

Surface designing of carbon fabric polymer composites with nano and micron sized PTFE particles

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Abstract The new technique to tailor carbon fabric-polyethersulphone (CF-PES) composite surface with polytetrafluoroethylene (PTFE) nano particles; to improve wear performance has been reported. Cold remote nitrogen oxygen plasma (CRNOP) treatment was employed to alter the CF surface to promote fiber/matrix adhesion and further; inter laminar shear strength and wear performance of the composites. The atomic force microscopy and high resolution transmission microscopy; studies confirms the topographical modification on the fiber surface due to CRNOP treatment. The dipper ridges and perforations introduced on the fiber surface were analyzed with field emission scanning electron microscopy. The PTFE particles film formation on the worn composite surface was supportively analyzed by Raman spectroscopy and energy dispersive X-ray techniques. The topographical smoothing and rolling effect during the wearing of surface designed composites with PTFE nano particles; endorse to enhance its sliding wear properties and life.

Introduction

Polymers form very important class of engineering tribomaterials, especially for dry bearings or gears applications [1, 2]. However, polymers are mostly used in composite form with the reinforcements such as fibers/fabrics of carbon, glass, Aramid etc., and solid lubricants (SLs) such as PTFE, graphite etc., in right amount and combinations. SLs have very low surface energy, which enhance the tribological performance of a composite at the cost of strength. Tribology is a science of surfaces and hence it is wise to tailor the surface with various fillers rather than incorporating these in the bulk and sacrificing the important strength properties of an engineering component apart from increasing the cost. However, efforts in this direction are numbered [3]. A series of composites using commingled fibers of carbon and Polyetheretherketone (PEEK) was developed with designing the surfaces with various SLs (micron sized) such as PTFE, graphite, MoS₂ and copper powder either in isolation or in combination in different proportions in top layers. It was reported that the triboperformance got enhanced significantly without appreciable loss in strength of a composite [3].

Use of nano scale fillers especially nano-SLs in the polymer composites has become very attractive solution for enhancing friction and wear performance as compared to micron or sub-micron sized fillers. A lot is reported on the nano-composites for tribological exploitation; however, no literature is available on inclusion of nanoparticles (NPs) or SLs for surface tailoring which could be very wise solution for engineering of the composite surfaces [4–6].

While designing the advanced composites, carbon fiber reinforcement is most preferred because of its excellent performance to cost ratio. The only limitation of its inertness towards matrix is overcome by surface treatment with

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various methods [7, 8]. Cold remote nitrogen oxygen plasma (CRNOP) is a very recent technique [9, 10] and has been explored by the group recently for CF [11, 12]. However, changes in the CF on nano-scale due to such treatment were not reported in details and hence presented in this research paper.

In this work, the concept of surface engineering of a composite with PTFE of varying sizes (from nano to micro scale) is explored by developing a series of composites with CF (untreated and CRNOP treated) and polyether-sulphone (PES). In depth investigations are reported on the induced distortions in the CF due to treatment along with the mechanical and tribological performance of surface engineered CRNOP treated composites.

Experimental

Materials

The carbon fabric (CF) was procured from Fibre Glast Development Corp. USA. PES polymer Veradel 3600P was supplied by Solvay Advanced Polymers, India in powder form. PTFE powders of three sizes (50–80 nm, 150–200 nm and 450–500 nm) were supplied by Shanghai SMEC Trading Co. China. Figure 1 shows the Field emission scanning electron micrographs (FESEM) of PTFE fillers. CRN(0.5%)OP was employed to CF and details are discussed in our earlier article [11].

Development of composites

Composites based upon CRNOP treated and untreated CF were developed using prepreg impregnation followed by compression molding technique and details are discussed elsewhere [12].

Surface designing of composites with PTFE

The top two prepregs of the composites were separately prepared with incorporation of PTFE. Since uniform

dispersion of NPs beyond 2 wt% is generally difficult, the amount of each type of PTFE on the surface was restricted to 2 wt%. This also enabled to bring out comparative aspects of PTFE sizes on enhancement of surface properties could be revealed. Powders of PES and PTFE (2 wt% of each size separately) were mixed in a high shear ball mill using zirconia balls in alcohol media for 16 h, followed by drying in a vacuum oven for 2 h. For deagglomeration of NPs, the dried mix was then sonicated with high intensity probe (chromtech, probe diameter 25 cm) in an alcohol medium for 20 min. After sonication in alcohol, the dried PES + PTFE mix was dissolved in dichloromethane, sonication process was also followed in this step to ensure deagglomeration of suspended PTFE particles. Hence the sonicated suspension of PTFE in the solution of PES was used for preparing two prepregs for each composite by impregnation technique as per method standardized in the laboratory [12]. The two PTFE tailored prepregs (on top surface) with eighteen untailed prepregs were compression molded at optimized temperature of 300 °C at a pressure 2 MPa. The composites were then cooled in a compressed condition. The five composites (Table 1) were developed and then cut with the help of isomet diamond cutter for different characterizations.

Characterization

The surfaces of fibers prior and after the CRNOP treatment were examined with FESEM (ZEISS, Supra 55). Finer details of the fiber surface were studied on the high resolution transmission microscopy (HRTEM): TechnaiG2 20 S-Twin model, operating at 200 kV. A longitudinal tow of CF was cut and embedded in epoxy resin solution (araldite LY-556 with HY-951 hardener). After solidification for 24 h, ultrathin sections (≈ 30 nm) from both the CF, CRNOP treated and untreated fibers were cut with ultramicrotome and supported on copper micro grids for HRTEM studies. Atomic force microscopy (AFM) studies were carried out to analyze the fiber surface roughness before and after plasma treatment. The fiber surface

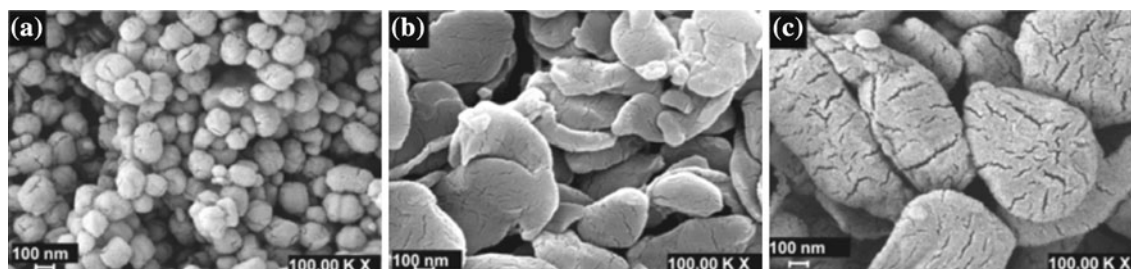


Fig. 1 High resolution FESEM ($\times 100$ k) micrographs of PTFE particles of different size **a** N—50 to 80 nm **b** SM—150 to 200 nm and **c** M—400 to 450 nm

Table 1 Details of developed series of composites

Designation of composites	Treatment of CF	Size/designation of PTFE fillers	Shape of fillers
PES _{CFU}	NIL	–	–
PES _{CF^T}	CRN(0.5)OP	–	–
PES _{CF^{TN}}	CRN(0.5)OP	PTFE 50–80 nm (N)	Highly spherical
PES _{CF^{TSM}}	CRN(0.5)OP	PTFE 150–200 nm (SM)	Sub rounded
PES _{CFTM}	CRN(0.5)OP	PTFE 400–450 nm (M)	Sub angular

CF carbon fabric, U untreated, T CRNOP treated, N nanometer PTFE 50–80 nm, SM submicron 150–200 nm, M Micrion-PTFE 400–450 nm, CRN(0.5)OP 0.5% oxygen in nitrogen

roughness was analyzed over a $2\ \mu\text{m} \times 2\ \mu\text{m}$ area. Studies were done on Nanonics MultiView scanning probe microscope, with transparent glass cantilever OptoProbe (tip diameter $< 10\ \text{nm}$).

X-ray diffraction studies in bulk and thin film diffraction geometry were done with Glancing angle X-ray diffraction (GAXRD); Phillips X'Pert, PRO-PW 3040. SEM (ZEISS, EVO-MA10) was used to study worn surfaces of composites. Renishaw inVia Raman spectrometer with 514 nm He–Ne laser and 785 nm near infrared laser excitation wavelength was used to record the spectra of fibers, polymers and composites. Theoretical void content in composites was calculated using ASTM 2734 and were in the range of 0.5% which confirms the void free composites.

Wear studies

Sliding wear studies were carried out on UMT-3MT Tribometer supplied by CETR, USA; in a pin-on-disc configuration discussed elsewhere [12]. The composite pin ($10\ \text{mm} \times 10\ \text{mm} \times 4\ \text{mm}$) was slid against a mild steel disc ($R_a \sim 0.2\ \mu\text{m}$) at a constant speed of 1 m/s and 1 sq. cm nominal contact area. The coefficient of friction (μ) as a function of time during sliding was recorded with the help of viewer software. The specific wear rate (K_0) was calculated using the equation:

$$K_0 = \frac{W}{\rho L d} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1} \quad (1)$$

where W is the weight loss in kg, ρ the density of pin in kg/m^3 , L the load in N and d the sliding distance in meters. The experiment was repeated for three times and the average of two closest values of weight loss was used for specific wear rate calculations.

Results and discussion

The plasma treatment has beneficially improved the physical and mechanical properties of CF-PES composites [12]. The interlaminar shear strength (ILSS) values of

composites increased up to 27% due to the CRNOP treatment which indicates the enhanced fiber matrix adhesion. Micrographs (FESEM) in Fig. 1a, b and c show the size and shape of three types of PTFE particles used for surface designing of composites. Nanometer range (50–80 nm) particles are highly spherical, while submicron (200–250 nm) and micron (400–450 nm) sized are sub rounded and sub angular, respectively. Figure 2a and b shows the FESEM images of treated and untreated fibers, treatment increased perforations and roughness on the fiber surface. As compared to crenulations on the untreated fiber surface, the deeper and narrower ridges at nanoscale can be easily visible on the treated fiber surface (Fig. 2b). Figure 3 shows HRTEM images of longitudinal thin section for untreated (Fig. 3a) and CRNOP treated (Fig. 3b) fibers. Both types of fibers have inter-planar spacing of 0.34 nm; typically observed for (210) planes of PAN-based CF and high purity carbon and graphite materials [13–15]. The micrographs show the orientation of small graphite crystallites for untreated and treated CF. Coexistence of crystalline and amorphous phases was observed, which is accordance to the literature [16, 17]. Warner et al. [18] suggested that the structure of PAN fibers is constitutive of ordered and amorphous domains with the length of the ordered regions ranging from 80 to 100 Å, roughly twice that of the disordered regions. During the process of fiber manufacturing the uneven distribution of stresses during the drawing step is the reason for existence of both the phases [16]. The distorted graphitic plane can be seen in the case of treated CF (Fig. 3b) which supports the results from the MRS studies as reported in our earlier article, [11] in which I_D/I_G ratio increased in the case of treated CF due to treatment. The planes are more smother and regular in the case of untreated CF (Fig. 3a). Distortion indicates the pitting on the fiber (as seen in FESEM studies Fig. 2) which eventually is responsible for improving its adhesion with the matrix.

AFM images for untreated and treated carbon fibers (Fig. 4) revealed that the surface etching was more on treated fibers which is in tune to the observations in FESEM studies (Fig. 2). Moreover, the deeper and narrower

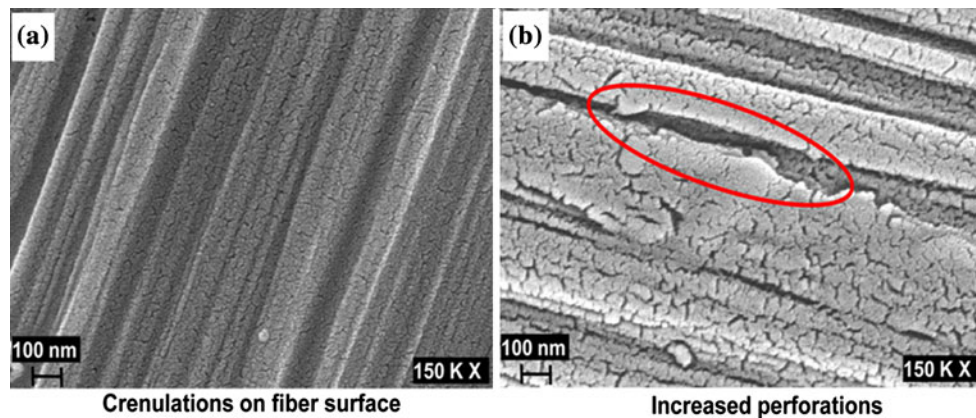


Fig. 2 High resolution FESEM ($\times 150$ k) micrographs of a carbon fibers **a** before treatment and **b** after CRNO(0.5)P treatment (Color figure online)

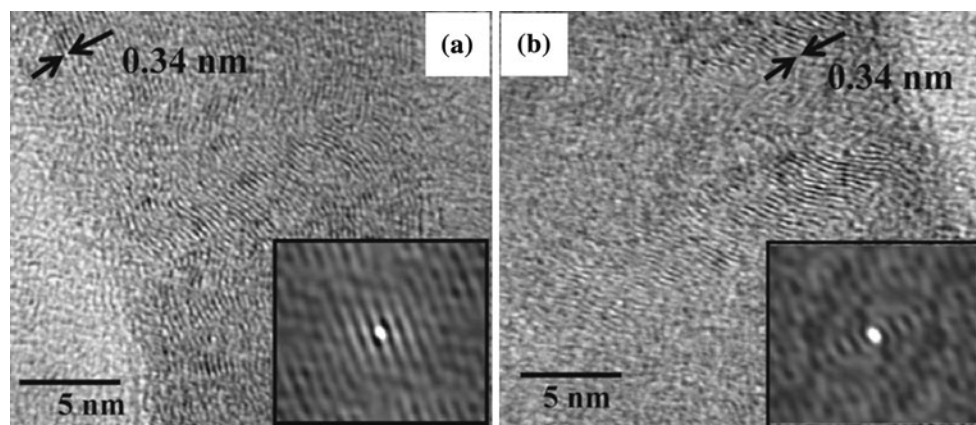


Fig. 3 HRTEM images of carbon fibers **a** untreated and **b** treated fibers

ridges were observed from both the studies, which are in accordance to the literature [19]. The fine striations on the untreated fiber surface were due to the spinning of the fiber precursor [20]. The average surface roughness (R_a) values for untreated and treated fibers were 38.4 nm and 66.3 nm, respectively, which confirmed the increase in surface area and alteration in the morphology. The increase in surface roughness of treated carbon fibers is beneficial for enhancing its reactivity towards matrix, since rougher fiber topography would lead to a higher degree of mechanical interlocking between the fiber and matrix [21].

The diffraction peak for carbon fibers (untreated and CRNOP treated) at $2\theta = 26.3^\circ$, 44.2° , 54.5° and 77.4° can be assigned to (002), (100), (004) and (110) planes, respectively (JCPDS-76-0152) in Fig. 5a, which appeared for PAN-based CF and well coherent to the literature [22]. The (002) diffraction profiles for both treated and untreated fibers are much narrower than the other peaks. Less prominently with the effect of CRNOP treatment, the main peak shifted from 26.3° to 26.5° with little broadening in size. In our earlier work ATR-FTIR studies

revealed the presence of oxygenated polar functional groups was confirmed on treated fibers [11]. The inclusion of O-atom on the treated fibers surface, (which is bigger than the C- atom) leads to the enhancement in lattice parameter and slight peak shifting as seen in Fig. 5a. Figure 5b shows the diffraction peak for PES micron powder; PTFE powder (N—50 to 80 nm, table 1) and ball milled PES and PTFE mix. (100) peak for crystalline nano PTFE is sharp as compared to its mixture with PES; micro PTFE and PES (M + PES) and amorphous PES. All above characterization results confirmed the changes on the fiber surface in nano-scale, due to CRNOP treatment, which is further responsible for enhanced fiber-matrix adhesion and improved performance properties of the composites.

Figure 6 shows the comparative tribo-performance (μ and K_0) for composites confirming that the inclusion of PTFE fillers on the surface of composites affected the sliding wear performance positively. The μ values for composites were in the range (0.07–0.25) while K_0 varied from 1.25 to 2.2×10^{-15} m³/Nm. The limiting load value

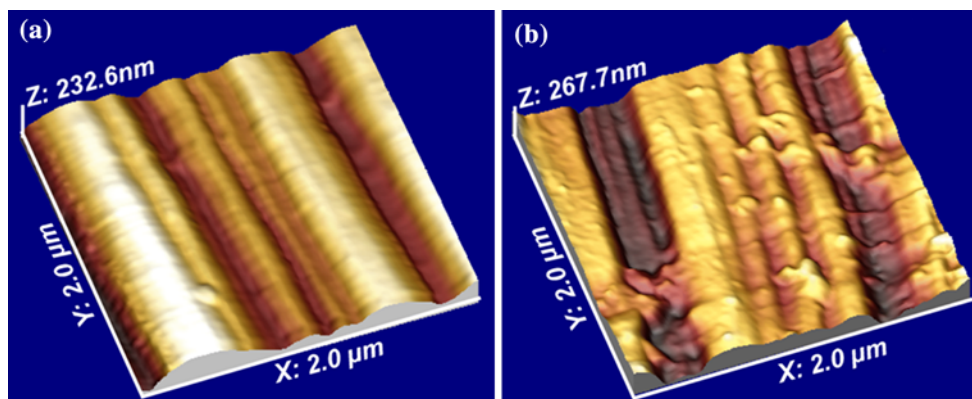


Fig. 4 AFM images of carbon fibers **a** untreated **b** CRNOP treated indicating increase in R_a value from 38.4 nm to 66.3 nm (Color figure online)

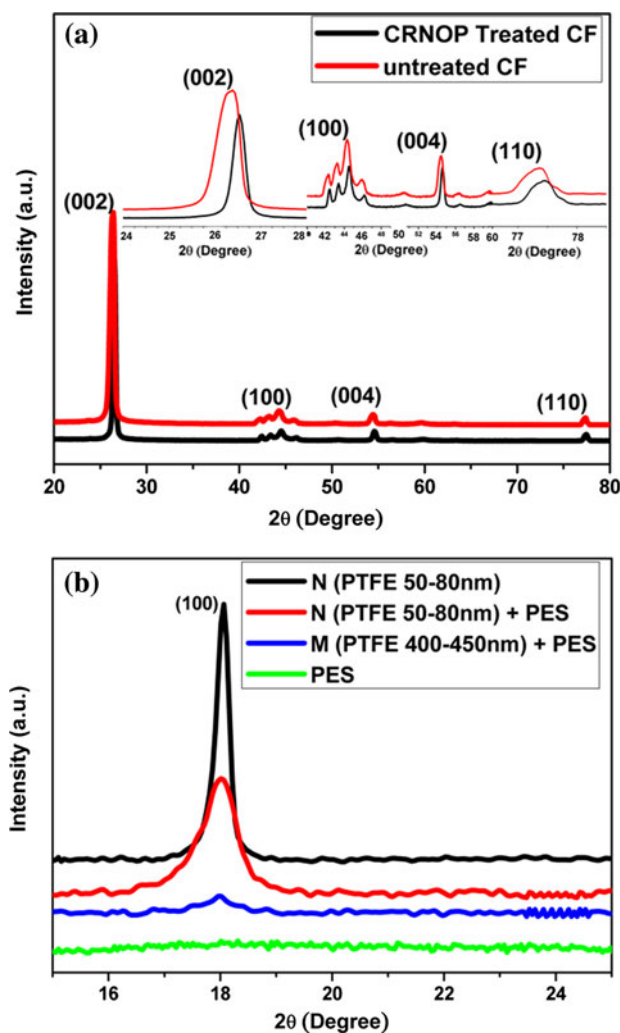


Fig. 5 GAXRD pattern for **a** CRNOP treated and untreated CF, **b** PTFE powders (N-nano powder; N + PES and M + PES are surface designed composites with nano and sub micron PTFE powders) (Color figure online)

for PES_{CFU} and PES_{CFT} composites was up to 700 N, while for tailored composites it increased from 800 to 950 N [23]. Especially for composite PES_{CFTN} (tailored with 50–80 nm

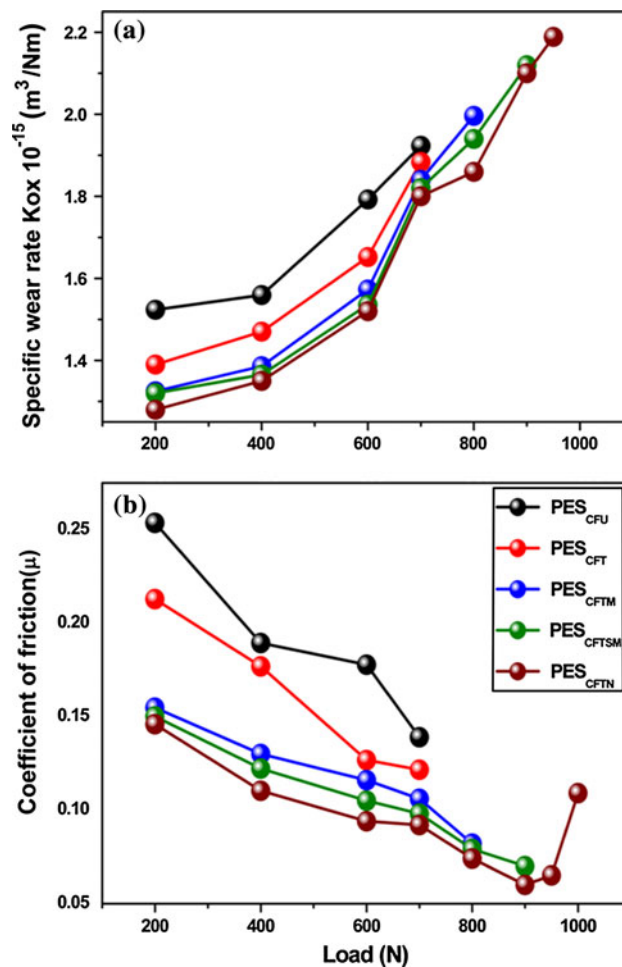


Fig. 6 **a** Specific wear rates. **b** Coefficient of friction, as a function of increasing load for all composites (Color figure online)

size PTFE) limiting load value was 950 N, μ value ≈ 0.07 and specific wear rate was $2.2 \times 10^{-15} \text{ m}^3/\text{Nm}$.

NPs have a very high surface area to volume ratio and hence provide large interfacial surface area, as a driving force for enhanced interaction with the counter surface [5].

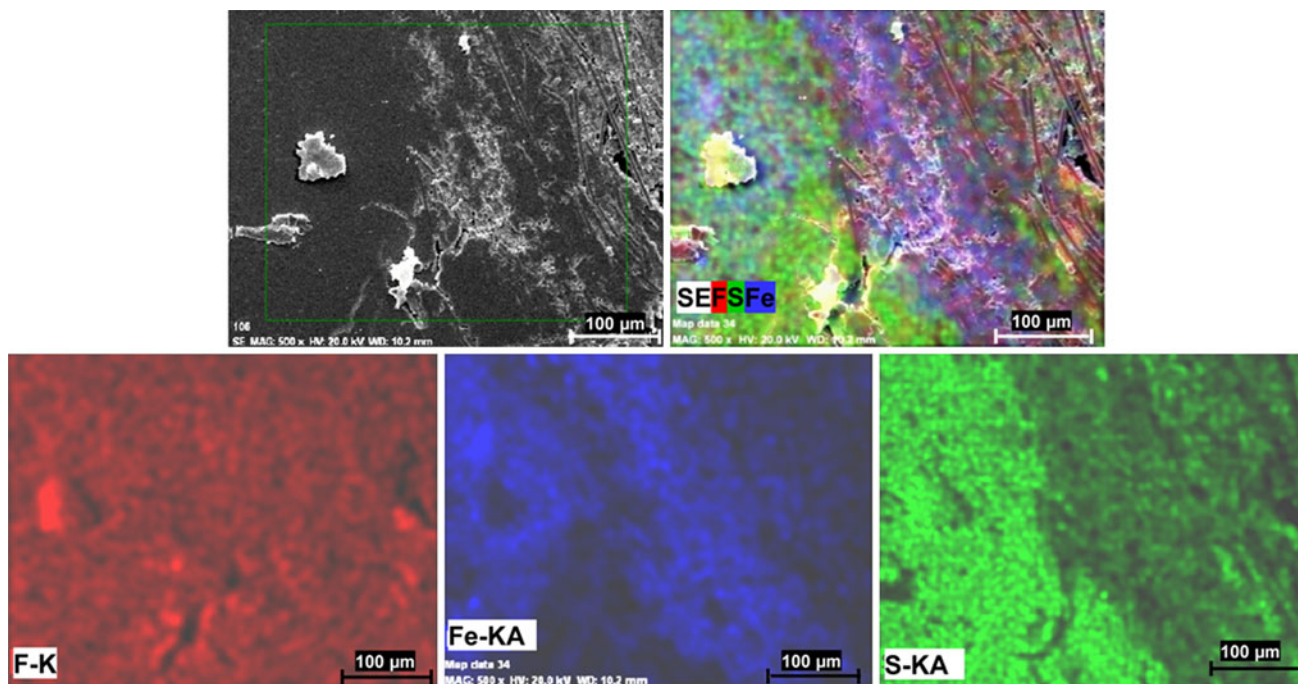


Fig. 7 Areal mapping EDAX analyses for PES_{CFTN} composite (Color figure online)

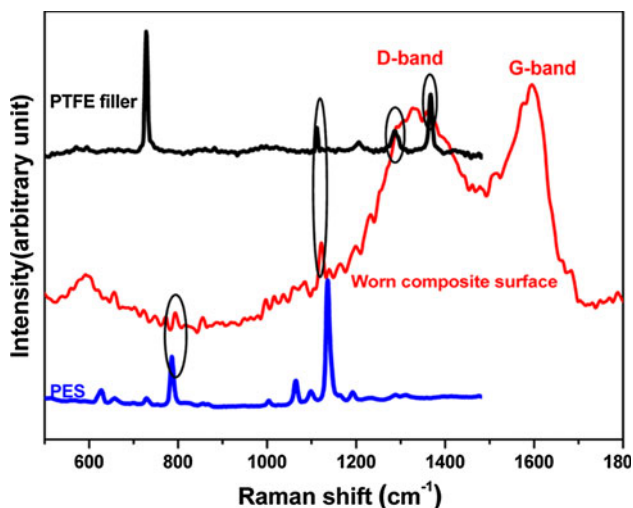


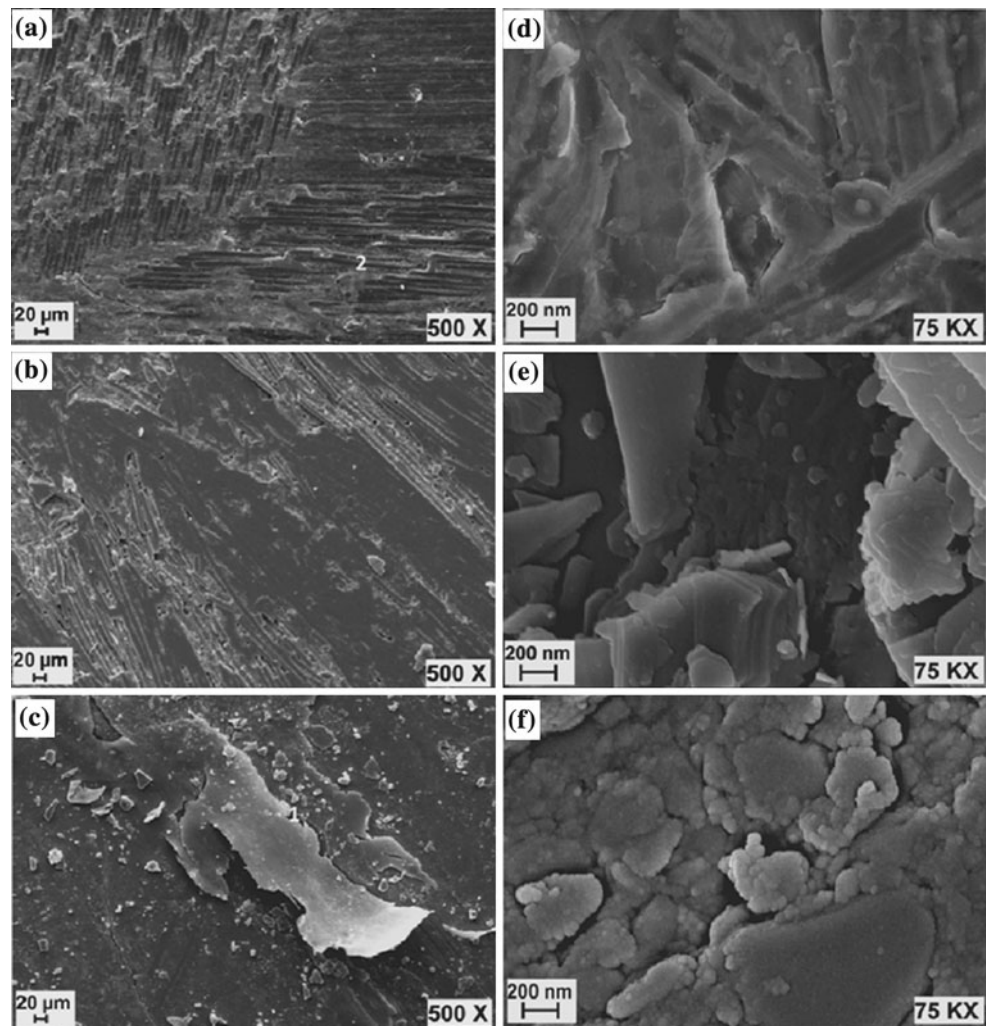
Fig. 8 Raman spectra for PTFE filler, PES polymer and worn PES_{CFTN} composites surface (Color figure online)

Spherical NPs provide high interfacial area between the fillers and matrix also. This leads to a better bonding between the two phases and hence better properties [24, 25]. PTFE, a high molecular weight fluorocarbon compound demonstrates mitigated London dispersive forces due to highly electronegative F⁻ atoms. In PTFE molecule, C–F forms non reactive and instantaneous polarized multi poles, with the increases in surface contact, the polarizability increases due to the dispersed electron clouds hence closer interaction between different molecules. At larger scale, the long chains of PTFE orient on the counter face

during sliding creating a fine coherent transfer film. The transfer film creates a low shear-strength interface with the bulk PTFE material [26]. Hence the interaction is between PTFE film and the PTFE containing composite leading to least possible adhesion and hence very low μ .

The film transferring ability depends on operating conditions and the size and amount of PTFE particles. Its application in nanosize however, is not reported in the literature. It was anticipated that nano-size PTFE would lead to the highest interaction with the counterface and hence would lead to the lowest μ and wear. Topographical smoothening and a rolling effect due to the inclusion of nano-fillers at the surface is the reason for improved friction and wear performance of PES_{CFTN} composite. During the wear process, NPs are removed from the surface of a matrix and can act as third body element in the contacting regions. The rolling effect of the NPs, especially at the edge of exposed fibers, reduce the shear stress in the contact region and hence the μ . This leads to the smoothening of topography of a composite surface. It also protects the fibers adhered to the matrix and results in increased fiber thinning before final removal of fibers from the matrix [27]. The rolling effect is also observed in the case of micro particulate inclusions, for which the small particles tends to tumble through the contact region and larger particles plough through it. There is a critical size of particle governing the transition from rolling to ploughing. To achieve the rolling, the ratio of maximum particle dimension to the minimum gap of contacting bodies must be exceeding the

Fig. 9 SEM micrographs ($\times 500$) of surface designed composites after wearing **a** PES_{CFT}, **b** PES_{CFTM} and **c** PES_{CFTN}; **d**, **e** and **f** are their respective high resolution FESEM images ($\times 75$ k) (700 N load at 1 m/s speed)



critical value which depends on the particle size. The hard micro sized particles and fillers abrade the counterface. This prevents the formation of a beneficial protective transfer film and increase the counter face roughness and hence the μ of the composite [28]. The NPs have potential to reduce abrasion that leads to these cascading events. NPs (<100 nm) are of the same size as the counterface asperities and polish the highest asperities and promote the development of transfer films. The transfer films shield the composite from direct asperity contact and damage [5]. These mechanisms as reported in the literature are responsible for beneficial influence of NPs on the tribo-performance in the present case.

Figure 7 shows the areal mapping EDAX analyses for worn PES_{CFTN} composites which confirm the uniform distribution of Fluorine on the surface (Red color). Blue color shows back-transferred Fe on the composite surface from the counter face. Existence of sulfur can be visible from green color mapping which confirms the PES matrix phase. MRS studies for CF in our earlier work supports the

HRTEM results in Fig. 2 by indicating the increased I_D/I_G ratio; hence induced distortion (reduced crystallinity) with plasma treatment to CF [11]. To confirm the inclusion of PTFE filler at the worn composite surface, MRS studies for worn composites and polymers were carried out. Figure 8 shows comparison among Raman spectra for pristine nano PTFE powder, PES powder and worn CF-PES composite surface tailored with nano PTFE filler. For PES, main peak of symmetric C–O–C stretching at 1154 cm^{-1} matches with the spectra for composite, also the deformation peak at 791 cm^{-1} [29] can be visible in the spectra. The main PTFE peaks at 1216 and 1300 cm^{-1} can be traced from the spectra of composites. An additional signal from PTFE spectra at 1118 cm^{-1} matches with the spectra of composites.

Figure 9 shows SEM micrographs of worn surfaces of surface designed composites; (a) PES_{CFT}, (b) PES_{CFTM} and (c) PES_{CFTN}. Micrographs (d), (e) and (f) are their respective high resolution FESEM images ($\times 75$ k) at 600 N load, 1 m/s speed and sliding time 2 h. When the

topography of composites with and without PTFE is compared, it can be clearly seen that PTFE has smoothed the surface and spread over the fibers and matrix. Nano-PTFE has spread over in such a way that it has formed a thin and coherent film on the surface (marked as 1 in Fig. 9c) which was responsible for its lowest μ . The elongated and uplifted film during shearing in the middle of the micrograph indicates how thin ($<0.1 \mu\text{m}$) and coherent the film was. The nano-fillers (Fig. 9f) and micro fillers (Fig. 9e) are clearly visible with high resolution FESEM images of worn composites surfaces. Increased fiber damage and easy peeling off of fibers leading to breakage (Fig. 9a) is responsible for high wear of untailed composite.

Conclusions

The concept of CRNOP treatment and surface designing with micron, sub-micron and nano sized PTFE proved beneficial for achieving high wear resistance, low friction and high life span of a composite containing CF and Polyethersulphone. The treatment to the fibers led to changes in the surface roughness (as evident from AFM studies), deep crenulations and pitting (as evident from FESEM studies), distortion in graphitic structure (as evident from HRTEM studies). All these led to better fiber-matrix adhesion and hence stronger composite. The idea of surface engineering of a composite with SLs (rather than incorporating in the bulk) to safeguard the composite from an un-intentional reduction in the strength properties and increase in the cost proved successful. The nano-PTFE proved most beneficial followed by sub-micron sized PTFE and then micron sized PTFE. Based on SEM and FESEM analyses it was concluded that the enhanced fiber-matrix adhesion led to the reduction in the severity of wear-events such as wear breakage, fiber peeling off from the matrix, fiber pulverization etc. Instead, wear thinning was prominently observed and was concluded to be responsible for less wear of treated fabric composites.

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