300V working reverse voltage after 10^{12} n/cm^2 (in EAR2 area).

In Fig. 4 the spectrum obtained after the irradiation is shown, note that the peaks are much better defined compared to the ones of Fig. 2, thanks to the vacuum conditions. The resolution of the triton peak increase from 7,6% to 8.3%, indicating a degradation of the performance of the device.

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4. Conclusion

Neutrons diagnostic in plasma is fundamental in most physics' cases, like magnetic and inertial confinement fusion, neutron spallation or nuclear fission. At present, diamond is the most widely used semiconductor for diagnostic is harsh environments in facilities like ITER and ISIS. SiC are a very promising alternatives with similar properties such as energy gap, minimum energy to create a defect in lattice, electron and hole mobility that make it suitable to work in these extreme environments. For this reason, an experimental campaign was conducted on a new generation of 100 μm thick SiC detector at the n_TOF facility at CERN, to evaluate the resistance to intense neutron fluence. In particular, in the EAR1, EAR2 and in NEAR areas, the SiC detector was irradiated with high flux neutrons (up to a total of 10^{12} n/cm^2), with energies from thermal to GeV. The preliminary results showed a worsening in the charge collection, but the loss charge can be compensated by increasing the working reverse voltage. There was also a worsening in the energy resolution, with limited impact on the detector performance, and well defined peak for the products of the ^{6}Li(n,t) reactions are observed after a total neutron flux of 10^{12} n/cm^2.

5. Acknowledgements

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A novel test-facility based on X-ray imaging and mm-wave polarimetry for plasma diagnostics

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Abstract

At INFN-LNS, a non-invasive plasma multidiagnostics system has been developed in the frame of the PANDORA (Plasma for Astrophysics, Nuclear Decay Observation and Radiation for Archaeometry) project and synergically with the SAMOTHRACE ecosystem funded by the EU Next Gen Program, aimed at fundamental nuclear and plasma physics research. Magnetically confined plasmas generated in a powerful and unconventional superconducting ion source equipped with tens of detection and diagnostic devices (RF polarimeter, optical emission spectroscopy, X-ray imaging and space and time-resolved spectroscopy, RF probes, scope, HPGe detector array) can be properly investigated. High precision measurements of the thermodynamic plasma parameters (electron temperature and density) and of the plasma structure and elemental composition can be carried out. Recently, within the synergic SAMOTHRACE (Sicilian MicronanoTech Research And Innovation Center) project frame, two new diagnostics testbenches – the PYN-HO prototype and the VESPRI 2.0 setup – were designed and they aims to develop and improve detectors and techniques beyond the state of art. The PYN-HO (Probing x-raYs by imagiNg and pin-Hole spectrOscopy) prototype is conceived to operate in four different configurations. It will allow to perform X-ray imaging and space-resolved spectroscopy by CCD pin-hole camera setup and advanced algorithms for Single Photon-Counted (SPhC) and High-Dynamic-Range (HDR) analysis, with the related calibrations and characterizations, both on test-benches and in magnetically confined plasmas. Two PYN-HO configurations will be instead dedicated on high energy resolution diffractometric spectroscopy measurement in X-ray and optical domains based on the use of gratings. The design of the VESPRI 2.0 mm-wave polarimeter is based on a heterodyne approach to measure the magnetoplasma-induced Faraday rotation, providing measurement of the plasma line-integrated electron density. The analysis method is based on the detection of Lissajous figure from a two channels scope in an x-y representation of a direct probing RF signals crossing the magnetoplasma.

Keywords: Plasma diagnostics, magnetized plasmas, polarimetry, X-ray imaging and space-resolved spectroscopy

1. Introduction

Plasma diagnostics plays a crucial role in investigating laboratory magnetized plasmas of interdisciplinary interest, spanning from operations of Electron-Cyclotron-Resonance (ECR) plasma systems such as ion sources for accelerators, to plasmas for thermonuclear fusion and fundamental research. About this latter topic, a plasma multidiagnostics system has been developed in the frame of the PANDORA project [1], which represents the first attempt in the world to measure beta radioactive decay in a magnetized plasma under controlled thermodynamic conditions. Plasma diagnostics is indeed considered to be mandatory for plasma parameters control during online operations.

A powerful technique is the X-ray pinhole CCD camera setup [2], which allows X-ray plasma imaging and space-resolved spectroscopy [3, 4, 5, 6] through advanced analysis algorithms to obtain Single Photon-Counted (SPhC) images providing the local plasma emitted spectrum in a High-Dynamic-Range (HDR) mode, also removing the readout noise [7]. Further improvements of the algorithm [8] allowed to perform more quantitative space-resolved spectroscopic analysis, evaluating local thermodynamic plasma parameters [9].

Recent R&D activities deal with design and develop of new and advanced diagnostics testbenches where detectors and techniques can be properly developed and improved with respect to the state of art for application

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in controlled nuclear fusion plasmas [10, 11], plasma physics [12, 13] and nuclear astrophysics research [1], thus, tested, characterized, and used simultaneously. In the SAMOTHRACE ecosystem frame (EU next gen. program), two new diagnostics prototypes have been recently developed.

2. PYN-HO X-ray testbench

The PYN-HO prototype is conceived to operate in four different configurations. Two configurations will allow to enhance the X-ray imaging and space-resolved spectroscopy technique, with the related calibrations and characterizations in both test-benches and magnetically confined plasmas. Two other ones will be instead dedicated on high energy resolution diffractometric spectroscopy measurement in X-ray and optical domains, based on the use of gratings. The final design is shown in Figure 1 and it includes:

A. Configuration 1.0 – X-ray calibration and characterization to perform energy and quantum efficiency calibration of the CCD detector, particularly in the low energy domain (0.5-30 keV). The system includes an X-ray source to calibrate the spectroscopic CCD system and a SDD (sensitive to low energies) to be used as a reference to normalize the CCD space-resolved spectra and correct the post-processed SPhC algorithm effects.

B. Configuration 2.0 – X-ray imaging and spectroscopy in magnetized plasma by combining different detection systems (SDD and pin-hole focused CCDs, including multi-collimators and shutters). X-ray plasma tomography can be performed by using two CCD cameras. In addition, volumetric spectroscopy on high X-ray emission plasmas will be performed by means of SDD operating at very high counting rate.

C. Configuration 3.0 – Diffractometric measurements on test-bench and in plasma. The system, based on the use of gratings and motorized stages, will reach resolutions of the order of $\Delta\lambda/\lambda = 10^{-3}$ at 565 eV. It will allow to carry out XRF peak broadening measurements for the estimation of plasma ion temperature, by resolving charge-state-shifted peaks.

D. Configuration 4.0 – Optical emission spectroscopy on test-bench and in-plasma to investigate the cold electron component of plasma. The system is thought to absolutely calibrate the spectrometer by an in-lab built radiometric calibration system and calibrated focused light sources. This aiming in plasma transmission measurements for determining the plasma opacity [14].

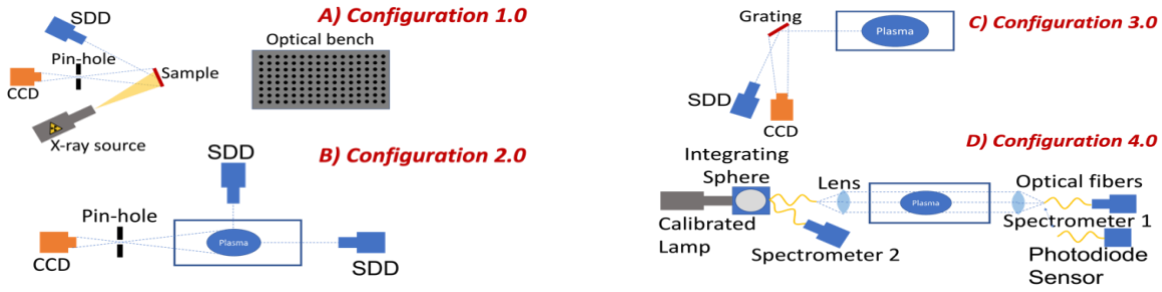

Fig. 1: Sketch of the PYNHO testbench configurations.

As a first step, the test bench was built to perform energy and quantum efficiency calibration of the CCD, i.e. configuration (A), as shown in Figure 2. Different X-ray sources were needed to calibrate and characterize the spectroscopy CCD system, and a SDD sensitive to low energies was required as a reference to normalize the CCD space-resolved spectra and correct the post-processed algorithm effects. Furthermore, the SDD is suitable to operate at a very high counting rate to perform volumetric spectroscopy on high X-ray emission fusion plasma. Specific multi-component (Cu, Al, Ti, Fe, Ag, Sn, Ta, W, Au) targets (see Figure 3) were supplied for measurements in the vacuum scattering chamber. The activity involved the simultaneous use of an X-ray tube, used as X-ray source in a scattering chamber to irradiate the target, inducing fluorescence emissions from the multi-component material, and of a SDD detector (interchangeable with CCD at high space and energy resolution) for the characterization of the CCD detector in terms of spatial and energy resolution response in single-photon counting (SPhC) operating mode. First characterization has been carried out and a total of 350 X-ray frames (100 seconds of exposure time) were acquired in SPhC mode. The X-ray post-processed image obtained using the diagnostics system processed via the developed algorithm is shown in Figure 3 (right). It is possible to perform spatially resolved spectroscopy and spectrally resolved imaging and thus distinguish the different elements that compose the target by detecting their characteristic fluorescence lines. In the X-ray image, each material has been highlighted using a different color.

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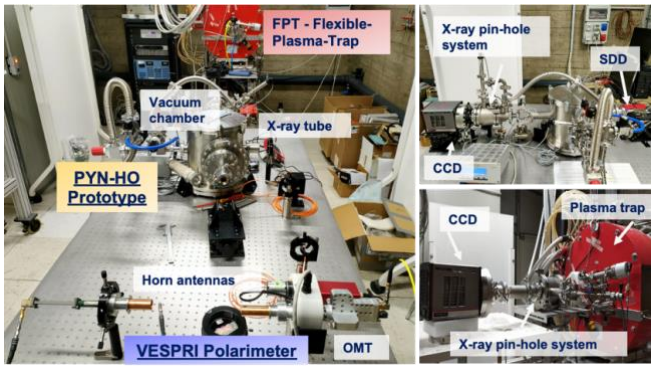

Fig. 2: Pictures of the PYN-HO prototype operating in the first configuration for testbench measurements.

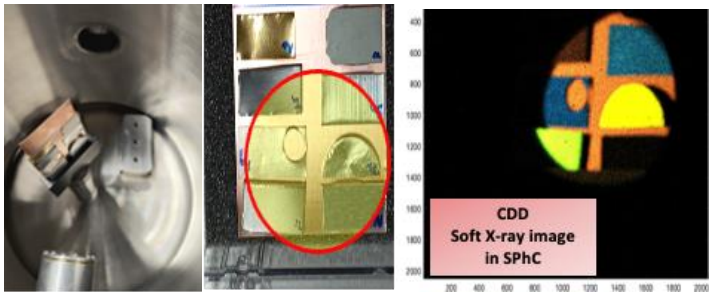

Fig. 3: Pictures of the multi-component target inside the vacuum chamber (left), the detail of the line of view of the CCD (middle) and the X-ray post-processed image acquired by the pin-hole CCD system**.**

The afore-mentioned systems are compatible to be installed and used in the plasma testbench - namely FPT (Flexible Plasma Trap) [14] - installed at INFN-LNS for R&D on diagnostics and detectors, where characterizations of ECR plasmas via the multi-diagnostic system (high resolution X-ray imaging and spectroscopy using CCD and SDD) can been carried out.

3. VESPRI 2.0 polarimetric setup

The polarimetric system VESPRI 2.0 for the evaluation of the total electron density based on the measurement of the Faraday rotation has been designed. The new design involves the use of a THz polarimetry system based on the superheterodyne approach and on the measurement of the Lissajous figures [15]. The first experimental tests to validate the technique were conducted on the optical bench (see Figure 2) using a down-sized polarimetric system (see Figure 4). It included a polarimeter operating in the 18-26 GHz probing frequency domain, with the following tools and devices: a signal generator for the probing wave, two high-directivity horn antennas of which the transmitting antenna was connected to the signal generator and the second rotatable receiving antenna was connected with an orthomode transducer (OMT) (a waveguide component to combine or separate two orthogonally polarized microwave signal paths). The setup operates following the Super-Heterodyne scheme, which allows to downshift the detected frequency (1 GHz) compared to the probing one (20 or 100 GHz) to be detected in a 80 GS/s scope to measure the Lissajous's figures. For this purpose, two mixers were installed and to each of them the output signal of the OMT and the signal coming from a second generator were connected. The measurements were carried out by interposing a wire polarizer (used to emulate magnetoplasma-induced Faraday rotation) measuring the Lissajous figures of the probing RF signal crossing the polarizer through a two channels scope (80 Gs rate) to which the two mixers outputs were connected. The scheme based on the Detection of Lissajous figure allows the real-time reconstruction of the State of Polarization (SOP) curve described by the electric field vector. This result can be obtained by using the two channels scope in an x-y representation.

As next step, the testbench will be installed on the FPT at INFN-LNS for in-plasma measurements, to test and characterize the approach directly in magnetized plasmas.

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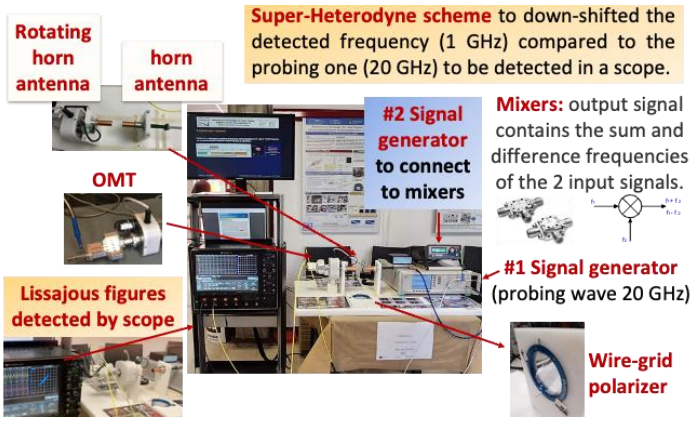

Fig. 4: Pictures of the polarimetric testbench.

4. Conclusions

Two new plasma diagnostics testbenches for laboratory plasma investigation have been developed. The PYN-HO prototype has been conceived for X-ray spectroscopy and imaging measurement and preliminary characterization have been carried out. The VESPRI 2.0 polarimeter is based on the super-heterodyne approach to measure the total electron density through Faraday rotation estimation. The analysis codes were updated to investigate the response of the detectors and tools, improving also the interpretative models to estimate the plasma parameters.

Acknowledgements

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Atmospheric Pressure cold Plasma processing of textiles –applications in functional finishings

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Abstract:

The Greige textile goods need to be converted in the finished product to make it comfortable to wear, attractive and feel good. The process of converting greige textile into finished fabrics is called wet processing. Classical textile wet processing techniques are chemical, water and energy intensive. Therefore, to make it non-aqueous, environmentally friendly Plasma processing is an economical and green alternative and hence it is becoming increasingly popular. This Paper presents the functional finishing of textile materials using etching and deposition process of low temperature atmospheric pressure plasma technology.

Plasma can be explained as the fourth state of matter where the constituents of gas atoms can be activated by addition of energy to produce highly energetic electrons, protons, neutrons, and radicals. The bombardment of these energetic particles results in cleavage of the chemical covalent bonds thereby giving rise to physico-chemical surface modification. The extent of physico-chemical surface modification of the textile material is dependent on the various plasma processing parameters including the power of plasma generation, duration of the exposure, type of gases used etc. In this study, atmospheric pressure, dielectric barrier discharge (DBD) cold plasma is used for functional finishing of the various textile materials including, cotton, silk, polyester, nylon, polypropylene etc.

for improving performance such as improved color up-take, enhancing adhesion with polymer coated fabrics, imparting functionalities like hydrophilicity, hydrophobicity, antibacterial antistatic, electrical conductivity, Multifunctional finish with superior wash durability compared to classical functional finishes is reported.

One of the functionalities imparted through plasma processing on the nylon fabric is depicted in the figure 1.

Keywords: Surface Etching, Plasma enhanced chemical vapour deposition (PECVD), hydrophilicity, hydrophobicity, antibacterial, antistatic, Multifunctional, durable

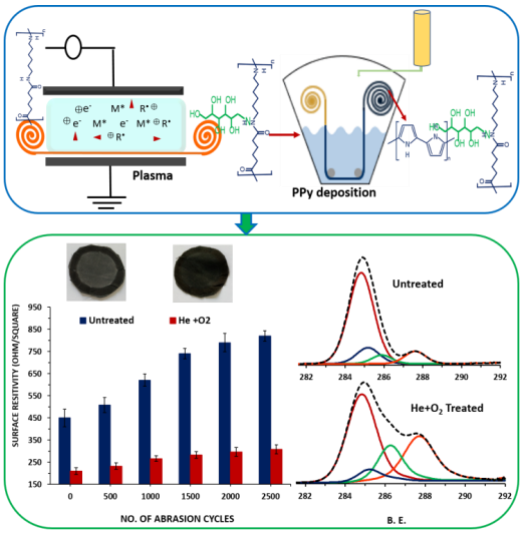

Figure 1: Figure illustrating the fundamentals of plasma reaction with the textile substrate to impart the conducting properties and durability study. It also represents the generation of functional groups after plasma as detected by XPS analysis. reference 1.

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Introduction:

The history of textiles is nearly as old as human civilization, and it has become richer with time. Earlier the main purpose of the clothing is to protect human from the different environmental conditions especially cold climate. The technologies used to produce textiles have changed continuously from antiquity to the present, and the variety of fabrics available has affected how people carry their belongings, dress, and adorns their environments.

The process of making the textile fabrics more beautiful must undergo the applications of different colorant and additions of chemicals is known as textile wet processing. The wet processing of the materials adds the value to final products and make it more attractive and comfortable to use. However, in the process of value addition the environment gets affected by the release of unused dyes and chemicals, by utilizing huge amount of water and energy. The coloration process of textiles needs large number of dyes, chemical and water. Out of the total dyes and chemicals used only 50 to 60% get transfer on to the fabric and remaining 40 to 50% goes in the effluent. Similarly, for finishing 60 to 70% chemicals are utilised the 30 50 40% goes into waste. Additionally, the water released after wet processing contents different hazardous chemicals and colours which is highly toxic to aquatic animals. Environmental safety and stringent policies have imposed strict rules to release such hazardous waste. Considering the facts that the conventional ways of textile wet processing are hazardous to the environment, the new techniques are being researched to reduce the consumption of water, energy and chemicals.

New techniques such as machine modifications to reduce the material to liquor ratio (MLR), recycle and reuse of water, recovery of some of the chemicals are being implemented.

The other way to reduce the environmental pollution is to develop alternative technologies such as spry coating, foam application, air dyeing, super critical carbon dioxide dyeing, digital printing etc plasma processing, E-beam treatment, UV modifications etc. Out of the above-mentioned technologies plasma processing of textiles is the better alternative to conventional wet processing techniques as it has many advantages over conventional processing techniques.

Plasma is commonly referred as partially ionised gas; it is also called as fourth state of matter. As we know, there are three states of matter namely solid, liquid and gas; when energy is provided to solid it is converted into a liquid. When further energy is provided liquid is converted into a gas. On further increase in energy gas is ionized and enters the plasma stat [2,3]. During plasma treatment bombardment of ions, reactive energetic species, electrons, highly energetic neutrals take place onto the surface. This makes plasma surface interactions a very complex phenomenon. Plasma processing parameters determine the nature and energy of bombarding species. Multiple interactions take place at surface due to the bombardment of species which results in change in surface chemistry and topography [4]. Mainly chemical and physical interactions takes place [5].

Physical Interactions

a) Surface cleaning and Ablation / etching:

Plasma removes adsorbed gases, low molecular weight ubiquitous contaminants, oligomers from the surface of the material and is known as plasma cleaning. After surface cleaning, ablation or etching begins. The energetic species in plasma react with material and remove the low molecular weight topmost layer. Depth of etching is influenced by the various plasma processing parameters and limited to ~10 nm or less. Breaking of bonds, chain scission and removal of the uppermost layer results in ablation of the surface. Morphological and topographical changes due to the etching results in rougher morphology and can be seen using SEM and or AFM [6].

b) Chain Scission:

Breakage of polymer chain into two or more parts is defined as chain scission. Chain scission can occur by rearrangement of backbone into two separate elements or by molecular division by bombardment of plasma species [7].

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Chemical Interactions

a) Surface activation or Radical formation

Active site (radical, amine, carbonyl, carboxyl, hydroxyl groups) formation on the polymer surface by plasma exposure can help in improving surface properties of polymer for various applications. Normally radicals formed by plasma are not stable and they rapidly undergo recombination. Therefore, plasma activation of polymer is subject of ageing effect [8].

b) Grafting:

It is often known as plasma graft-copolymerisation. Active site formed in plasma can directly graft on the surface of polymer (*in-situ* plasma grafting) or first formation of active sides, followed by exposure to monomer (post plasma grafting) [9].

c) Polymerisation:

Formation of polymeric material on the surface of substrate using vapours of organic liquids (monomers) in presence of plasma is called as plasma polymerization. It is also known as plasma enhanced chemical vapour deposition (PECVD) process. In the process of polymerisation fragmentation of monomer molecules, the formation of reactive sites (radicals), and recombination of the activated fragments takes place [10].

Application of plasma in textiles:

The above-mentioned plasma interactions give rise to endless number of possible plasma application in textiles. Wide range of research has been carried out and reported in literature. Some of the major applications commonly reported are:

1. Imparting hydrophilicity
2. Improving adhesion
3. Influencing dyeability and printability
4. Application of functional finish
5. Desizing/ degumming
6. Imparting hydrophobicity and oleophobicity (lipophobicity)
7. Shrink proof treatment of wool
8. Sterilisation
9. Changing electric conductivity and antistatic properties

Research papers published in above mentioned application areas are revised briefly and Research and development work done in the Bombay Textile Research Association is discussed in this paper.

Experimental setup:

An atmospheric pressure plasma machine working on the dielectric barrier discharge (DBD) principal is utilized in this research work to treat the different textile fabrics for various applications. The details of the Plasma machine are reported elsewhere [11].

Materials and Methods:

Fabrics such as cotton, silk, polyester, nylon, polypropylene etc were procured from local supplier in India. Plasma gases helium and oxygen were from INOX air India LTD. All other chemicals used were of analytical grad.

Methods:

Depending upon the functionality imparted on the fabric various characterization techniques were used to analyses the changes in the fabrics. Some of the majorly used analytical techniques are as below.

Wicking height measurement by IS 7093

Contact angle measurement using DSA 20 goniometer to determine the hydrophilicity or hydrophobicity.

Adhesion measurement by peel off method using test method IS 1706 part 5.

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Tensile strength as per ASTM D 5035

SEM: changes in surface morphology were analyzed using scanning electron microscope.

XPS: X-Ray photoelectron spectroscopy was utilized to see the incorporation of new chemical functional group. Similarly, Fourier Transform Infrared Spectroscopy was used to see the surface chemical changes.

Imparting hydrophilicity: Improvement in hydrophilicity after plasma treatment is the most studied application on almost every type of textile fibre. Plasma treatment basically aims to introduce hydrophilic functional groups such as –COOH, –OH and $–NH_2$. Wettability of the textile material is the prime requirement in many applications and hence it has got special attention. Kiran Kale et. al. [12] have studied the effect of APGD plasma of P/C blended fabric on hydrophilicity. The hydrophilic properties of the treated fabric was measured as capillary rise and it was reported that the plasma processing parameters vis treatment time, discharge intensity, gas flow rate, type of gas and inter electrode distance affects the wettability of P/C blended fabric. In most of cases, directly contact angle (CA) cannot be measure as a function of hydrophilicity because of irregular surface and large porosity of the textile surface affects the CA measurements. Therefore, wettability of textiles is monitored indirectly by absorbency and wicking measurements. R. Moretn et. al. [13] have modified the PET and PP non-woven with air, argon and helium plasma and studied its wettability by liquid absorptive capacity and shown that air plasma treatment were more efficient in incorporating oxygen containing groups such as C—O, O—C=O and C=O. Plasma treatment for hydrophilicity is reported for PET, cotton, nylon, PE, keratin, PP, natural and synthetic and blends have been reported [14-24].

The work done in BTRA on different fabric for wettability improvement is represented in figure 2. It can be seen from the figure 2, that each type of fabric has different wicking properties without plasma treatment. Further, it may be observed that for the same plasma processing parameters different fabrics respond differently. Maximum improvement in wettability is seen for the polyester fabrics. Whereas the, the least changes are seen for plasma treated polypropylene.

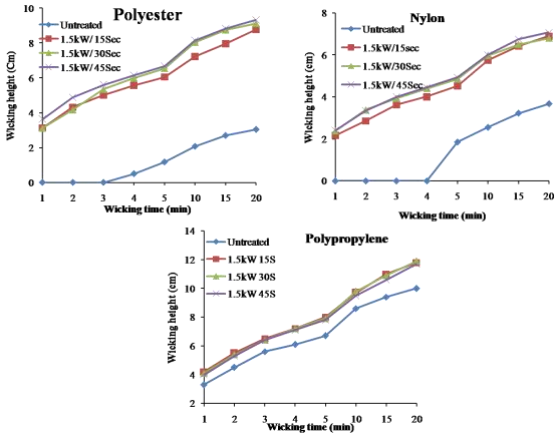

Figure 2. change in wettability of polyester, nylon and polypropylene fabrics after plasma treatment.

Hydrophobic and oleophobic finishing by plasma treatment: Hydrophobic or oleophobic surface can be achieved by grafting or deposition of functional groups. With plasma it can be done using fluorine containing gases or *in-situ* plasma polymerisation of monomer in single step. *In-situ* plasma polymerization of hexamethyldisiloxane (HMDSO) on cotton, Polyester, nylon and cotton/polyester blended fabrics have been reported for improved hydrophobic properties by contact angle studies. It is reported that, the formation Si-C and Si-O groups from HMDSO are mainly responsible for hydrophobic characteristics of plasma treated fabric [25-30]. Use of SF_6, CF_3CHF_2, $C4F_8$, vinyltrimethoxysilane, Tetraethyl orthosilicate etc. on cellulosic and synthetic fabrics for imparting hydrophobic finish by plasma have been reported [31-36]. The beauty of such hydrophobic finishing achieved by plasma is, it allows water vapours to diffuse from one surface of fabric to other surface making fabric comfortable for apparel purpose at the same time water cannot pass.

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Plasma enhanced chemical vapour deposition (PECVD) of 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA) monomer was carried out on filter paper and super hydrophobic and oleophobic surface was achieved. Studies with various fluorine containing monomers for deposition of oleophobic polymer with plasma have been reported by several research group [37-39]. Main drawback of the thin polymer layer deposited by plasma is durability. Thin layer of polymer gets removed when the substrate is subjected to washing and abrasive action. Two step approach; plasma activation followed by grafting or polymerisation can overcome the problem of durability of such treated fabrics. In another study by Ricardo Molina et. al. [40] a two-step process was carried out to impart hydrophilic- oleophobic coating on cellulosic materials. *In-situ* plasma polymerisation of acrylic acid was first done followed by treatment with dilute fluorosurfactant. Super-hydrophobic, oleophobic finish for self-cleaning by plasma activation followed by pad-dry-cure of fluoroalkyl-functional siloxane is also reporte [40].

Figure 3 shows the comparative results of the HMDSO plasma treated cotton, polyester and nylon fabrics.

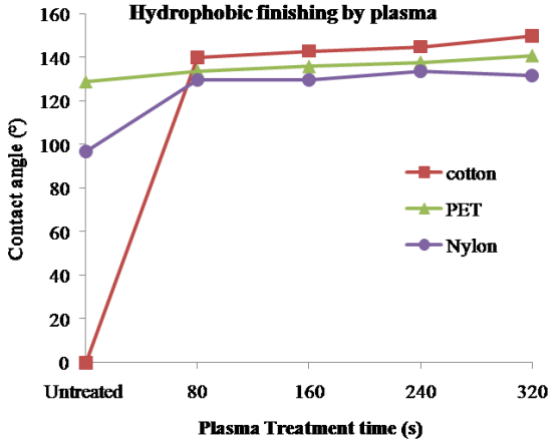

Figure 3, Hydrophobic finishing of the cotton, PET and nylon fabrics using HMDSO at BTRA.

It can be observed from figure 3, that initially the cotton fabrics showed the contact angle value 0° indication the water absorbent nature of the fabric. However, after treatment with HMDSO for only 80S made the cotton fabric hydrophobic and further increase in exposure the plasma it has become the super hydrophobic and contact angel 150° was achieved. Similarly, for polyester it has increased from 129° to 141° which was the least increment as compared to cotton and nylon. This could be due the hydrophobic nature of the polyester, which has already showed the contact angle of 129° hence further improvement after plasma polymer deposition was not very effective.

Plasma treatment for shrink proof wool:

Wool fibre surface has the unique structure of overlapping scale called cuticle cells. Due to scale structure, it has shirking/ felting tendency. Plasma treatment is being utilised for shrink proofing or antifelting treatment of wool by removal of the scale. Abundance of research work has been carried out on plasma treatment wool fibres/fabrics for antifelting, shrink proofing, dyeing, etc. [41-55]. An excessive literature review is given by C. W. Kan et. al. [56] covering the dyeing, printing, shrink proofing, antifelting, finishing of wool by plasma treatment. The reaction mechanism of plasma interaction with wool surface is given. Also, the effect of various plasma processing parameters is discussed. Plasma removes the outermost layer (scale) of wool by etching. Oxidisation of fatty hydrophobic layer takes place at the beginning and further increase in plasma exposure time cause removal of F-layer.

Plasma sterilization:

There are evidence in literature stating antimicrobial effect of plasma treatment [57-62]. Plasma sterilization is an alternative method, which is user friendly and more effective on the wide spectrum of prokaryotic and eukaryotic microorganisms [63]. Basically, the main inactivation factors for cells exposed to plasma are ion bombardment, UV radiation and various reactive species. Plasma exposure

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can kill micro-organisms on a surface in addition to removing adsorbed monolayer of surface contaminants [63-66].

Plasma for changing electric conductivity and antistatic properties:

Plasma treatment of textile material improves wettability by removal of surface contamination, oxidisation or introduction of polar functional groups. When hydrogen is bond with atmospheric water surface resistivity of material reduces. Melek Gul Dincmen et. al. [67] have grafted three different hydrophilic monomers on nylon 66 fabric and studied the antistatic properties. It was found that, diallyldimethylammonium chloride (DADMAC) gave the best results. Reduction in surface resistivity of nylon 66 fabric was found to be influenced by plasma power and treatment time. C. W. Kan [68] has reported the antistatic properties of plasma treated polyester fabric. The relationship between moisture content and half-life decay time for static charge was found to be inversely propositional. Reduction in surface resistivity of cotton and polyester fabric is reported by different authors [69,70] mentioned the cause for reduction in surface resistivity is because of increase in moisture content after plasma exposure. T. mehmood et. al. [71] have used low pressure oxygen plasma treatment on PET film and fabric to study the plasma induced effect on binding of polypyrrole. They have found that formation of carboxylic groups and nano surface roughness are responsible for improved conductivity. Plasma treatment of cotton, polyester, polypropylene, viscose, nylon, wool fabrics for improved conductivity and abrasion resistance is also reported [72-77]. Work done in the BTRA to improve the electrical conductivity and durability to washing is shown in figure 1.

Plasma for Adhesion improvement

Adhesion is the tendency of two dissimilar materials to cling to each other. Textile fabrics normally synthetic one are used for coated technical applications. The synthetic materials such as polyester, nylon, polypropylene (PP) etc are used for coating using different chemical as per application. These synthetic materials have good tensile strength, resistance to abrasion, resistance to chemical and low cost also. Hence, they are widely used. However, the hydrophobic nature and low surface energy of these materials limit its application in various areas. Especially, in coating due to the low surface energy, the adhesion between textile fabric and coating chemical inferior. Therefore, using the plasma surface modification, surface energy of the synthetic fabrics can be modified the adhesion between coating chemical and fabrics can be improved. In this regard BTRA has treated various synthetic fabrics and coating adhesion was studied with polyurethane (PU) foam coating [78-80]. The comparative result of PET, Nylon and PP fabrics is shown in figure 4.

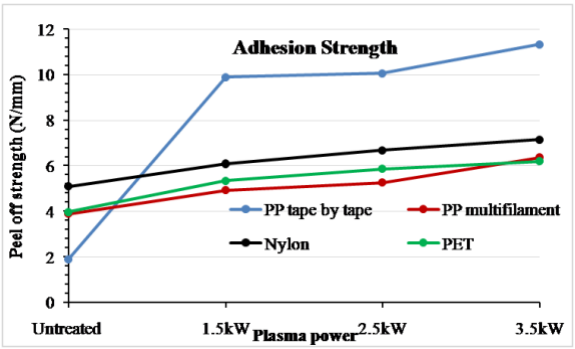

Figure 4 Adhesion studies of different fabric treated with plasma and coated with PU.

The main advantage of plasma technology is the effect of plasma treatment is only limited to the surface of the material and bulk properties remained unchanged. The tensile strength of the plasma treated different fabrics is depicted in figure 5. As can be seen from the figure 5, that after plasma treatment the tensile strength of the PP tape by tape, nylon and PET fabrics remained unchanged whereas in case of PP multifilament there was slight improvement in the tensile property. This could be attributed to the surface roughness created by the plasma treatment which is mainly responsible for the increase in the cohesive forces and hence increased the tensile strength.

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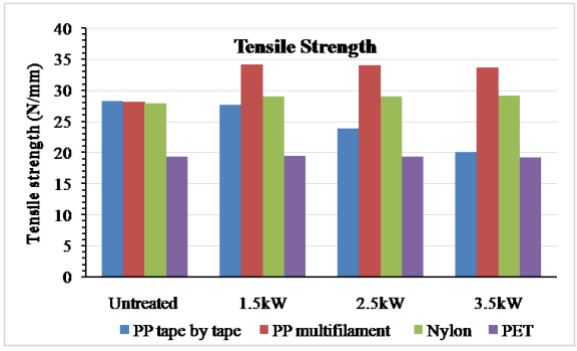

Figure 5 comparative analysis of the tensile strength of the different fabrics treated with plasma at different power levels.

Plasma for Multifunctional Finishing

Multifunctional finishing of the cotton fabric using plasma technology and nano finishing have be reported for functional properties including UV resistance, flame retardants and crease resistance and antibacterial protection [81,82]. The experimental results of the optimised samples are reported in the figure 6. Sample 1 represent without plasma and sample 2 shows the results for plasma treated materials. As can be seen from the figure 6, that UV protection that the UPF factor of the untreated fabric was around 5 was increased initially to 100 for both the samples. However, after repeated washing the plasma treated sample showed the better results and UV protection factor of 20+ was achieved even after 20 washes. This indicates that the plasma treatment improves s the adhesion of nano particles on the surface of the material and impart the durable functional finish. Further the flame retardancy of the treated samples was measured by Limiting Oxygen Index (LOI) and time to burn the specific length of the samples. As can be seen from the figure 6 that LOI vaule increased from 18 to 27.4 and 28.5 for without plasma treated and plasma treated samples respectively. Burn time is increased up to 25sec which provide as time to escape in case of fire hazards indicating the sample is having a good flame-retardant property. Further the preference of the easy-care finish was assist by crease recovery angle measurement (CRA) and found to have very good resistance to form a crease.

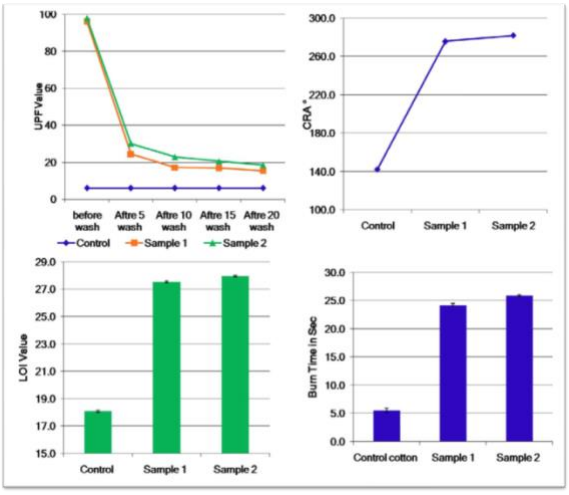

Figure 6 multifunctional finishing of the cotton fabric using plasma and nano technology.

Figure 7 a and b represent the antibacterial activity of the treated samples against the *Staphylococcus aureus* and *Klebsiella pneumonia* bacteria. After 24hr no bacteria is preset in the pleat hence showing the very good antibacterial activity of the treated samples.

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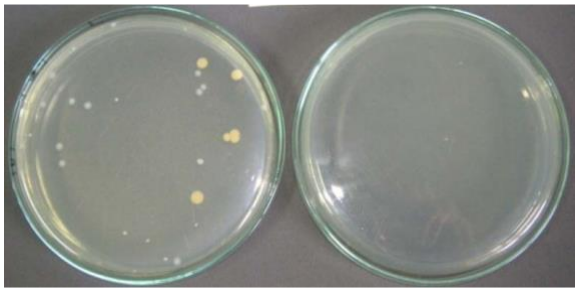

Figure 7a, Antibacterial activity of treated samples after 24hr against *Staphylococcus aureus* bacteria

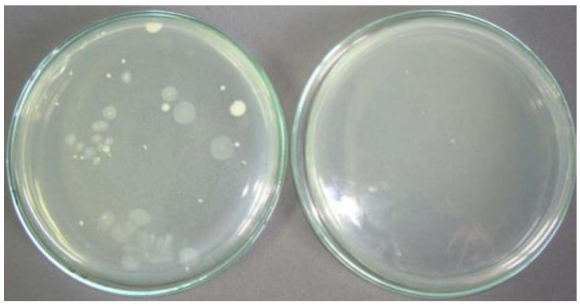

Figure 7b, Antibacterial activity of treated samples after 24hr against *Klebsiella pneumonia* bacteria

Conclusions:

Plasma technology is the new eco-friendly solution the conventional textile wet processing. Using the atmospheric pressure plasma technology various functional finishes including hydrophilicity, hydrophobicity, adhesion improvement, multifunctional finish and electrical conductivity was introduce on the various textile fabrics such as cotton, polyester, nylon, PP etc.

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Atmospheric-pressure Plasma Enhanced Chemical Vapor Deposition of size agents on glass fibers

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Abstract

The current limitation in mechanical properties of fiber reinforced plastics, mainly caused by poor adhesion at the fibers-polymer interface, are a limit to their usage and consequent huge market opportunities. The current work presents a novel approach to overcome such limitation. A PECVD step carried out at atmospheric pressure resulting in organosilicon-based thin films, rich in suitable functional groups, deposited between the glass fibers interface and the adhesion-promoting size agent. Extensive characterizations of the plasma source and the resulting thin films have been carried out, including adhesion tests. Numerical simulations helped create an enclosed reaction chamber suitable to be installed in-line at industrial production facilities, so to render the process viable and economically competitive. Preliminary results show an increase of adhesion of 30% on the macro-scale, and around 100% on the micro-scale, thus making the process an already feasible alternative to the current state of the art.

Keywords: PECVD, atmospheric plasma torch, adhesion-promoting layer, glass fibers, size agent, industrial applications.

1. Introduction

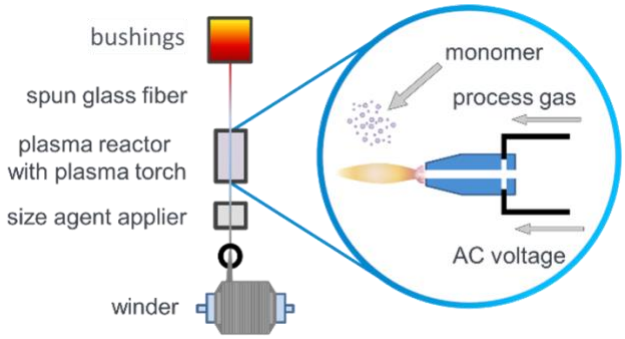

Fig. 1: Schematic representation of the in-line PECVD process: The adhesion-promoting thin film is deposited by means of several atmospheric plasma torches in a reactor chamber (for further details see also Fig. 4) located between the bushings from which the glass fibers are extruded and the roller which applies the size agent.

Fiber reinforced plastics are a class of composite materials consisting of a polymeric matrix in which fibers are embedded. The resulting material offers improved mechanical properties, while remaining light-weight and cost-effective. The yearly growth of such market is estimated to be around 5% by 2025 [1]. On the European stage, glass fibre reinforced plastics alone account for 95% of the total market, with 30% or more used in the transport sector [2,3] and around 10% in the manufacture of wind turbines, at the cost of around 1 €/kg [2]. The main limitation to the mechanical properties and lifetime of such materials is constituted by the adhesion forces at the glass-polymer interface. As such, the state-of-the-art dictates the application of an aqueous dispersion of a bonding agent and additives, in order to offer for the glass fibers a highly-functionalized surface with superior adhesion properties for the subsequent polymer matrix. Such method can however, nowadays, only reach a 10-20% coverage of dried glass fibers [3].

The current work proposes a further deposition step, carried out by means of Plasma Enhanced Chemical Vapor Deposition at atmospheric pressure, on the newly-extruded glass fibers, resulting in a thin film with suitable

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chemistry so to act either as coadjuvant or a complete replacement of the size agent, thus improving the properties of the composite material and reducing the CO_2-footprint associated both to its production and usage. The method must be implementable on industrial scale and be competitive, commercially too, with the current state-of-the-art.

A schematic representation of the proposed PECVD step is shown in Figure 1: the glass fibers are extruded from the bushings at different speeds and are immediately swept through the plasma reactor, where the adhesion-promoting thin film is deposited in an after-glow PECVD step by means of several atmospheric plasma torches. A size agent is then applied to the thus coated fibers by a sizing roller, and the fibers are finally spun around the winder.

2. Materials and Methods

All deposition processes have been carried out by means of a commercially available atmospheric plasma torch by Plasmatreat, powered by a FG5001 Openair-Plasma® generator and equipped with a PTF 160 nozzle in two variations: a standard configuration with a single injection point for the plasma feed, and one which allows for the precursor of the thin films to be injected laterally in the plasma zone. A further configuration for the PECVD step, carried out with the pilot prototype on a glass fibers with a variable number of plasma torches, involved a standard PTF 160 nozzle with a separate spray injection of the monomer in the remote after-glow region, once the first method proved too inefficient. The ranges of operating parameters employed are listed in Table 1.

Table 1: Operating parameters of the plasma torch for the deposition processes.

Voltage [V]	250 ÷ 400	Frequency [kHz]	19 ÷ 25
Duty Cycle [%]	20 ÷ 100	Feed gases	dry air, nitrogen 5.0
Feed glas flow [slm]	30 ÷ 60	Monomer	Organosilicons

2.1. Thin films characterization

For preliminary analyses, all thin films have been deposited on soda-lime glass plates. The films morphology has been characterized by means of scanning electron microscopy with a VEGA Plus TS 5135 MM SEM from the company Tescan. A previous metallization of the samples, by means of a Sputter Coater 108auto from Cressington equipped with a gold target and resulting in a nominal gold film of 30 nm has also been carried out. The chemical composition of the resulting thin films has been investigated by means of absorption IR spectroscopy in single reflectance modus, both at normal and grazing incident angles, via a Bruker FTIR spectrometer Vector 22. Adhesion tests on glass plates as substrates have been carried out via an Elcometer 106 Pull-Off Adhesion Tester. For all adhesion tests, a two-components epoxy resin has been used as glue.

2.2. Numerical simulations

CFD numerical simulations of the plasma jet have been carried out via a finite element method by means of the software COMSOL Multhyphisics®, version 5.1 and following [4]. The cold gas simulations are based on Reynolds-averaged Navier-Stokes equations [5] and assume a turbulent flow for all the simulated scenarios. The sub-physic models employed have been: k-ω, k-ε, Low Reynolds k-ε, and Realizable k-ε, both in stationary and time-dependent modus. Further time-dependent simulations have also been carried out by means of a Large Eddies Simulation (LES Smagorinsky) model.

3. Results and Discussion

The morphology of the thin films resulting after the PECVD and their chemical composition are shown in Figure 2. Despite an obvious effect of the operating duty cycles and the distance between plasma torch and glass substrate, all films exhibit the typical signal in the 3900-2500 cm^{-1} region attributed to hydroxyl, amino- and methyl-groups, all suitable for increased adhesion properties.

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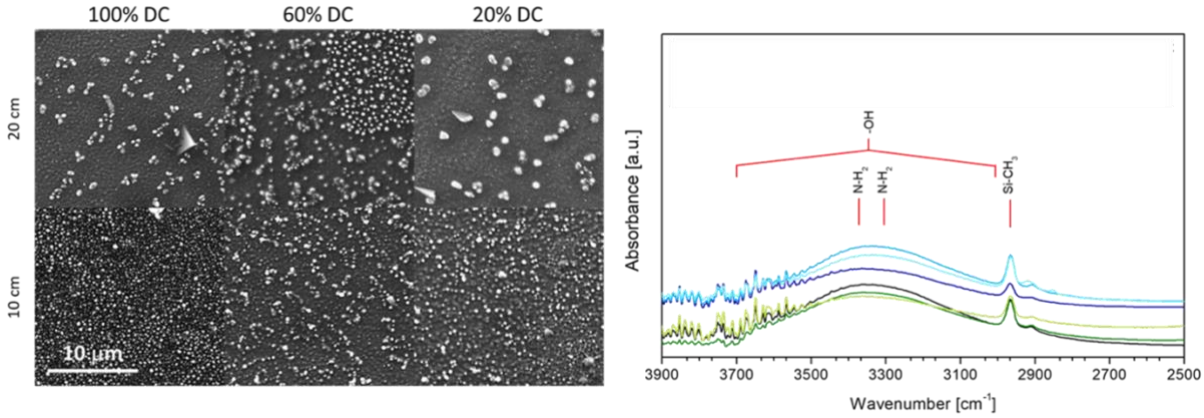

Fig. 2: Left: SEM pictures of the resulting thin films for different duty cycles and at different substrate-plasma torch distances. Right: FTIR spectra of the films in the 3900-2500 cm^{-1} region of the films, and signal attributions.

The adhesion tests on glass plates showed in several cases an increase (up to around 30%) when compared both to the untreated glass and the glass treated with a non-depositing plasma acting as references (Figure 3): in most cases, only a lower-limit adhesion force could be determined, since either the detachment took place at the wrong interface, or the glass substrate shattered before detachment. In some cases, the thin plasma film has also been tested in conjunction with a commercial size agent (Hydrosize® U6-01): the samples, labelled with the "+ H." tag, show no conclusive trend, since the significant increase in the overall thickness of the to-be-tested samples makes the latter more prone to cohesive instead of adhesive failures. In these cases, too, the measured adhesion forces cannot therefore be considered but as lower-limits values. Subsequent tests on the microscale, i.e. on single coated fibers, have thus become necessary. These tests showed an increase of more than 100% wrt uncoated fibers and still 20% better than commercially available coated fibers [7,8].

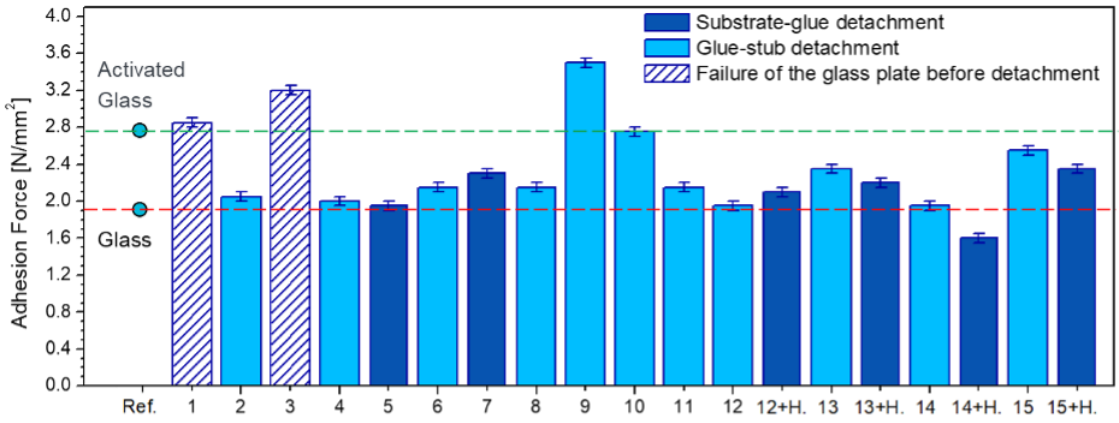

Fig. 3: Left: SEM pictures of the resulting thin films for different duty cycles and at different substrate-plasma torch distances. Right: FTIR spectra in the 3900-2500 cm^{-1} region of the films, and signal attributions.

Finally, Figure 4 shows the first iteration of the reactor chamber's prototype, and how the four torches for the deposition step have been arrayed. Results of the cold gas simulations, i.e. the impinging velocities of the plasma stream on the surface of the glass fibers wedge show that in most configurations only three, and sometimes two, reactors are necessary to attain a complete coverage of such wedge, leading to a more efficient and cost-effective second iteration of the prototype with fewer torches needed.

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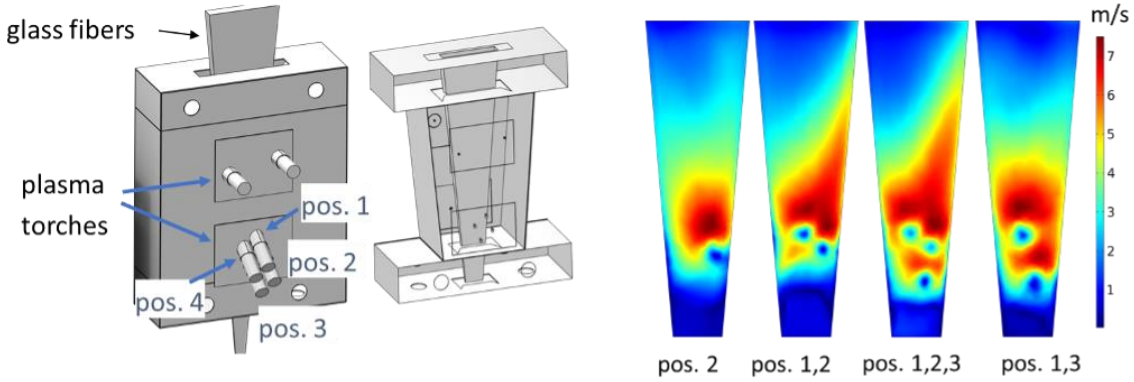

Fig. 4: Cross-section of the reactor chamber's prototype with the attachment points for the plasma torches (left). Velocities of the plasma jet impinging on the glass fibers wedge running through the chamber for different numbers and position of the plasma torches (right).

4. Conclusions and Outlook

The current work showed a new method for improving the mechanical properties of fiber-reinforced plastics by introducing a thin adhesion-promoting coating on the glass fibers' surface by means of a plasma enhanced chemical deposition step carried out at atmospheric pressure. The process is carried out in a reaction chamber suitable to be installed in an industrial line, at conditions compatible with large-scale applications. Results of the adhesion tests performed show vast improvements for a wide range of employed monomers, in some cases exceeding the performances of industrially-coated glass fibers, thus making the method already competitive with the current state-of-the-art technology. Future steps are the installation of a pilot test in a real facility and further optimization of the process and the associated costs.

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