

Nano and Micro PTFE for Surface Lubrication of Carbon Fabric Reinforced Polyethersulphone Composites

Jayashree Bijwe and Mohit Sharma

Abstract Carbon fibre/fabric (CF) is a privileged reinforcement for advanced polymer composites in tribological applications where performance is primary criteria rather than the cost due to the combination of distinct properties such as high specific strength, thermo-oxidative resistance, thermal and electrical conductivity along with self-lubricity etc. However problems associated with its chemical inertness and surface lipophobicity towards majority of matrix materials need special attention, as these directly affect final properties of a composite. From tribological point of view, surface engineering of composites is very much advantageous in addition to fibrous reinforcement. This chapter reports on the newly developed technique to modify the surface of carbon fabric—Polyethersulphone (CF-PES) composite with Polytetrafluoroethylene (PTFE) micro and nano particles; to improve the tribological properties. Prior to the composite preparation plasma treatment was employed for CF surface modification to promote fiber matrix interfacial adhesion and mechanical interlocking which further improves final composites strength and wear resistance properties. Both the treatment methods; first for fiber surface alteration and secondly for composite surface, proved beneficial to enhance composites performance. The inclusion of nano scale PTFE particles on the surface of a composite proved to be more efficient than the micro-scale PTFE particles to improve tribo-performance of CF-PES composite.

J. Bijwe (✉)

Industrial Tribology Machine Dynamics and Maintenance Engineering Centre (ITMMEC),
Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India
e-mail: jbijwe@gmail.com

M. Sharma

Leibniz-Institut für Polymerforschung Dresden, e.V. Hohe Strasse 6, 01069 Dresden, Germany
e-mail: mohittiet@gmail.com

1 Introduction

1.1 Fabric Reinforced Polymer Composites

For most applications virgin polymers are not the right choices mainly because of poor strength properties. Reinforcements for polymers, in various forms such as particulates, spheres (hollow, solid etc.) and fibrous (short, long, woven, nonwoven etc.) are preferred depending on prerequisite application. Each reinforcement form has its own advantages and limitations. Short fibers, for example offer easy injection moldability for thermoplastic polymer composites. The strength offered, however, is moderate and depends on fiber alignment with respect to the loading direction. Long fibers on the other hand offer very high strength, but only in one direction and that too at the cost of easy processability. These are generally processed by compression molding and hence fiber handling is a tough job. Fabric reinforcement on the other hand offers very high strength in two directions along with easier processability compared to the composites with long fibers. For tribo—materials, most popular fibrous reinforcements consists of glass, carbon, graphite, Aramid etc. Again each has its own advantages and limitations. Glass fibers are least expensive and offer moderate strength and wear resistance (W_R) at the cost of increased coefficient of friction (μ); damage the counterface, by abrasion generally and are used in combination with solid lubricants (SLs). Aramid fibers are of moderate cost, offer considerable W_R resistance and strength without excessive incremental in the μ value, neither damages the counterface. However, their temperature resistance is poor. On the other hand Carbon/graphite fibers are most expensive with excellent; specific strength, thermal conductivity and self-lubricity properties.

1.2 Solid Lubricants for Improving Tribological Performance

For tribological applications, advanced polymer composites are preferably used with fibers/fabric reinforcements along with SLs. SLs have lower surface energy and offer less resistance to shearing and hence low μ values. For tribological purpose the most popular SLs are PTFE, graphite, white graphite (hexa boron nitride/hBN), MoS_2 etc. [1, 2].

1.3 Need for Surface Tailoring of Composites

While designing the high performance tribo-composite (e.g. dry bearing) which can survive under harsh operating conditions; matrix, fillers and reinforcement are selected very judiciously. Such specialty polymers and reinforcements are

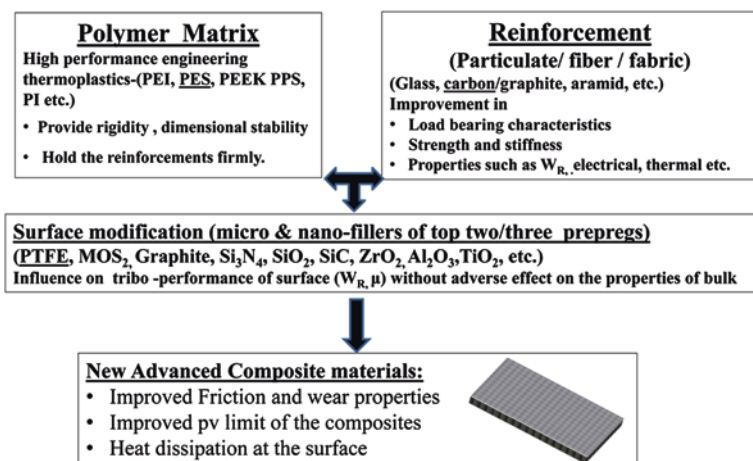


Fig. 1 Schematic surface designing of Polymer Composites

essential but generally expensive. Since tribological composites need high performing surfaces from friction and wear point of view, use of these expensive materials in the bulk is not essential always. SLs being low surface energy materials if added in the bulk of composite, improves tribo-performance at the cost of significant deterioration in the strength apart from unnecessary increase in the cost. It will be wise use the SLs only on surface rather than in the bulk or implement the concept of graded composites in which surface, subsurface and bulk are tailored judiciously with various matrices and reinforcements in such a way that the desired performance can be achieved with adequate cost. (For dry bearings, surfaces should have very low μ , low wear, high thermal conductivity, low expansion and high counter face friendliness, fatigue resistance while bulk should have desired mechanical strength and high thermal conductivity). Interestingly no such efforts are reported in open literature though peripheral information is available in few patent forms [3, 4].

Figure 1 shows the schematic to signpost the judicious importance of each constituent for surface designed advanced polymeric composites which finally attributes to enhanced tribological performance.

A little is reported on the exploration of concept of surface engineering of polymeric bearings [5]. Bijwe et al. [5] prepared surface-tailored composites based on commingled yarns of carbon fiber and Polyetheretherketone (PEEK) using autoclave method. The composites were surface modified with micro sized particles of graphite, MoS_2 , copper and PTFE either in isolation or in combination in different proportions in the top fabric layers rather than their inclusion in the bulk. PTFE in various forms, such as particulate (micron sized), wool, short fibers, long fibers, etc., was used to investigate benefits endowed by the surface modifications. Among all SLs PTFE proved

most promising. The long PTFE fibers on the surface proved most beneficial as compared to other forms to improve tribological performance of composites without appreciable loss in the strength. PTFE fiber inclusion removed the stick–slip problem associated with the unmodified surface; reduced μ from 0.6 to 0.12 and enhanced the W_R approximately by 70 times. The placement of SLs however, was done manually and proper technique was not evolved in these preliminary studies.

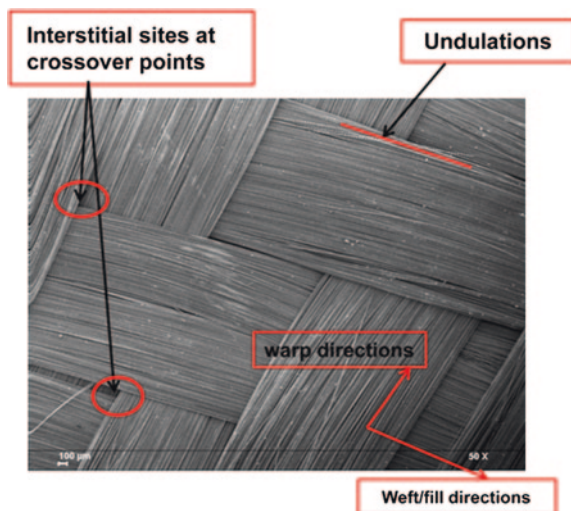
1.4 Nano-Fillers for Tribo-Performance Enhancement and Involved Mechanisms

Development of polymeric nano-composites is the most sought research area from last decade due to the multi-fold potential of nano fillers as performance enhancers when added in small doses [5–13]. The prominent features of nano-fillers are;

1. Nano-particles (NPs) have a very high surface area to volume ratio and hence provide very large interfacial surface area, as a driving force for enhanced interaction with other surface, diffusion, especially at elevated temperature etc.
2. A very low content (generally <2–3 wt %) provides exceptional increase in mechanical strength properties apart from thermal, electrical and biological.

During the wear process, NPs are removed from the surface of a matrix and can act as a 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 [14]. This leads to the spontaneous reduction of grooving/cutting wear by the hard counterpart asperities and smoothening of topography of a surface of a composite. It also protects the fibers adhering to the matrix and results in increased fiber thinning rather than breaking before final removal of fibers from the matrix [6–8, 15]. The rolling effect of NPs attributes to the reduction in μ and hence the frictional heating at the tribo couple. The rolling effect is also observed in the case of micro particulate inclusions, for which the small particles tend to tumble through contact region and larger particles plough through it [5, 15]. There is a critical value of the size of a particle governing their transition from rolling to ploughing. To achieve the rolling, the ratio of maximum particle dimension to the minimum gap of contacting bodies must exceed the critical value which depends on the particle itself [16]. The hard micro sized particles and fillers may abrade the counterface. This prevents the formation of a protective transfer film, which increase the counter face roughness and hence the μ of the composite [17]. The NPs have the potential to reduce the abrasion that leads to these cascading and problematic events NPs (<100 nm) are of the same size as the counterface asperities and polish the tallest asperities and promote the development of transfer films. The transfer films shield the composite from direct asperity contact and damage [14]. This film converts the adhesive wear to “like on like” sliding pairs and hence the severity of wear reduces drastically [7, 18].

Fig. 2 Fiber architecture of 2×2 twill weave carbon fabric [20]



The quantification of advantages in tribology due to variation in size of fillers (nano-sub-micro, micro etc.) is essential. Unfortunately it is not addressed in the literature and needs to be investigated in details. Recently authors have reported on such efforts using PTFE as a solid lubricant for surface modification, Polyethersulphone (PES) as a matrix and carbon fabric (surface treated and untreated) as a reinforcement [19] and the essence of the findings are reported in the subsequent sections.

2 Materials and Methodology

2.1 Details of Selected Materials and Methods

2.1.1 Reinforcement

The carbon fabric (CF) 3 K, 2×2 twill weave (Fig. 2) was used as reinforcement and was procured from Fiber Glast Corporation, USA.

2.1.2 Matrix Material

Thermoplastic Polyethersulphone (PES) Veradel 3600P procured from Solvay Advanced Polymer India was selected as a matrix material for development of composites. PES is an amorphous, amber colored, transparent, high performance, heat-resistant and semi tough engineering thermoplastic polymer having density



Fig. 3 FESEM micrographs of selected PTFE particles [19, 20]

1.37 g/cm³. It has a good thermal stability and high continuous use temperature (up to 200 °C). PES has a glass transition temperature (T_g) of 215 °C and a melting temperature (T_m) range of 300–380 °C. It has high hydrolytic stability as compared to the other transparent thermoplastics polymers.

2.1.3 Selection of a Solid Lubricant: Polytetrafluoroethylene

PTFE is a white colored thermoplastic crystalline polymer with a density of 2.2 g/cm³. Its T_g and T_m are −20 and 321 °C; respectively. Due to the robust nature of molecular bonds in its structure; PTFE is highly resistive to UV radiation and most of the chemicals except alkali metals and elemental fluorine. It retains these properties over a very wide range of temperatures. For surface modification of composites, three sizes of PTFE (micro- 400–450 nm, sub-micro- 200–250 nm and nano- 50–80 nm) as confirmed from FESEM studies (Fig. 3) were selected.

2.2 Surface Treatment of Carbon Fabric

2.2.1 Cold Remote Nitrogen Oxygen Plasma

Generally fibers are not always compatible with the polymer matrices and are provided with various types of sizing by the supplier to enhance their wettability with the selected matrices. Carbon fibers are known for their inertness towards the matrices leading to less performing composite and hence require special attention after procuring from the supplier. Various CF surface treatments; such as acid, plasma, rare earth, gamma treatment are reported successfully in the literature with varying benefits [21–24] and newer and more effective methods are continuously being tried by researchers.

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 research areas. In this regards, cold remote nitrogen plasma (CRNP) treatment with 0.5 % oxygen is a modified process and recently proved

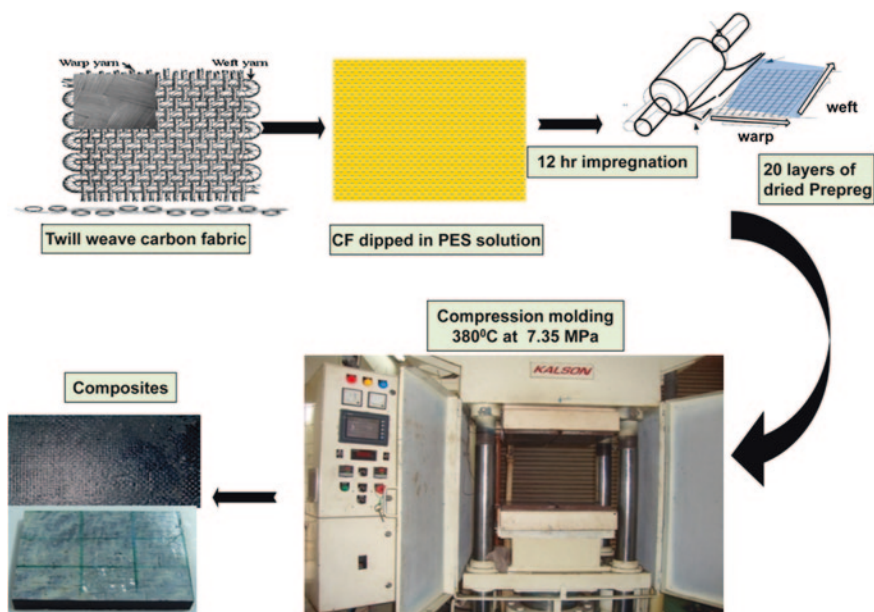


Fig. 4 Schematic of fabrication of CF-PES composites using compression molding [20]

to be successful [22]. The carbon fabric modified with this Cold Remote Nitrogen Oxygen Plasma (CRNOP) technique this was used for reinforcement. Unmodified CF was also selected to quantify the benefits due to surface modification of fabric. (The work involves two surface modifications; first that of fibers and second that of surface of a composite with PTFE.)

2.3 Development of Composites

2.3.1 Selection of a Processing Technique

Solution impregnation technique was selected since it leads to homogenous distribution of a matrix throughout the prepregs including cross-over points in the weave which results the best performance of the composites. Figure 4 shows the schematic for fabrication of composites [20]. Twenty pieces of CF plies (28×28 cm) were cut from the roll were immersed in the solution of PES in dichloromethane (DCM) (20 wt %) for twelve hrs in a properly sealed steel container. The prepregs were taken out carefully avoiding the misalignment of the weave and dried in an oven for an hour at 100°C in a stretched condition and were stacked in a steel mold. PTFE coated glass fabric was placed on the top and bottom of the stacked prepregs as a mold release agent. The mold was then heated in

a compression molding machine to a temperature of 380–390 °C for 20 min under a pressure of 7.3 MPa. The composites were then cooled in a compressed condition and then cut with the help of diamond cutter for different mechanical (as per ASTM standards) and tribological characterizations. This composite was treated as a composite with unmodified surface. Two such composites were developed containing CF with and without CRNOP treatment.

2.3.2 Novel Technique for Surface Modification of Composites

A modified impregnation method was used to develop surface tailored composites with PTFE of different sizes. The surface designing was done for only top two layers.

PES and PTFE powders in a selected composition (2 wt % of PTFE in PES) were mixed in a high shear ball mill using zirconia balls in an alcohol media for 16 h. Batches prepared with all PTFE powders were dried in vacuum oven for 2 h. The dried mix was then probe sonicated in an ethyl alcohol medium for 20 min to achieve more homogeneous mixing and de-agglomeration of NPs. The solution impregnation technique (discussed in [Sect. 2.3.1](#)) was then used to prepare two prepregs for the surface.

The sequence of applying temperature and pressure was optimized (temperature from 280 to 380 °C in the steps of 20 °C and pressure in the steps of 1 MPa up to 6 MPa). At higher applied temperature and pressure, matrix bleeding and displacement of fibers were observed. Hence, the two tailored prepregs with eighteen untailored prepregs were compression molded under optimized conditions followed by natural cooling under compressed state to the ambient temperature.

3 Characterization of Carbon Fibers

Various surface characterization techniques were adopted to analyze the effect of plasma treatment on the CF surface.

3.1 Field Emission Scanning Electron Microscopy

The surfaces of fibers prior and after treatment were examined by Field emission Scanning Electron Microscopy (FESEM). Figure 5 shows the FESEM images of untreated and plasma treated fibers indicating the increased perforations and roughness of the fiber due to the treatment, which was responsible for better fiber-matrix mechanical interlocking and hence enhanced adhesion. High resolution FESEM micrographs in Fig. 5b indicate deeper and narrower ridges along the length of the treated fibers. In the process of composite manufacturing during

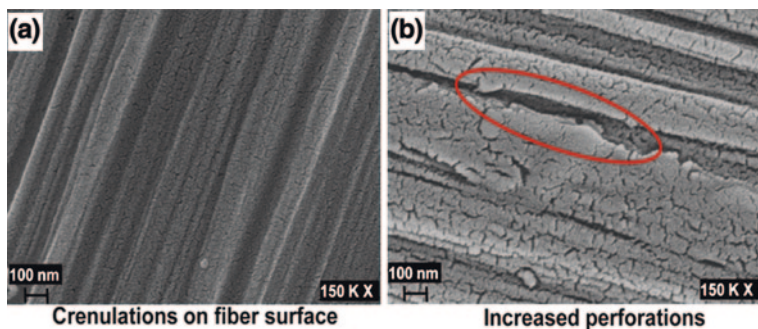
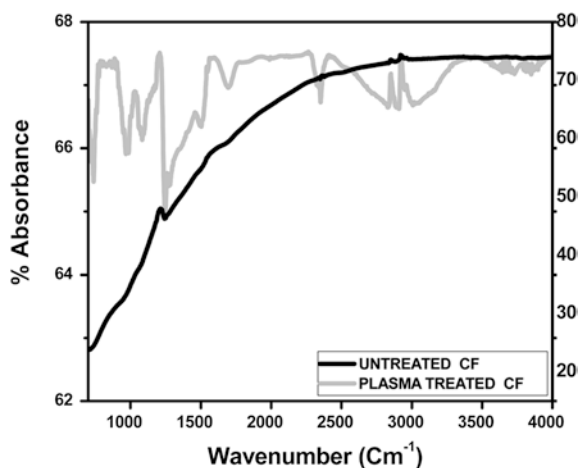


Fig. 5 High resolution FESEM (Mag. $\times 150$ K) micrographs of a carbon fiber **a** before treatment **b** after plasma treatment [19, 20]

Fig. 6 ATR-FTIR spectra of untreated and plasma treated CF [22]



compression molding, groves on the fiber surface acts as duct for polymer melt to flow and hence melt trapped in between the ridges. Hence, fiber-matrix mechanical interlocking with treated fibers is better.

3.2 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

In order to investigate the possible changes in chemical composition of CF by plasma treatment, Attenuated total reflectance Fourier transform infrared spectroscopy (ATRF-TIR) analysis (Fig. 6) was done in mid infrared range ($700\text{--}4,000\text{ cm}^{-1}$). Spectrum of untreated fiber does not show any significant peaks

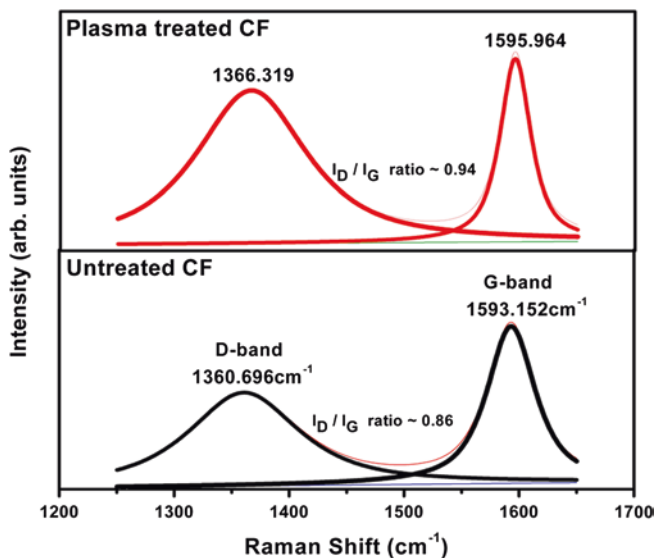


Fig. 7 Raman spectra of the untreated and plasma treated carbon fibers [22]

while that of plasma treated fibers, presence of oxygenated polar functional groups was observed. Ether, carboxyl and carbonyl groups were observed corresponding to wave number range $950\text{--}1,200$, $1,650\text{--}1,710\text{ cm}^{-1}$, respectively. These functional groups were responsible for improvement in adhesion between the matrix and fabric.

3.3 Micro Raman Spectroscopy

Carbon materials, such as carbon fibers and other sp^3 bonded amorphous carbons are strong Raman scatterers and the Micro Raman Spectroscopy (MRS) technique enables to distinguish between various structural organizations in these materials [25–27]. The first-order Raman spectra bands with peak positions $1,360$ and $1,593\text{ cm}^{-1}$ are the main features of carbon materials and are called D bands (disordered) and G bands (graphitic), respectively [28–31].

The degree of structural disorder on the surface of CF due to CRNOP treatment was characterized by the ratio of integrated intensity of disorder induced (I_D) to Raman allowed band (I_G). The ratio I_D/I_G (Fig. 7) showed slight increase and a decrease in surface crystallite size (L_a). The size of crystallites located in the surface regions (L_a) was calculated using the empirical formula by Tuinstra and Koenig [32]; L_a for treated and untreated CF was 4.68 and 51.6 nm , respectively. During surface treatment graphitic microstructure of CF is partially destroyed,

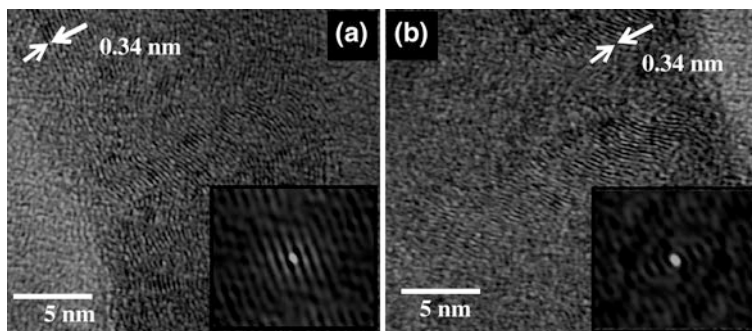


Fig. 8 HRTEM images of carbon fibers; **a** untreated, **b** plasma treated fibers; **c** and **d** are their corresponding auto correlated images, respectively [20]

the crystallite size is reduced, and the activity of the graphite crystallite boundary is improved [33, 34]. Figure 8 supports this by indicating the increased I_D/I_G ratio, hence induced distortion (reduced crystallinity) due to treatment to CF.

3.4 High Resolution Transmission Electron Microscopy

High Resolution Transmission Electron Microscopy (HRTEM) is an indispensable tool for examining the finer details of the fiber surface. It was preferred to compare the induced distortion in the graphitic planes of treated and untreated CF.

Figure 8 shows HRTEM images of longitudinal thin section for untreated and treated fibers. Both 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 [35–37]. The micrographs show the orientation of small graphite crystallites in CF. Both shows the coexistence of crystalline and amorphous phases which is accordance to the literature [38, 39]. Warner et al. [40] 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 fiber manufacturing process uneven distribution of stresses during the drawing step leads to the existence of both the phases [38]. The auto correlated images of small sections are shown in respective inserts. While comparing the inserts, the distorted graphitic plane can be easily seen in the case of treated CF which supports the results from Raman spectroscopic studies (I_D/I_G ratio found increased in case of treated CF). The planes are more smoother and regular in case of untreated CF. Distortion can be correlated with pitting on CF and hence improves their compatibility with the matrix material (FESEM studies in Sect. 3.1).

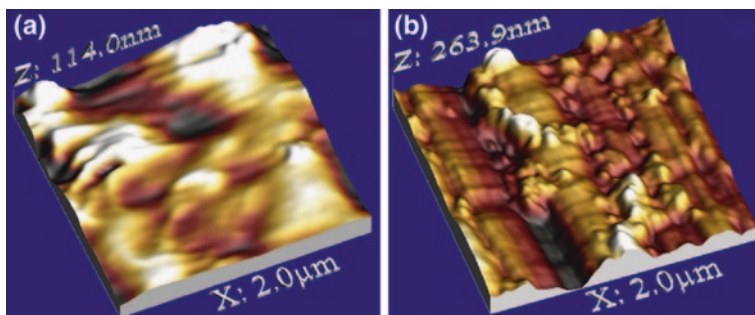


Fig. 9 AFM images of carbon fibers; **a** untreated **b** Plasma treated indicating increase in surface roughness from 114 to 264 nm [19, 20]

3.5 Atomic Force Microscopy

Atomic Force Microscopy (AFM) studies (Fig. 9) were carried out to analyze the topographical and morphological changes induced on the surface of CF due to plasma treatment. Fiber tows of untreated and treated CF were mounted separately on the stainless steel magnetic stubs. The fine striations on the untreated carbon fiber surface were due to the spinning of the fiber precursor [41]. The observed features similar to FESEM studies such as surface etching, increased perforation and presences of deeper and narrower ridges were more clearly seen on the treated fiber. The average surface roughness values for untreated and treated carbon fibers were 23.28 and 52.43 nm respectively, which confirmed the increase in surface area and alteration in morphology due to the treatment. The increase in surface roughness of treated carbon fibers is beneficial for enhance their reactivity towards matrix materials, since a rougher fiber topography would lead to a higher degree of mechanical interlocking between fiber and matrix [42].

3.6 Fiber: Matrix Adhesion Test

A simple test was performed to ensure enhancement in fiber-matrix adhesion due to treatment. A small sample of fibers (treated and untreated) was dipped in PES solution (in DCM 20 wt %) for 10 min followed by careful withdrawal of the fibers and drying in identical way. The difference in layer of matrix adhering to the fiber strand was examined with SEM (Fig. 10). Figure 10b confirms more polymer adhered to the treated fiber rather than the untreated one. As compare to untreated fibers (Sect. 3.1) deeper channels (along longitudinal axis) on the treated CF surface provide more surface areas (denier per filament) for polymer to adhere adequately, which in turns responsible for enhanced adhesion and hence the better mechanical interlocking between the fiber and matrix.

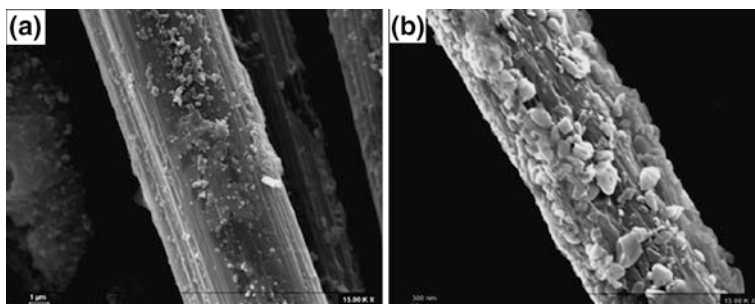


Fig. 10 SEM ($\times 15$ K) of impregnated fibers; **a** before treatment **b** after plasma treatment [20]

The analysis from all surface characterization techniques revealed that the plasma treatment on fiber surface altered its original inertness of and led to enhancement in fiber matrix adhesion, which resulted in improved performance properties of their composites as discussed in subsequent section.

3.7 Mechanical Strength of CF

The reduction in single fiber strength due to the fiber modification methods is a critical issue. Generally, fiber surface modification method increase the fiber-matrix interfacial strength but at the cost of decremented single fiber strength properties. The CRNOP treatment reduced the strength of a carbon fiber (5 to 10 %) [22].

4 Characterization of Developed Composites

The composites developed were characterized for their physical, mechanical and tribological properties as discussed in following sections.

4.1 Characterization of Composites with Treated and Untreated CF

Table 1 shows the details and designations of composites with tailored surfaces while Table 2 summarizes the properties of composites and positive changes due to CRNOP treated fabric in a composite. The reinforcement influenced the heat distortion temperature of PES appreciably (25–30 °C). However, the CF treatment

Table 1 Details of unmodified and PTFE modified PES-CF composites [19, 20]

Designations of composites ^a	Av. PTFE particle size (FESEM studies) (nm)	Shape of PTFE fillers
PES _{CFU}	—	—
PES _{CF}	—	—
PES _{CF_{NT}}	50–80	Highly spherical
PES _{CF_{TS}}	200–250	Sub rounded
PES _{CF_{TM}}	400–450	Sub angular

^aPES_{CFU}—Composites with untreated CF

PES_{CF}—Composites with treated CF

PES_{CF_{NT}}—Composite with treated CF and nano- sized (50–80 nm) PTFE on the surface

PES_{CF_{TS}}—Composite with treated CF and submicron sized (150–200 nm) PTFE on the surface

PES_{CF_{TM}}—Composite with treated CF and micron sized (400–450 nm) PTFE on the surface

Table 2 Physical and mechanical properties of CF-PES composites reinforced with untreated and plasma treated CF [20]

Properties/materials	PES	PES _{CFU}	PES _{CF}	% changes due to CF treatment
Fiber weight (%)	—	67.50	68.24	—
Void fraction	—	0.47	0.37	↓ 21.3
Density (g/cm ³)	1.37	1.52	1.54	↑ 1.3
HDT ASTM D648 (°C)	204	227	233	↑ 2.6
Tensile strength (MPa)	84	744	778	↑ 4.4
Tensile modulus (GPa)	3	65	76	↑ 14.4
Toughness (MPa)	60	4.1	4.3	↑ 4.7
Flexural strength (MPa)	112	692	835	↑ 17.1
Flexural modulus (GPa)	2.8	54	68	↑ 20.6
Interlaminar shear strength (MPa)	—	36	46	↑ 21.7

had almost negligible effect on the HDT values of the composites (1.5–2.5 %). Composites containing plasma treated CF proved superior to those with untreated CF confirming the improved fiber-matrix adhesion as a result of treatment due to the increment in fiber matrix mechanical interlocking.

4.2 Tribo-Characterization of Composites

Performance of composites was evaluated in adhesive sliding wear mode using pin on disc configuration as discussed in following subsection.

4.2.1 Methodology for Tribo-Evaluation of Composites

Tribological studies in adhesive wear mode were carried out on UMT-3MT Tribometer supplied by CETR, USA. Prior to the experiment the composite pin slid against a rough mild steel disc for uniform contact. Initial weight of the pin

was measured after cleaning ultrasonically with petroleum ether followed by drying. The pin was slid against a mild steel disc (Ra values range 0.1–0.2 μm) at a constant speed of 1 m/s. After the experiment, pin was again weighed with an accuracy of 0.0001 g and weight loss readings were used to calculate the specific wear rate (K_0) of composites. 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.

4.2.2 Tribological Aspects of PTFE as a Solid Lubricant

PTFE has a peculiar morphological and molecular structure and has a high molecular weight inert fluorocarbon compound which 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. Tribological point of view, this is the most exploited solid lubricant in various amounts and sizes in the bulk of the composites barring nano-size, in general. In PTFE fluorine atoms are close enough to form a smooth cylindrical surface against which other molecules can easily slide. At larger scale, the long chains of PTFE orient on the counter face surface during sliding creating a fine coherent transfer film. The transfer film creates a low shear-strength interface with the bulk PTFE material [43]. Hence the interaction is between PTFE film and the PTFE in composite leading to least possible adhesion and hence very low μ . This film transferring ability depends on the size and amount of PTFE particles apart from operating conditions.

4.2.3 Tribo-Characterization of Composites

The essence of performance of composites is shown in Table 3 which elaborates on the influence of two modifications (plasma treatment to the CF and PTFE on the surface of a composite) on W_R wear resistance and μ . Overall W_R of the composites was in the range 4.8 to 7.8×10^{14} Nm/m^3 , which is rated as quite high and μ was in the range 0.06–0.25 which is a desirable range for such composites. In all the cases with increase in load W_R and μ decreased appreciably and these are the general trends reported in the literature.

Table 3 The essence of CF-PES composites performance due to treatments (plasma treatment to the CF and PTFE on the surface of a composite) [20]

Composites	Limit load* (N)	Wear resistance (W_R) $\times 10^{14}$ Nm/m ³ under load ($\times 100$ N)						Coefficient of friction (μ) under load ($\times 100$ N)					
		2	4	6	7	8	9.5	2	4	6	7	8	9.5
PES _{CFU}	700	6.5	6.4	5.6	5.2	F	F	0.25	0.19	0.18	0.14	F	F
PES _{CFT}	700	7.2	7.1	6.0	5.3	F	F	0.21	0.18	0.13	0.12	F	F
PES _{CFTM}	800	7.5	7.2	6.4	5.7	5.0	F	0.16	0.13	0.11	0.11	0.09	F
PES _{CFTSM}	900	7.6	7.3	6.5	5.4	5.1	F	0.15	0.12	0.10	0.10	0.08	F
PES _{CFTN}	950	7.8	7.4	6.6	5.6	5.4	4.8	0.14	0.11	0.09	0.09	0.07	0.06

*Shows failure of composite under the selected load

Influence of Plasma Treatment on Fibers

The plasma treatment led to increase in W_R and decreased μ (Table 3) of CF-PES composites which is a significant improvement. As compared to the untreated ones, μ values of treated CF-PES composite lowered by $\sim 15\%$ with almost equal increment in wear resistance. The treatment to the fibers led to the increase in the surface roughness and inclusion of functional groups which resulted in more fiber-matrix adhesion as discussed in the earlier section; leading to more resistance to peeling off or breakage of fibers during sliding and hence lower wear.

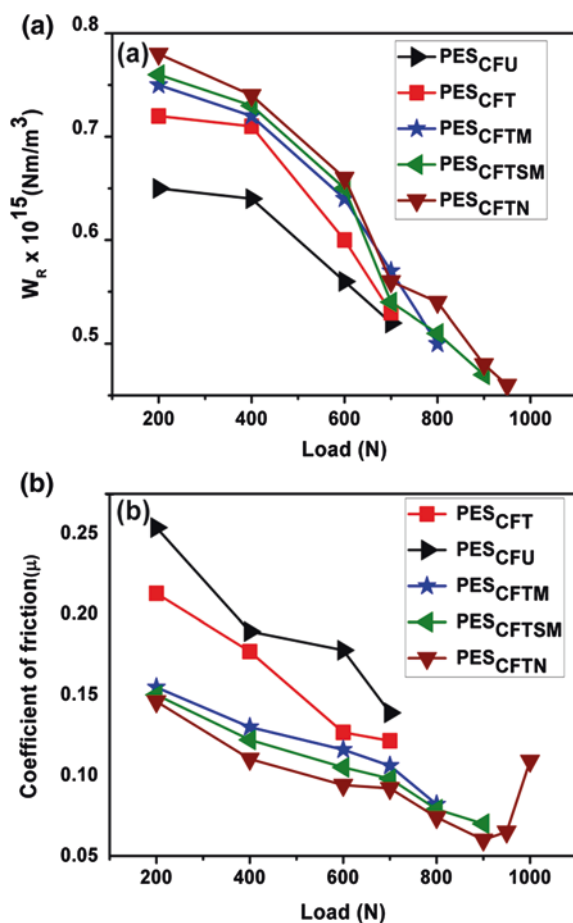
Influence of PTFE Modification on the Surface and Size of Particles

The μ and W_R were highly influenced due to PTFE modification rather than size of PTFE particles on the surface. PTFE inclusion improved the μ and W_R of composites to ~ 33 and $\sim 14\%$ respectively. Table 3 summarizes the trends in improvement (Fig. 11) due to various PTFE modifications on Tribo-performance parameters (μ , W_R and limiting load).

The incremented limiting load value has established the efficacy of PTFE surface modification, the limiting load for PES_{CFU} and PES_{CFT} composites was up to 700 N, while for tailored composites it was from 800 to 950 N. For PES_{CFTN} composite (tailored with 50–80 nm size PTFE); limiting load value was 950 N with $W_R \approx 4.8 \times 10^{14}$ Nm/m³ and μ value ≈ 0.06 confirming potential of nano-PTFE.

Sliding wear performance of the composites improved with decrement in the size of PTFE fillers. Well spherical nano fillers provide high interfacial area between the fillers and matrix. This leads to a better bonding between the two phases and hence better strength and toughness properties [6, 44]. 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. It is of utmost importance that the NPs should be uniformly dispersed to get the best property profile. To avoid agglomeration the minimum wt % of fillers is to be

Fig. 11 **a** Coefficient of friction; **b** specific wear rates as a function of increasing load for all surface designed series of composites [19, 20]



used. In literature on polymeric NCs generally 2–3 wt % of nano-fillers is claimed [45–48] to be the optimum amount. The main feature of PTFE NPs which influence the wear performance is their huge interfacial surface area.

It was desired to see the service life of the designed surfaces. The CF-PES composites (without and with PTFE particles at the surface) were slid against steel disc till the steady state friction value starts fluctuating at high friction torque. This signposted the limiting life of modified composites when few or no PTFE particles left on its surface for replenishment of transferred film on the steel disc.

Higher the limiting time, more is the tribo-utility of the surface. In the long experiment at 700 N load, the limiting sliding times for the composite surface without PTFE, with micro sized PTFE and nano—PTFE were; 8.33, 17.7 and 21.3 h respectively; indicating beneficial effects of PTFE on the composite surface [19]. For PES_{CFTN} composites, the transfer of thin tenacious PTFE film on the steel disc surface was effective in maintaining steady μ values for long time.

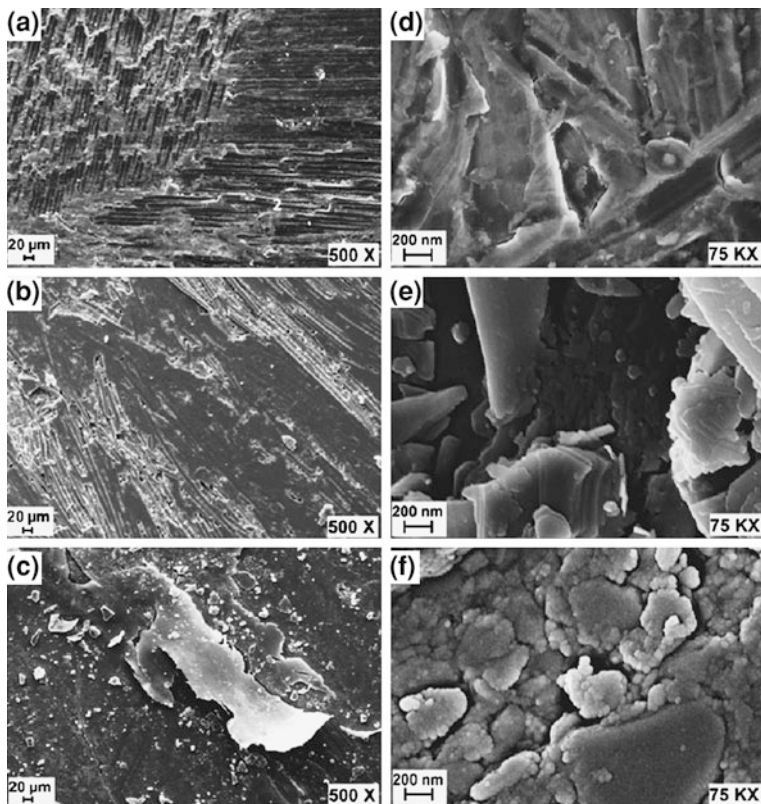


Fig. 12 SEM micrographs ($\times 500$) of surface designed composites after wearing; **a** PES_{CFT}, **b** PES_{CFTM} and **c** PES_{CFTN}; **d**, **e** and **f** are their respective high resolution FESEM images ($\times 75$ k) at 700 N load at 1 m/s speed (permission required) [19, 20]

Figure 12 shows SEM and FESEM micrographs of worn surfaces of surface designed composites. The fibers were fully covered with the nano PTFE fillers. PTFE layer is efficiently transferred on the counter surface and sliding is between PTFE layer on the composite surface and thin tenacious layer transferred on the counter surface. The existence on nano-fillers (Fig. 12f) and micro scale (Fig. 12e) is clearly visible with high resolution FESEM images of worn composites surface, which were absent for composites without tailored surface (Fig. 12d).

5 Concluding Remarks

Surface designing of PES_{CFT} composites with micro, sub-micro and nano-scale PTFE fillers improved the overall tribo-performance of composites; though the reduction in μ was significant rather than the wear resistance. The idea of

surface treatment of a composite with solid lubricants to safeguard the composites from an un-intentional reduction in strength properties and increase in the cost (if solid lubricant is employed in the whole composite rather than the surface both factors viz. strength and economics are affected significantly) proved successful. Surface designing enhanced limiting load values of composites significantly from 700 to 950 N, limiting running time from 8 to 21 h; reduction in μ (from 0.12 at 700 N load to 0.065 at 900 N load) and W_R (from 5.2 to 5.6×10^{14} Nm/m³ at 700 N load) especially in the case of PES_{CFTN} composite. The increased surface area of contact due to the inclusion of nano—PTFE at the composite surface was responsible for enhanced tribo-performance of PES_{CFTN} composite.

References

1. Donnet C, Erdemir (2001) A Historical developments and new trends in tribological and solid lubricant coatings. *Surf Coat Technol* 180:76–84
2. Teer DG (2001) New solid lubricant coatings. *Wear* 251:1068–1074
3. Blanchet TA, Kennedy FE (1992) Sliding wear mechanism of Polytetrafluoroethylene (PTFE) and PTFE composites. *Wear* 153:229–243
4. Nejhad MNG, Veedu VP, Yuen A, Askari D (2007) Polymer matrix composites with nano-scale reinforcements. Patent US 2007(0142548):A1
5. Bijwe J, Hufenbach W, Kunze K, Langkamp A (2008) Polymeric composites and bearings with engineered tribo-surfaces. In: Schlarb AK, Friedrich K (eds) *Tribology of polymeric nano-composites*. Elsevier, Amsterdam
6. Friedrich K, Zhang Z, Schlarb AK (2005) Effects of various fillers on the sliding wear of polymer composites. *Compos Sci Technol* 65:2329–2343
7. Friedrich K, Fakirov S, Zhang Z (2005) *Polymer composites—from nano to macro scale*, Springer, US
8. Chang L, Zhang Z, Ye L, Friedrich K (2008) Synergistic effect of nanoparticles and traditional tribo-fillers on sliding wear of polymeric hybrid composites. In: Schlarb AK, Friedrich K (eds) *Tribology of polymeric nano-composites*. Elsevier, Amsterdam
9. Zhang MQ, Rong MZ, Friedrich K (2006) Wear resisting polymer nanocomposites: repairation and properties. In: Mai YW, Yu ZZ (eds) *Polymer nanocomposites*. CRC Press, Washington
10. Zhang ZZ, Su FH, Wang K, Jiang W, Men XH, Liu WM (2005) Study on the friction and wear properties of carbon fabric composites reinforced with micro- and nano-particles. *Mater Sci Eng A* 404:251–258
11. Su FH, Zhang ZZ, Guo F, Wang K, Liu WM (2006) Effects of solid lubricants on friction and wear properties of nomex fabric composites. *Mater Sci Eng, A* 424:333–339
12. Kuo MC, Tsai CM, Huang JC, Chen M (2005) PEEK composites reinforced by nano-sized SiO₂ and Al₂O₃ particulates. *Mater Chem Phys* 90:185–195
13. Rong MZ, Zang M, Liu H, Zeng HM, Wetzel B, Freidrich K (2001) Microstructure and tribological behavior of polymeric nanocomposites. *Ind Lubr Tribol* 53:72–77
14. Burris DL, Boes B, Bourne GR, Sawyer WG (2007) Polymeric nanocomposites for tribological applications. *Macromol Mater Eng* 292:387–402
15. Friedrich K, Lu Z, Hager AM (1993) Overview on polymer composites for friction and wear application. *Theoret Appl Fract Mech* 19:1–11
16. Dwyer-Joyce RS, Sayles RS, Ioannides E (1994) An investigation into the mechanisms of closed three-body abrasive. *Wear* 175:133–142

17. Bahadur S (2000) The development of transfer layers and their role in polymer tribology. *Wear* 245:92–99
18. Vaziri M, Spurr RT, Stott FH (1988) An investigation of the wear of polymeric materials. *Wear* 122:329–342
19. Sharma M, Bijwe J (2012) Surface engineering of polymer composites with nano and micron sized PTFE fillers. *J Mater Sci* 47:4928–4935
20. Sharma M (2011) Carbon fabric reinforced polymer composites: development, surface designing by micro and nano PTFE and performance evaluation, Ph D thesis, Indian Institute of Technology, Delhi, India
21. Tiwari S, Bijwe J, Panier S (2011) Tribological studies on Polyetherimide composites based on carbon fabric with optimized oxidation treatment. *Wear* 271:2252–2260
22. Tiwari S, Sharma M, Panier S, Mutel B, Mitschang P, Bijwe J (2011) Influence of cold remote nitrogen oxygen plasma treatment on carbon fabric and its composites with specialty polymers. *J Mater Sci* 46:964–974
23. Tiwari S, Bijwe J, Panier S (2011) Role of Nano-YbF₃ treated carbon fabric on improving abrasive wear performance of polyetherimide composites. *Tribol Lett* 42:293–300
24. Tiwari S, Bijwe J, Panier S (2011) Polyetherimide composites with gamma irradiated carbon fabric: studies on abrasive wear. *Wear* 270:688–694
25. Meyer N, Marx G, Brzezinka KW (1994) Raman spectroscopy of carbon fibres. *J Anal Chem* 349:167–168
26. Sarraf H, Škarpová L, Louda P (2007) Surface modification of carbon fibers. *J Achievements Mater Manuf Eng* 25:24–30
27. Montes-Morán MA, Young RJ (2002) Raman spectroscopy study of high-modulus carbon fibres: effect of plasma-treatment on the interfacial properties of single-fiber-epoxy composites part II: characterisation of the fibre-matrix interface. *Carbon* 40:857–875
28. Morita K, Murata Y, Ishitani A, Murayama K, Ono T, Nakajima A (1986) Characterization of commercially available PAN (polyacrylonitrile)-based carbon fibers. *Pure Appl Chem* 58:455–468
29. Sharma SP, Lakkad SC (2011) Effect of CNTs growth on carbon fibers on the tensile strength of CNTs grown carbon fiber-reinforced polymer matrix composites. *Compos Part A* 42:8–15
30. Liu Y, Pan C, Wang J (2004) Raman spectra of carbon nanotubes and nanofibers prepared by ethanol flames. *J Mater Sci* 39:1091–1094
31. Nemanich RJ, Solin SA (1979) First and second order Raman scattering from finite-size crystals of graphite. *Phys Rev B* 20:392–401
32. Tuinstra F, Koenig JL (1970) Raman spectrum of graphite. *J Chem Phys* 53:1126–1130
33. Chaudhuri SN, Chaudhuri RA, Benner RE, Penugonda MS (2006) Raman spectroscopy for characterization of interfacial debonds between carbon fibers and polymer matrices. *Compos Struct* 76:375–387
34. Cao WW, Zhu B, Jing M, Wang CG (2008) Raman spectra of PAN-based carbon fibers during surface treatment. *NCBI PubMed* 28:2885–2889
35. Tressaud A, Chambon M, Gupta V, Flandrois S, Bahl OP (1995) Fluorine-intercalated carbon fibers III. A transmission electron microscopy study. *Carbon* 33:1339–1345
36. Sharma SP, Lakkad SC (2009) Morphology study of carbon nanospecies grown on carbon fibers by thermal CVD technique. *Surf Coat Technol* 203:1329–1335
37. Gaskell DR (1981) Introduction to the thermodynamics of materials. McGraw-Hill, New York
38. Bai YJ, Wang CG, Lun N, Wang YX, Yu MJ, Zhu B (2006) HRTEM microstructures of PAN precursor fibers. *Carbon* 44:1773–1778
39. Hai XS, Ying ZF, Huan LS, Dong-mei H, Qing-yun C (2010) Catalytic graphitization of Mo-B-doped polyacrylonitrile (PAN)-based carbon fibers. *J Central South University Technol* 17:703–707
40. Warner SB, Uhlmann DR, Peebles LH (1975) Ion etching of amorphous and semicrystalline fibers. *J Mater Sci* 10:758–764

41. Zhang X, Huang Y, Wang T (2006) Surface analysis of plasma grafted carbon fiber. *Appl Surf Sci* 253:2885–2892
42. Paredes JI, Alonso AM, Tascón JMD (2000) Atomic force microscopy investigation of the surface modification of highly oriented pyrolytic graphite by oxygen plasma. *J Mater Chem* 10:1585–1590
43. Schadler LS, Brinson LC, Sawyer WG (2007) Polymer nanocomposites: a small part of the story. *J Miner Met Mater Soc* 59:53–60
44. Kocsis JK, Zhang Z (2005) Structure-property relationships in nanoparticle/semi-crystalline thermoplastic composites. In: Calleja JFB, Michler G (eds) *Mechanical properties of polymers based on nanostructure and morphology*. CRC Press, New York
45. Xian G, Zhang Z, Friedrich K (2006) Tribological properties of micro and nanoparticles-filled Poly(etherimide) Composites. *J Appl Polym Sci* 101:1678–1686
46. Chang L, Zhang Z, Zhang H, Friedrich K (2005) Effect of nanoparticles on the tribological behaviour of short carbon fibre reinforced Poly(etherimide) composites. *Tribol Int* 38:966–973
47. Zhang ZZ, Sua FH, Wang K, Jiang W, Mena XH, Liu WM (2005) Study on the friction and wear properties of carbon fabric composites reinforced with micro- and nano-particles. *Mater Sci Eng, A* 404:251–258
48. Park DC, Kim SS, Kim BC, Lee SM, Lee DG (2006) Wear characteristics of carbon-phenolic woven composites mixed with nano-particles. *Compos Struct* 74:89–98



<http://www.springer.com/978-3-642-33881-6>

Tribology of Nanocomposites

Davim J. P. (Ed.)

2013, X, 102 p., Hardcover

ISBN: 978-3-642-33881-6