

Influence of cold remote nitrogen oxygen plasma treatment on carbon fabric and its composites with specialty polymers

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Abstract The parameters controlling performance of a fiber-reinforced polymer composite are type of matrix and fibers, their amount, aspect ratio, fiber orientation with respect to loading direction, fiber–matrix interface, and processing technique. In the case of carbon fiber reinforcement, fiber–matrix interface has always been a serious concern, because of chemical inertness of carbon fibers toward matrix and hence efforts are continued to enhance the fiber–matrix adhesion. A recent technique of cold remote nitrogen oxygen plasma was employed for surface treatment of carbon fabric (CF) to enhance its chemical reactivity and mechanical interaction toward matrix material. Untreated and plasma treated CF were used as bidirectional reinforcement for developing high performance composites with various specialty polymer matrices such as Polyetherimide, Polyethersulfone, and Polyetheretherketone. Treated CF reinforced composites showed appreciable

improvement in most of the mechanical properties, which varied with type of plasma, its dosing and matrix used. X-ray Photoelectron Spectroscopy confirmed improvement in O/C and N/C ratio indicating inclusion of Oxygen and Nitrogen on the surfaces of fibers due to plasma treatment, which was responsible for enhanced adhesion. Similarly, Fourier Transform Infrared–Attenuated Total Reflectance Spectroscopy indicated presence of ether, carboxylic, and carbonyl functional groups on the plasma-treated surface of fibers. Raman spectroscopy indicated slight distortion in graphitic structure of treated CF. Scanning Electron Microscopy also indicated changes in the topography of treated CF, indicating enhanced mechanical interlocking with matrix.

Introduction

Specialty engineering thermoplastics such as Polyetheretherketone (PEEK), Polyethersulfone (PES), Polyetherimide (PEI), etc. are used as matrices for advanced composites, because of their additional advantages such as higher specific strength, thermal stability, resistance to fatigue and crack, recyclability up to an appreciable extent, unlimited shelf life, etc. Among various reinforcements, fabric reinforcement is the most promising for fiber-reinforced composites typically used for aircraft structures that encounter harsh operating conditions such as high stresses, speeds, temperatures, etc. [1, 2]. Carbon fibers are chemically inert in nature and hence have poor wettability and adsorption with most of the matrices. For enhancing fiber–matrix interfacial adhesion, chemical bonding and mechanical interlocking are the most effective methods. To date several surface treatment methods viz. electrochemical, chemical, thermal and discharge plasma treatments are

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practiced [3–8]. In most of these methods, fiber surface is roughened by pitting of surface leading to more mechanical interlocking between fiber and matrix.

Classical plasma treatment is a well-proven technique for improving adhesion between fiber and matrix. Its improvisation for enhancing effectiveness is one of the most sought fields. In this view, cold remote nitrogen plasma (CRNP) treatment is recently developed plasma process [9, 10]. Such plasma, located far from the discharge is exempted to ionic bombardment or UV light, so it allows a better control and a greater understanding of the chemistry of the treated surface. In comparison with classic plasma treatment, CRNP treatment is a significantly less destructive method allowing a greater control over the number of unwanted reaction pathways. The main reactive species of the CRNP are atomic nitrogen and vibrationally and/or electronically excited nitrogen molecules with a long radiative or collisional relaxation time. A low level of oxygen (<2%) added to the nitrogen flow allows oxygen atoms to be produced in the plasma without altering the extra volume. Cold remote nitrogen–oxygen plasma (CRNOP) is a modified version of CRNP when traces of O₂ are added to nitrogen during treatment. In literature, efforts are reported to evaluate potential of CRNP and CRNOP on polymers such as polypropylene, polyethylene, etc. to modify their surfaces [9, 10]. However, efforts on exploitation of combination of these two for carbon fiber treatment and its effect on mechanical properties of specialty polymer composites are not yet reported. Hence, in this work, carbon fabric (CF) was treated with CRNP and CRNOP (with varying % of O₂) to assess the changes on the fiber surface as analyzed by various techniques such as Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy (RS), and Fourier Transform Infrared–Attenuated Total Reflectance (FTIR–ATR). Several composites based on PEI, PES and PEEK matrices with untreated and treated CF were developed and evaluated for various performance properties (strength and modulus) and findings are presented in this paper.

Experimental

Procurement of materials

Twill weave (2 × 2, 3k and thickness 3.4 mm) CF was supplied by Fibre Glast Developments Corporation, USA. PEI material (ULTEM 1000) in the form of granules was supplied by GE plastics, USA. Two grades of PES (GAFONE B2500 and GAFONE B3500) were supplied by Solvay Advanced Polymers, India as granules and PEEK powder (VICTREX 150XF) was from Victrex, USA.

Supplier's data on these grades are presented in various tables along with their composites.

CRNP and CRNOP treatment

An experimental setup available at university of science and technology of Lille, France was used for plasma treatment. In this process, gaseous flow (N₂ or N₂ + O₂) provided by a continuous pumping with rotary pump (33 m³/h). It was excited by an electrodeless discharge provided by a microwave generator (2,450 MHz) with a capacity of delivering a transmitted power up to 1,200 W [9]. The discharge was produced in a quartz tube (inner diameter 30 mm) coupled to the Pyrex cylindrical treatment chamber (diameter 150 mm and volume 15 l). The distance between the discharge and the treatment zone was 900 mm. The gaseous flow was controlled by means of a mass flow regulator and the pressure was measured with a Pirani gauge.

Carbon fabric as received was used for treatment. After placement of fabric sample in chamber, pressure was reduced to 10 Pa for 5 min followed by treatment with selected plasma (CRNP or CRNOP) for 15 min. Nitrogen flow rate was always 2.5 slm (standard liter by minute) and the working pressure was 4 hPa (hectopascal). For CRNOP treatment, oxygen (0.5 and 1%) was added to nitrogen before its excitation. This value was not optimized and was arbitrarily chosen. After the treatment, samples were stored in ambient air before use.

Surface analysis

Treated and virgin fabrics were analyzed with various techniques as follows to investigate chemical and mechanical changes on the surfaces.

Scanning Electron Microscopy analysis of untreated and CRNOP treated fibers after gold coating was done on Zeiss EVO MA10 microscope at Indian Institute of Technology (IIT) Delhi, India to characterize the topographical changes on fiber surface due to treatment.

X-ray Photoelectron Spectroscopy analysis was performed at The University of Lille, France on Escalab VG220XL spectrometer working with a monochromatic Al K α X-ray source at 1,486.6 eV. The angle between the collector and the sample was 90°. Spectra were analyzed by casa XPS 2310 software calibrated by setting the aliphatic carbon to 284.6 eV. A Gaussian Lorentzian mix function and a linear background subtraction were used for photo peak decomposition. The atomic % of an element *i*, denoted by Xi (such as $\sum Xi = 100\%$, excluding hydrogen which is not detected) was calculated from the atomic ratio. The % of a functional group was calculated from Xi and

from the area of the component provided by the decomposition of photo-peaks. XPS analysis was performed after storage of treated fabric in ambient conditions approximately for 2 weeks.

In order to investigate the possible changes in chemical composition of carbon fibers by plasma treatment, ATR-FTIR analysis was done on Perkin Elmer SPECTRUM BX in mid infrared range (4,000–700 cm^{-1}).

Ranishaw in Via Raman spectroscope with 514 nm He-Ne laser was used to get Raman spectra of untreated and plasma treated CF. The fibers were fixed on microscope slides. The intensity ratio between the D-line (1,360 cm^{-1}) and G-line (1,590 cm^{-1}) of Raman spectra was employed to evaluate the size of the crystalline surface of the carbon fiber samples.

Fiber–matrix adhesion studies

A reported method based on thermogravimetry analysis (TGA) was tried in this work to quantify the pick-up of matrix by fibers [5]. However, even after trying for three times, results did not show correlation. Hence, new and simple method was tried to find the effect of treatment on improvement in adhesion between matrix and CF. Small pieces of fabric (100 × 100 mm) {virgin and plasma treated (CRNP, CRNO(0.5)P and CRNO(1)P)} were accurately weighted and then dipped simultaneously in PEI solution for 3 min. They were then carefully taken away from the solution and allowed to drip in identical conditions followed by complete drying and weighing. Percentage gain in weight was calculated expecting that treated fabric would show higher pick-up of matrix. Each experiment was done twice and good repeatability was observed. It was of interest to examine if there was a difference in layer of matrix adhering to the fiber strands, two small pieces of such strands were cut and cross-sections were examined under SEM after gold coating.

Development of composites

Composites based on PEI and PES matrices were developed at IIT Delhi, India, while composites based on PEEK matrix were developed at IVW (Institut für Verbundwerkstoffe) GmbH, Germany. For PEI and PES composites, impregnation method (solution in dichloromethane-DCM) followed by compression molding technique was used, while for PEEK composites powder spraying method was used, since no proper solvent exists for PEEK to enable the use of impregnation method. The pieces (280 mm × 260 mm) were cut from the CF roll and the open strands from all the four sides were sealed with a PTFE-coated glass fabric tape

to avoid the fiber misalignment. These pieces were immersed individually in separate containers filled with viscous solution of PEI/PES (prepared with Dichloromethane) for 12 h. The containers were properly sealed to avoid evaporation of solvent, which was required for adequate wetting of fiber strands with the PEI solution. The plies were taken out carefully to avoid misalignment in weave and dried in oven for 2 h at 100 °C in a stretched condition. These 20 prepregs were used to attain the desired thickness in the range of 3.5–4 mm and were stacked in the mold carefully to avoid misalignment. PTFE coated glass fabric was placed on the top and bottom of the stacked prepregs. During compression molding, the mold was heated to attain the temperature in the range of 385–390 °C within 2 h. The prepregs were then compression molded at this temperature at an applied pressure of 7.35 MPa. During the total compression time of 20 min at high temperature four intermittent breathings (each of 2 s) were applied to expel any residual solvent. The composites were then allowed to cool under ambient conditions and applied pressure. The test specimens were cut from the composites with the help of diamond cutter as per required standards for mechanical and tribological testing. In all the composites, which differed in the treatment of plasma, amount of resin was managed to be same.

Initially PEI composites were developed with four types of CF viz virgin (VCF); treated with pure cold nitrogen plasma (CRNP); mixture of CRNP and 0.5% Oxygen (CRNO(0.5)P) and mixture of CRNP and 1% Oxygen (CRNO(1)P). For remaining composites of PES and PEEK, however, only one plasma-treated CF (mixture of cold nitrogen plasma and 0.5% Oxygen) was used.

CF–PEI composites—Four composites were developed with CF and PEI matrix as indicated in Table 3. These composites were designated as PEI_{VCF}, PEI_{NPCF}, PEI_{NO(0.5)PCF}, and PEI_{NO(1)PCF} prepared with VCF, CRNP, CRNO(0.5)P, and CRNO(1)P-treated CF, respectively.

CF–PES composites—Four composites were developed from CF and two grades of PES {PES2500, which is a blended polymer (details not provided by the supplier) and designated as A and PES3500 designated as B in this article}. PES-B had slightly better strength and modulus properties than PES-A as evident from supplier's data reported in Table 4. The composites were designated as PES-A_{VCF}, PES-A_{NO(0.5)PCF}, and PES-B_{VCF} PES-B_{NO(0.5)PCF} prepared with VCF, CRNO(0.5)P-treated CF, respectively.

CF–PEEK composites—Two composites were developed from CF and PEEK matrix as indicated in Table 5. The composites were designated as PEEK_{VCF}, PEEK_{NO(0.5)PCF} prepared with VCF, CRNO(0.5)P-treated CF, respectively. These composites were manufactured by using the static press method, which has the characteristics of heating and cooling stages of one production cycle takes place in the

same tool. Prior to the manufacturing process, the CF is coated with PEEK powder, 24 g per sheet for the inner layers and 12 g for the top and bottom layers, resulting in a computed fiber volume content of 50 %. In the next step, fourteen layers of CF-prepreg were stacked between the heating/cooling plates using maximum temperature of 380 °C within 120 min, held for 30 min and then cooled down to 20 °C at a cooling rate of 1.2 K per minute. The operating pressure is maintained at 0.7 mPa during the entire process.

Characterization of composites

Physical properties

The composites were characterized for physical and mechanical properties. In physical characterization, density of composites was determined as per ASTM D792 specifications. Weight and volume fraction of CF in composites were determined by Soxhlett apparatus using dichloromethane as a solvent and keeping extraction time as 36 h. It was obvious from Tables 4–6 that in each series of composites, volume percentage of CF was almost constant. For PEEK composites, it was slightly on lower side. Void contents in composites was calculated as per ASTM D2734 standards based on following equation

$$\text{Void content (Vol.)} = 1 - \rho_c(W_m/\rho_m + W_f/\rho_f), \quad (1)$$

where ρ_c , ρ_m , and ρ_f are density of composite (experimental), matrix and fiber (as per literature), W_m and W_f are weight fraction of matrix and fiber. It was observed that void percentage was in the range of 0.5% for developed composites.

Mechanical properties

The tensile properties of composites were determined according to ASTM D638 specifications on Zwick 250 Universal testing machine. Strain was measured with extensometer. Cross head speed during test was 2 mm/min.

Flexural tests were performed on Lloyd UTM as per ASTM D790 specification. Span to thickness ratio for specimen was 32:1. Cross head speed during test was 2.71 mm/min.

Interlaminar shear strength (ILSS) tests were performed on Lloyd UTM as per ASTM D2344 specifications. Span to depth ratio for specimen was 5:1. Cross head speed during test was 1 mm/min. Five samples were tested for each type of test and average of best three was taken into consideration. Coefficient of variation value was given in parenthesis in Tables 4–6.

Results and discussion

The SEM micrographs of untreated and plasma-treated CF are shown in Fig. 1. It can be seen that surface of the fiber after plasma treatment was rougher than that of virgin CF. The grooves were deeper and closely spaced on the surface of treated fibers indicating increased surface roughness of

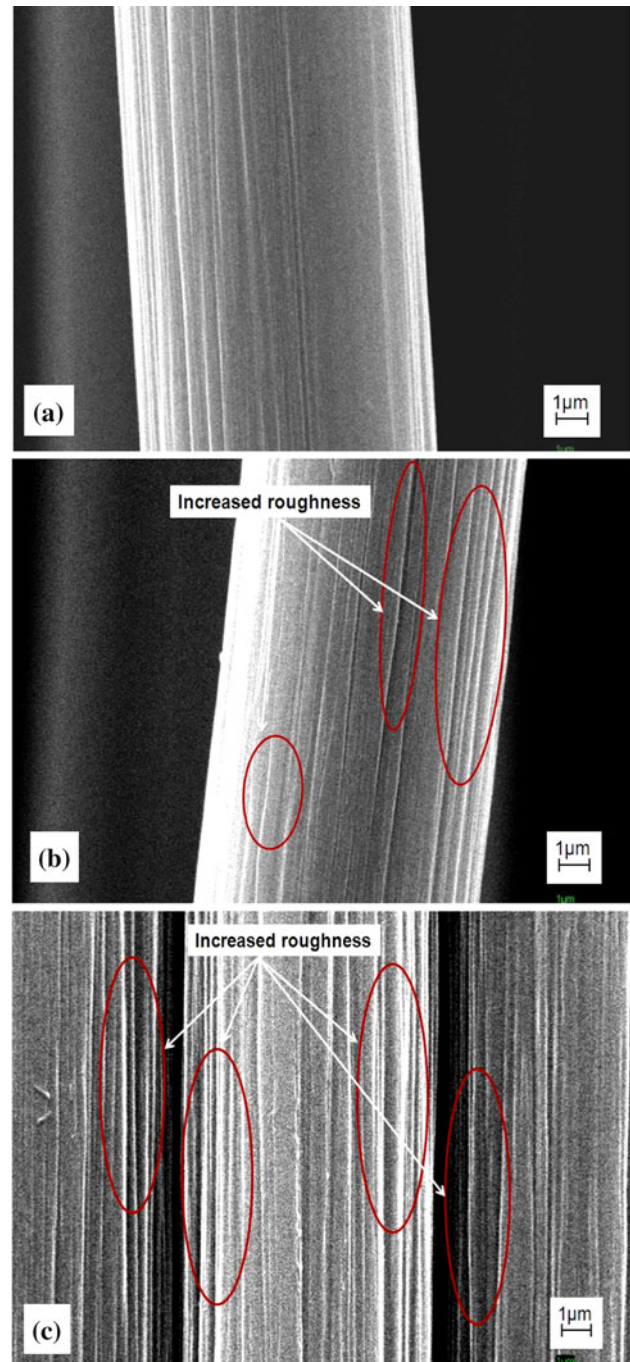
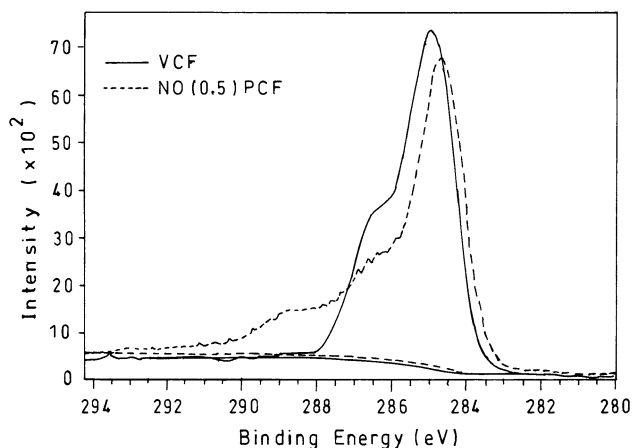


Fig. 1 SEM (20kx) of carbon fibers—(a) for virgin fiber, (b) for fiber treated with mixed plasma (N_2 and 0.5% O_2), and (c) for fiber treated with mixed plasma (N_2 and 1% O_2)

Table 1 XPS results for untreated and treated carbon fibers

Designations of fibers	O/C	N/C	XO (%)	XN (%)	XC (%)
Virgin CF	0.23	–	18.7	–	81.3
Treated (CRNOP)	0.35	0.04	25.1	2.9	72.0

Treatment time 15 min. Addition of O₂ to N₂ plasma was 0.5%

**Fig. 2** XPS of virgin CF and for fiber treated with mixed plasma (N₂ and 0.5% O₂)

carbon fibers. This causes better mechanical interlocking between carbon fiber and matrix [8].

In order to study the chemical changes occurring on CF during the CRNOP treatment, XPS analyses were performed. The wide scan spectrum of the untreated CF only shows C1s and O1s signals. For the CRNOP-treated CF, N1s signal is also detected. The elemental compositions of untreated and treated CF surfaces are shown in Table 1. As can be seen, O/C ratio, initially equal to 0.23 for untreated CF, increases to 0.35 after the CRNOP treatment. In comparison to the one of untreated CF, the C1s peak of the treated CF (Fig. 2) shows a broadening and a shoulder toward high binding energies, giving evidence for oxygen and nitrogen (N/C = 0.04) incorporation on CF surface. For the untreated CF, C1s, and O1s photo-peaks were fitted in 4 (C1, C2, C4, and C6) and 2 (O1 and O2) components, respectively (Table 2). The chemical assignments of each peak are proposed in accordance with the literature data [11, 12]. The oxygen incorporation rate was calculated from the relationship:

$$X'_O = X_{C2} + X_{C4},$$

where C2 and C4 correspond to $\text{CH}_2\text{-O}$ and >C=O functions. Good agreement between the calculated X'_O value (17.6%) and the experimental one (18.7%) gives evidence for the validity of the peak fitting. Moreover, there was a good agreement between X_{C2} and X_{O2} , where

Table 2 Results of the C1s and O1s decomposition for untreated CF

	C1	C2	C4	C6	O1	O2
BE (eV)	284.9	286.4	288.9	291.5	531.4	533.0
FWHM (eV)	1.42	1.42	1.42	1.42	1.74	1.74
Function	C–C	C–O	C=O	Plasmon	C=O	C–O
% Area	77.5	20.2	1.50	0.83	7.47	92.53
Xi (%)	63.00	16.41	1.21	0.67	1.39	17.30

O2 corresponds to C-O , and between X_{C4} and X_{O1} , where O1 corresponds to C=O . For the treated CF (O₂% added to N₂ = 0.5%), C1s and N1s peaks were fitted in 6 (C1 to C6) and 3 (N1 to N3) components, respectively (Table 3). New carbon components are C3 corresponding to >C=NH , and C5 corresponding to -C(=O)-O and -C(=O)-NH_2 functions. In this case, the oxygen incorporation rate can be calculated from:

$$X''_O = (X_{C2} - X_{N1}) + X_{C4} + 2(X_{C5} - X_{N3}) + X_{N3}.$$

Once again, X''_O calculated value (25.5%) is of the same order as the experimental X_O value (25.1%) and X_{C3} and X_{N2} are also of the same order, giving evidence for the validity of the decomposition. So, during the CRNOP treatment, the main grafted function on CF surface are C=O (which increases from 1.2 to 8.5%) and -C(=O)-OH (2.7%). These functional groups seem to favor the increase of the carbon fiber and the interface adhesion between CF and resin.

Figure 3 indicates FTIR–ATR spectra of untreated and CRNO (0.5)P-treated CF. Spectra of untreated fiber was not showing any significant feature. However, for treated fibers, presence of oxygenated polar functional groups was observed. Ether, carboxyl and carbonyl groups were observed on spectra corresponding to wave number range 950–1,200, 1,650–1,710 cm^{-1} , respectively. These groups were responsible for improvement in adhesion between matrix and fabric.

The phases and structural changes that take place in materials were analyzed by Laser RS technique. The bands with intensity 1,360 and 1,593 cm^{-1} are the main features of carbon materials and are called D bands (disordered) and G bands (graphitic), respectively. Figure 4 shows Raman spectra of untreated and CRNO(0.5)P-treated fibers.

The degree of structural disorder of the fibers was characterized by ratio of integrated intensity of disorder induced (I_D) to Raman allowed band (I_G). Lorentzian functions were used to obtain the intensity (I_D/I_G) ratio and the respective surface crystalline size (L_a) of the carbon fibers from Raman spectra. I_D/I_G ratio for treated and untreated CF was 0.94 and 0.86, respectively, and surface crystalline size (L_a) for the same were 46.8 and 51.6 Å,

Table 3 Results of the C1s and N1s decomposition for CRNP-treated CF

	C1	C2	C3	C4	C5	C6	N1	N2	N3
BE (eV)	284.9	286.4	287.5	288.7	289.9	291.5	398.2	400.5	402.1
FWHM (eV)	1.37	1.37	1.37	1.37	1.37	2.34	2.35	2.35	2.35
Function	C–C	C–O H ₂ C–NH ₂	HC=NH	C=O	C(=O)–OH C(=O)–NH ₂	Plasmon	CH ₂ –NH ₂	CH=NH	C(=O)–NH ₂
% Area	61.5	18.1	3.9	11.5	3.2	1.8	7.2	82.1	10.7
Xi (%)	44.3	13.0	2.8	8.3	2.3	1.3	0.2	2.4	0.3

Treatment time = 15 min. Addition of O₂ to N₂ = 0.5%

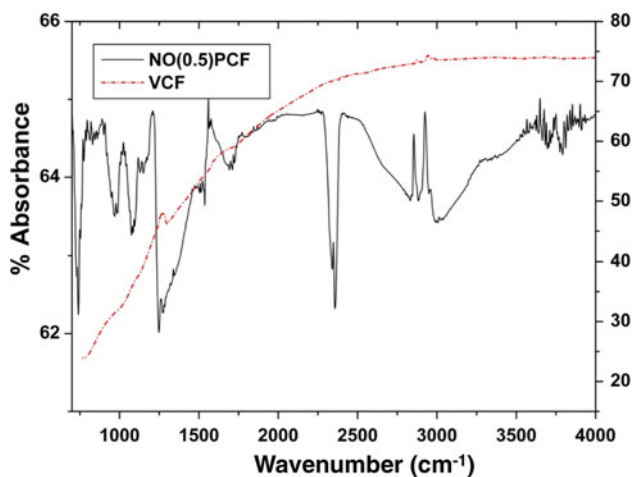


Fig. 3 FTIR–ATR of virgin fiber and for fiber treated with mixed plasma (N₂ and 0.5% O₂)

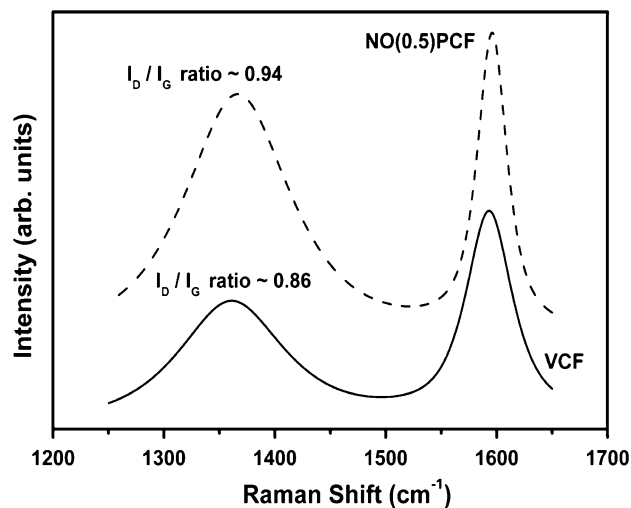


Fig. 4 Raman spectra for virgin fiber and for fiber treated with mixed plasma (N₂ and 0.5% O₂)

respectively. As evident I_D/I_G increased, consequently, the crystalline size decreased after treatment of CF, which indicates the slight distortion in graphitic structure of CF.

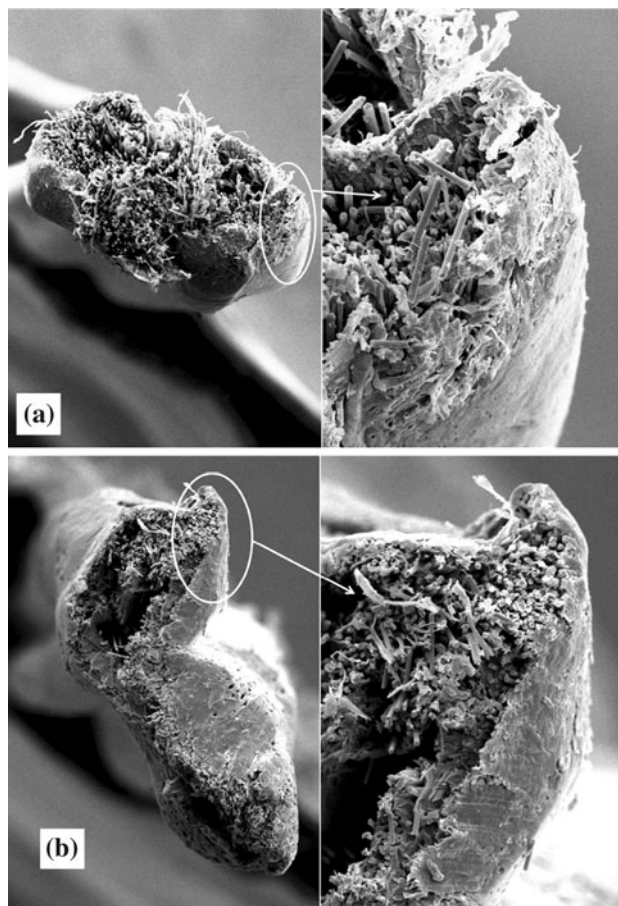


Fig. 5 SEM surfaces of fiber strands after adhesion test (100× and zoom 4); (a) for virgin fiber strand and (b) for treated fiber strand indicating variation in amount of matrix adhering to the strands

Fiber–matrix adhesion studies

Weight gained by plasma treated fabric was more than untreated fabric and was in the order; CRNO(1)P (64.88%) > CRNO(0.5)P (63%) > CRNP(55.90%) > VCF(51.96%).

This enhanced weight gain in treated fabric was due to improved adhesion of matrix with fabric, which was caused by changes in morphology, and inclusion of some oxygenated functional groups on CF after plasma treatment as confirmed by SEM and FTIR–ATR analysis.

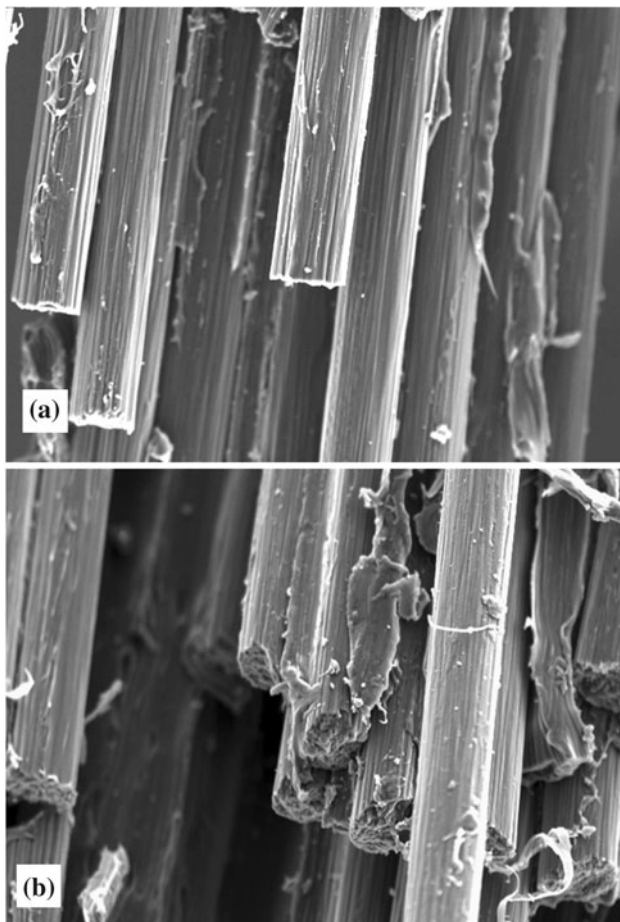


Fig. 6 (a, b) SEM of fractured surfaces during tensile testing for composites (a) with untreated fabric and (b) treated (0.5% O₂ plasma) fabric indicating more amount of matrix adhering to fibers in (b)

Figure 5a, b shows the cross-section of strands (untreated and treated) containing various fibers. Though the quantitative estimation of surface layer at the edge was not possible, it can clearly be seen that the treated strand shows thicker layer on the edge and surface.

It is expected that the treatment to the fibers should affect its own mechanical properties and extent of deterioration depends on the method selected for the treatment. In this case, tensile strength of untreated and treated fibers was measured as per ASTM D4018 standard and it was observed that for untreated fiber and treated fiber, it was $136 \pm .641\%$ MPa and $133 \pm 7.78\%$ MPa, respectively, indicating that plasma treatment has affected the strength reduction nominally.

Studies on composites

It was of interest to see if the fiber–matrix adhesion had increased due to treatment. Hence, surfaces of two

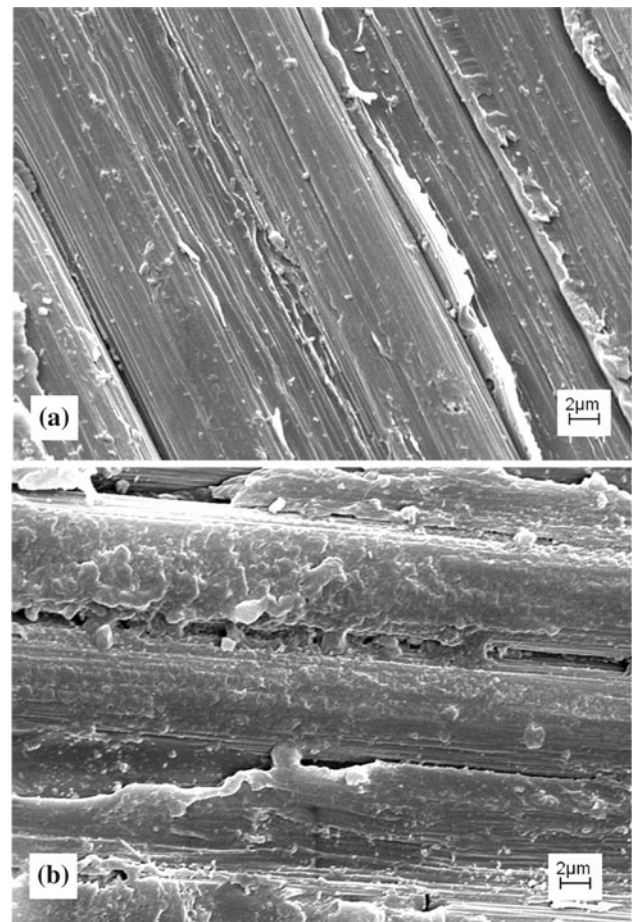


Fig. 7 (a, b) SEM of surface of composite (virgin and plasma treated fabric) after abrading with SiC paper (800 grade)

composites fractured during tensile testing were studied with SEM and micrographs are shown in Fig. 6a, b. It is clearly seen that fibers in treated composite (Fig. 6b) showed more matrix adhering to the fibers as compared to those in untreated composite (Fig. 6a). Though roughening of fiber due to treatment is already shown in Fig. 1, it was also of interest to examine how this affects fiber–matrix adhesion. Hence small pieces of composites (10 mm × 10 mm) were uniformly abraded against SiC abrasive paper (800 grade) to remove the skin of matrix. The details of process are explained elsewhere [13]. The micrographs of Fig. 7a, b clearly show more fiber–matrix adhesion (as consequences of mechanical interlocking of matrix with fiber and chemical bonding of matrix with fibers due to various functional groups added during treatment) in the case of composite with treated fabric rather than untreated fabric composite.

Micrographs of Fig. 8a(i)–(iii) show fractured surfaces of virgin CF-, CRNO(0.5)P-, and CRNO(1)P-treated CF-reinforced composites during ILSS test. Figures indicate extent of debonded plies in failed composites. As clearly seen that

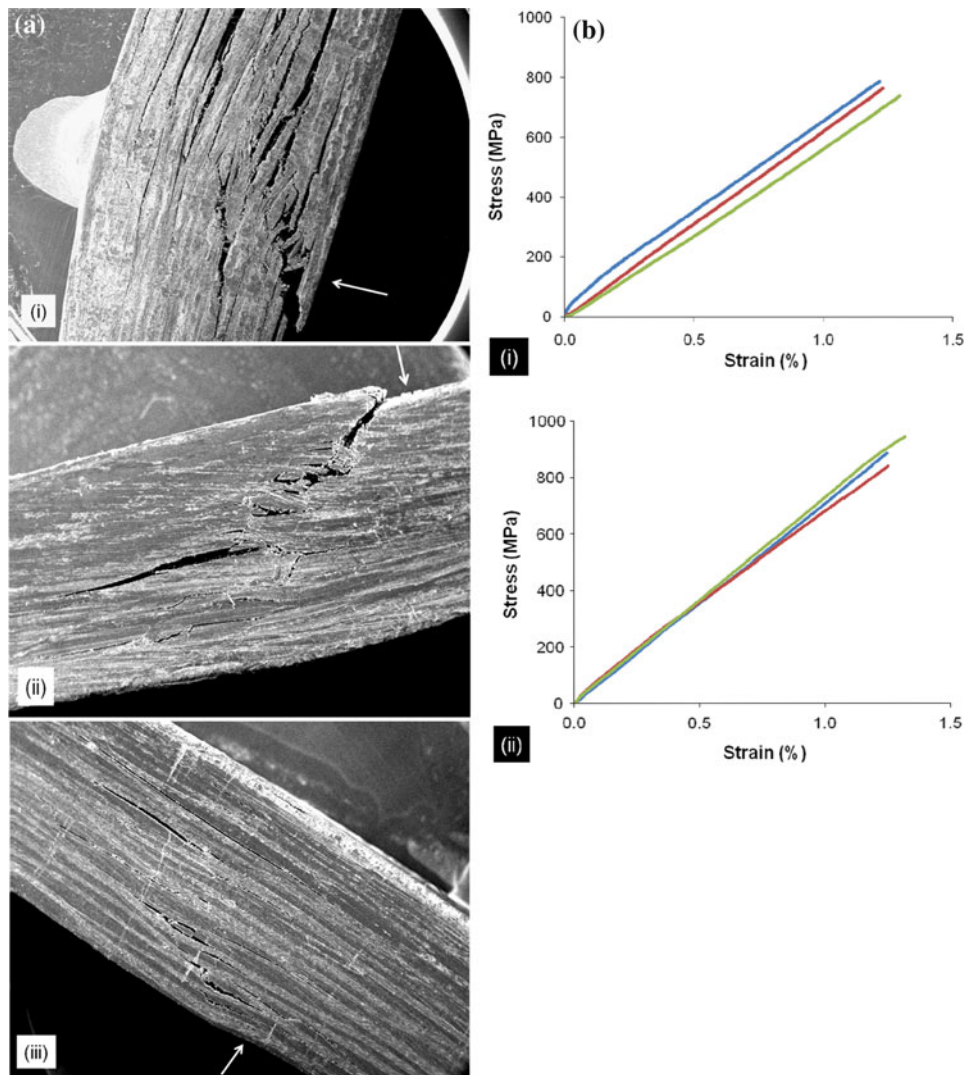


Fig. 8 (a) Fractured surfaces of composites during ILSS test. ($\times 50$); (i) composite with virgin CF, (ii) composite with NO(0.5)PCF and, (iii) composite with NO(1)PCF. Arrows mark on figures show

direction of loading. (b) Stress-strain curves for fabric reinforced composites (i) composite with virgin fabric and (ii) composite with treated fabric

with treatment, extent of debonding decreased and was minimum for 1% O_2 treatment (Fig. 8a(iii)). Figure 8b(i) and (ii) shows stress–strain curves for untreated (i) and treated (ii) fabric-reinforced composites of PEI.

Tables 4–6 show the data obtained on the physical and mechanical properties for CF–PEI, CF–PES, and CF–PEEK composites, respectively. It was observed that density of composites increased due to plasma treatment in most of the cases indicating beneficial effects of fiber–matrix adhesion.

Comparison of strength of unfilled matrices and composites indicated that CF reinforcement enhanced all properties of virgin polymers significantly. When PEI and PES systems containing similar range of fibers in amount (which were based on impregnation technique) were

compared, the strength of composite was higher whose matrix had higher strength (PEI in this case). This was as expected since all other parameters (reinforcement and processing technique) are similar. Comparison of PEEK system was not possible since processing technique was different.

For the sake of comparison, concept of % relative improvement was used by normalizing each performance property of composites based on treated fabric with respect to those based on virgin fabric and this is shown in Figs. 9 and 10. Figure 9 summarizes the data on only PEI composites with different doses of CRNOP, while Fig. 6 is for all composites containing CF treated with CRNOP (0.5% O_2).

As seen from Fig. 9, N_2 plasma showed relative improvement (though small) in all properties (modulus,

Table 4 Physical and mechanical properties of CF–PEI composites reinforced with virgin CF and various CRNP- and CRNOP-treated carbon fabric

Properties	PEI ^a	PEI _{VCF}	PEI _{NPCF}	PEI _{NO(0.5)PCF}	PEI _{NO(1)PCF}
Fiber weight (%)	–	67.15	70.23	67	68.45
Volume (%)	–	55.53	58.08	55.42	56.61
Void content (vol.%)	–	0.48	0.47	0.45	0.55
Density (g/cm ³)	1.27	1.54	1.53	1.55	1.58
Tensile strength (MPa)	105	758 (5.46)	750 (1.2)	810 (0.75)	893 (5.9)
Tensile modulus (GPa)	3	66 (2.08)	67 (5.99)	72.5 (0.78)	79 (0.97)
Strain at break (%)	60	1.15	1.10	1.10	1.23
Toughness (MPa)	–	4.35 (0.81)	4.12 (5.97)	4.66 (5.46)	5.51 (8.47)
Flexural strength (MPa)	150	927 (2.39)	951 (3.56)	1,134 (2.99)	1,174 (9.17)
Flexural modulus (GPa)	3.3	59 (5.21)	61 (5.89)	65 (1.10)	73 (6.55)
ILSS (MPa)	–	34 (7.73)	38 (7.22)	45 (6.90)	52 (3.35)

Parenthesis shows coefficient of variation value

^a Supplier's data

Table 5 Physical and mechanical properties of CF–PES 2500 and CF–PES 3500 composites reinforced with untreated and CRNO(0.5)P-treated carbon fabric

Properties	PES-A 2500 ^a	PES-A _{VCF}	PES-A _{NO(0.5)PCF}	PES-B 3500 ^a	PES-B _{VCF}	PES-B _{NO(0.5)PCF}
Fiber weight (%)	–	67.57	71.52	–	67.50	68.24
Volume (%)	–	58.09	60.45	–	57.98	57.9
Void content (vol%)	–	0.47	0.44	–	0.47	0.37
Density (g/cm ³)	1.37	1.57	1.58	1.37	1.52	1.54
Tensile strength (MPa)	80	742 (1.25)	747 (4.53)	83	744 (1.34)	778 (5.82)
Tensile modulus (GPa)	3	60 (1.32)	74 (1.35)	3.22	65 (3.88)	76 (4.22)
Strain at break (%)	> 60	1.1	1.06	> 60	1.1	1.1
Toughness (MPa)	2.97	4.1(2.45)	4.4 (4.72)	3.2	4.1 (2.43)	4.3 (3.48)
Flexural strength (MPa)	112	685 (0.74)	736 (1.51)	112	692 (1.2)	835 (3.06)
Flexural modulus (GPa)	2.8	56 (5.35)	63 (7.49)	2.8	54 (7.31)	68 (8.17)
ILSS (MPa)	–	30 (6.76)	46 (4.34)	–	42 (4.76)	44 (4.72)

Parenthesis shows coefficient of variation value

^a Supplier's data

Table 6 Physical and mechanical properties of CF–PEEK composites reinforced with virgin and various CRNOP-treated carbon fabric

Properties	PEEK ^a	PEEK _{VCF}	PEEK _{NO (0.5)PCF}
Fiber weight (%)	–	68.17	67.90
Volume (%)	–	51.46	52.87
Void content (vol.%)	–	0.56	0.58
Density (g/cm ³)	1.32	1.43	1.44
Tensile strength (MPa)	97	576 (1.23)	627 (3.91)
Tensile modulus (GPa)	3.6	57 (8.03)	60 (8.38)
Strain at break (%)	60	1.0	1.1
Toughness (MPa)	–	3.0 (6.93)	3.4 (7.29)
Flexural strength (MPa)	170	622 (0.49)	726 (1.72)
Flexural modulus (GPa)	4.1	51 (5.17)	78 (3.91)
ILSS (MPa)	–	43 (4.65)	46 (4.52)

Parenthesis shows coefficient of variation value

^a Supplier's data

flexural strength, and ILSS) at the cost of tensile strength and toughness. The mixed plasma (0.5 and 1% O₂) showed distinct improvement in all the properties. Higher (1%) dosing of O₂ in N₂ plasma proved more beneficial and all properties improved in the range of 20–50%. This improvement was due to the introduction of new polar oxygenated functional groups on CF surface during CRNOP treatment as well as increased roughening of fibers and hence mechanical interlocking with matrix.

As seen from Fig. 10, mixed plasma treatment showed significant improvement in all properties, though it was most prominent for ILSS for PES-A and PEI composites. It was also observed that the benefits depended on the type of matrix also. Improvement in TS, toughness, and flexural modulus was maximum for PEEK matrix composites. Highest and lowest enhancement in ILSS and TS, respectively, was shown by PES-A composite. The order of

improvement in performance properties of composites with selected matrices due to treatment was as follows.

Tensile strength	PEEK > PEI > PES-B > PES-A
Tensile modulus	PES-A > PES-B > PEI > PEEK
Flexural strength	PEI > PES-B > PEEK > PES-A
Flexural modulus	PEEK > PES-B > PES-A > PEI
Toughness	PEEK > PEI = PES-A > PES-B
ILSS	PES-A > PEI > PEEK > PES-B

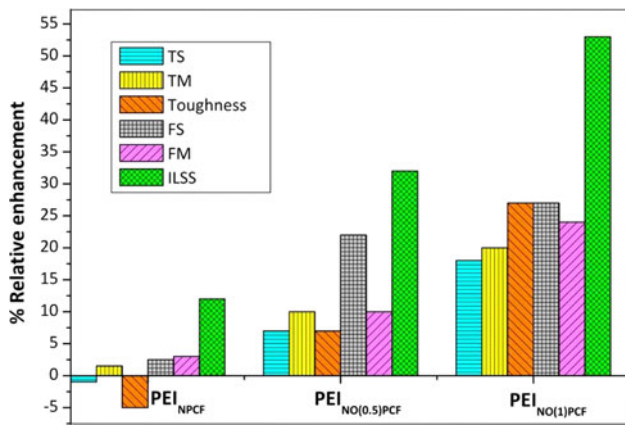


Fig. 9 Relative enhancement (compared to the composite with VCF) in mechanical properties of PEI composites due to plasma treatment of CF

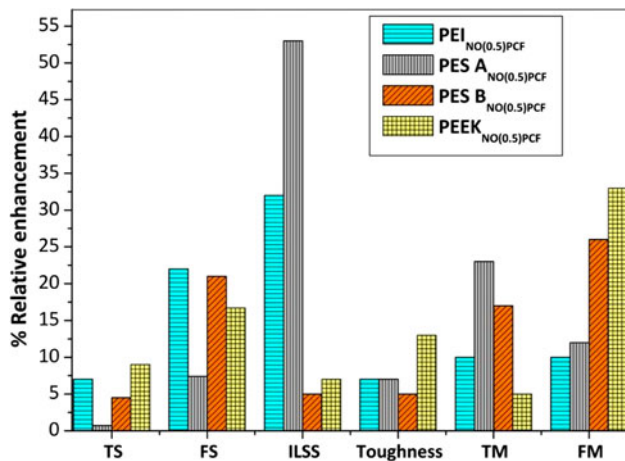


Fig. 10 Relative enhancement (compared to the composite with virgin CF) in mechanical properties of all composites due to plasma treatment (mixture of N₂ and 0.5% O₂) of CF

It was also interesting to note that in the case of PEI and PES composites (which were developed using same technique), the extent of enhancement due to treatment in strength properties was more for PEI composites than PES

composites. This could be because of difference in intensity of chemical reaction of matrix with treated fibers. PEI which contains N atom which has more electron density (lone pair) than S atom in PES resulted in stronger chemical bonding leading to higher to strength properties.

Conclusions

Based on the studies on composites developed with different specialty matrices (PEI, PES, and PEEK) and CF of twill weave treated with different CRNPs, following conclusions were drawn.

Plasma treatment of CF proved beneficial for improvement in fiber–matrix adhesion, which was supported by the adhesion test performed on virgin fiber and various plasma-treated fibers. This enhanced adhesion led to improvement in all mechanical properties such as strength (tensile, flexural, and ILSS) and modulus (tensile and flexural). The enhancement was maximum for ILSS and minimum for tensile strength and toughness. The extent of enhancement depended on type of plasma and matrices used to develop the composites. Mixed plasma (containing mainly N₂ and traces of O₂) proved to be more effective than N₂ plasma. For PEI composites, 1% O₂ in N₂ plasma proved significantly better than that with 0.5% O₂ in N₂ plasma, which in turn was better than plain N₂ plasma. Plasma treatment benefited most to PEEK composites as evidenced from most of the properties followed by PES-A. PEI was least benefited.

The main reasons for enhanced fiber–matrix adhesion were: roughening of smooth surface of carbon fiber as supported by SEM leading to more mechanical interlocking sites and secondly inclusion of various reactive functional polar groups on fibers such as ether, carboxylic, carbonyl as evidenced by various techniques such as XPS, ATR–FTIR, etc. These groups on fiber surface altered the original inertness of carbon fiber and led to enhanced interaction with matrix resulting in stronger composites.

Overall, it was concluded that the recent technique of CRNOP when applied to carbon fibers first time, the inert nature of carbon fibers could be altered significantly leading to substantial enhancement in the performance properties of composites.

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