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Polytetrafluoroethylene (PTFE) fiber reinforced polyetheretherketone (PEEK) composites

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ABSTRACT

This work uses high tenacity expanded polytetrafluoroethylene (ePTFE) filaments as both a fiber reinforcement and a reservoir for solid lubricants. The goal is to reduce the wear of the composites by regulating the PTFE transfer. Expanded PTFE films are a porous network of PTFE nodes and fibrils, while highly oriented ePTFE filaments are aligned crystalline fibers that are regarded as high-tenacity fibers that can be woven into threads or yarns. Reported yield strength of these filaments can exceed 500 MPa. The best performing composites were those that had filaments of ePTFE aligned normal to the counterface. The wear rates obtained from the inclusion of expanded PTFE filaments were better than conventional powder filled PTFE–PEEK composites reaching values as low as $K = 7 \times 10^{-8}$ mm^3/N m and showed stable friction coefficients below $\mu = 0.125$ for over 2 million cycles.

1. Introduction

Polymeric composites are frequently used in applications where traditional fluid lubrication cannot be used [1–3]. Solid lubrication is advantageous due to cleanliness, simplicity and the available range of operating temperatures but achieving a combination of low friction and wear rates remains a challenge. Composite materials offer designers the ability to tune properties and achieve steady, low wear rates while maintaining a low friction coefficient. Fiber reinforced polymers have shown improved wear rates as well as excellent structural properties [4–6]. The traditional design approach has been to use fibers for strengthening and filler particles for lubrication. Recently there has been some thought with carbon nanotubes to try and have both strengthening and lubrication from the same fibers [7–9].

Polyetheretherketone (PEEK) is a popular matrix material for tribological composites due to its strength and wear resistance. It is an injection moldable polymer with a high operating temperature and chemical resistance. McCook et al. [10] surveyed fillers in PEEK in various environments. Others have examined ceramic nanofillers and polytetrafluoroethylene (PTFE) in PEEK [11–19]. The inclusion of PTFE in PEEK yielded a reduced friction coefficient μ; Burris et al. found unfilled $\mu = 0.36$ was improved to $\mu = 0.11$ at 50 wt.% PTFE. Wear rates and friction coefficients of various PEEK composites are shown in Fig. 1.

PTFE has many advantageous properties, such as low friction, low outgassing, high temperature capability and high chemical inertness, which make it an ideal filler material for a wide variety of applications. Expanded PTFE is a fibrillated form of PTFE that has a porous network of PTFE fibrils connected to dense nodes of PTFE. Expanded PTFE films can have a variety of densities and shapes, with porosities ranging from 5 to 90%. Expanded PTFE provides increased strength to weight ratio and creep resistance compared to fully dense PTFE. The mesh-like materials have been used previously in tribology as a coating material with an epoxy matrix [20]. Interestingly, highly oriented PTFE filaments that are extracted from high tenacity expanded PTFE threads have been entirely overlooked as a filler material. These filaments have high crystallinity and strength while maintaining the desirable properties of dense PTFE. While previous work with expanded PTFE has been limited to coating applications; the goal of this work is to design a bulk composite using expanded PTFE filaments in a wear resistant matrix (PEEK). The hypothesis is to regulate the wear by preventing PTFE transfer and subsequently forcing the transfer films to be thin.

2. Materials

Polyetheretherketone (Victrex 450 PF PEEK) powder of average particle size 10 μm was used as the matrix material in this study. The PEEK was filled with high tenacity expanded polytetrafluo-

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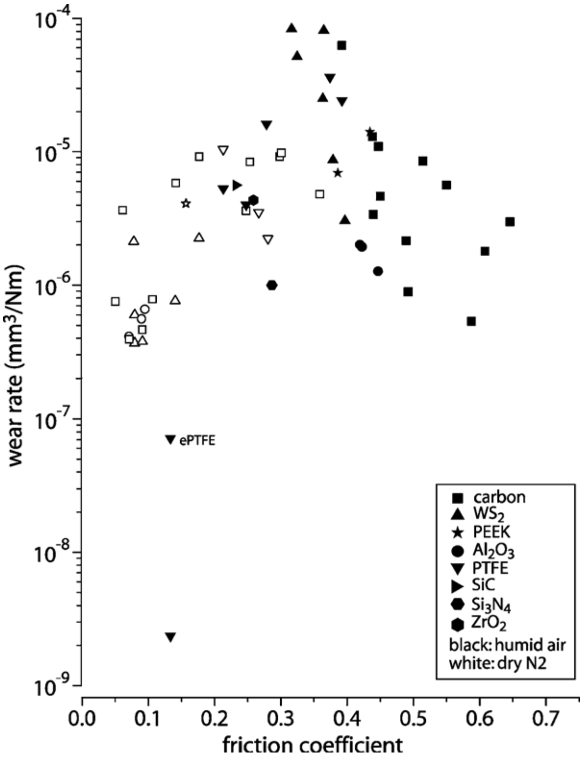

Fig. 1. The performance of various PEEK composites, with filler material labeled. The ePTFE composite from this study is included for comparison. The design goal is the bottom left quadrant, with low friction and wear. Data is from [10,13–18].

roethylene (ePTFE) thread (PlastomerTech Solar Thread) composed of three filaments of expanded PTFE with characteristic diameters of approximately 180 μm. Prior to processing, the threads were manually separated into individual filaments and trimmed to length (approximately 50 mm for most composites and 10 mm for a 15 vol.% chopped fiber composite).

The composites were constructed in a press by alternating the desired amount of PEEK powder with a prescribed number of filaments or threads. The majority of the constructed composites were designed with the filaments aligned perpendicular to the sliding direction (i.e. the filaments are normal to the counterface surface). For completeness, additional samples containing randomly oriented ePTFE were prepared. Additionally, a single sample of aligned ePTFE threads (a thread is a bundle of 3 filaments) was also prepared.

Aligning the ePTFE filaments or threads within a PEEK matrix requires a unique consolidation approach. Schematically the design and approach is similar to vintage cigar-presses. Here, the PEEK/ePTFE layers were aligned and stacked until a 12.7 mm diameter press was filled with material. The axial consolidation pressure was on the order of 40 MPa. The consolidated composites were transferred to a 12.7 mm diameter cylindrical molding chamber where they were lightly pressed and heated to 340 °C to ensure flow of the PEEK without melting the ePTFE. The cooled samples were machined at high speed into test specimens of approximately 7 mm × 7 mm × 12 mm. The surfaces were finished using 800 grit silicon carbide wet abrasive paper and a slurry polish, washed in soap and water and sonicated in methanol for 30 min. The final composites had 8, 10, and 15 vol.% aligned filaments, 13 vol.% aligned threads, and 18 and 25 vol.% randomly oriented filaments.

PTFE powder was used as a filler to compare performance to the ePTFE composites. The PTFE powder (DuPont 7C – characteristic particle size of ~30 μm) filled PEEK composites were made using a dual asymmetric centrifugal laboratory mixer to disperse the powders. The final dispersed powders were molded and machined using the procedure described previously. The resulting volume percents of PTFE powder filled PEEK composites were 6, 9, 13, 16 and 20 vol.%.

Samples for mechanical characterization were made from ensembles of ePTFE filaments of known length and randomly distributed among the powder. Plates were machined to a width of 16.5 mm. The final specimens were unfilled PEEK, PEEK with 10 mm long filaments of ePTFE and PEEK with 20 mm long filaments of ePTFE.

3. Experimental methods

The tribological properties of the samples were evaluated using a linear reciprocating tribometer described in Schmitz et al. [21]. The apparatus is contained in a soft-walled clean room at temperature of 20 °C and exposed to lab air of ~25% humidity. The samples were mounted directly to a 6-channel load cell and run against a rectangular lapped (R_a = 150 nm) 304 stainless steel counterface mounted to the linear reciprocating stage. A new counterface was used for each test and cleaned with methanol prior to use. A pneumatic cylinder/linear thruster assembly applied an average normal force of 250 N. The sliding distance was 25.4 mm and the speed was nearly constant 50.8 mm/s. Wear rate calculations were made utilizing mass loss measurements taken after a prescribed number of cycles and all uncertainties in wear rates followed the established methods [21–23]. Transfer films were characterized using a Perkin-Elmer XPS for chemical composition and a Veeco Dektak 8 for surface profilometry.

The interfacial shear strength between the ePTFE and PEEK was determined by performing filament pull out tests on samples fractured in tension. The interfacial shear strength is found by using the ultimate strength, diameter, and critical length of the fiber. The fractured samples were then studied under the SEM and optical microscope to determine if the ends of the fibers had pulled out of the PEEK or had fractured within the matrix and subsequently pulled out. The cut ends are easily distinguished from the fibrillated and fractured morphology of broken filaments. The lengths of each filament were measured in the optical microscope in an effort to estimate a critical filament length for pull out and the interfacial shear strength. The ultimate strength of the filaments was experimentally determined by hanging masses from individual filaments.

4. Results and discussion

Friction coefficients for unfilled PEEK was relatively high and noisy with average values of μ = 0.37. The addition of PTFE reduced the friction coefficient for all loading conditions. These data are plotted against filler loading in Fig. 2a. The addition of 8 vol.% aligned ePTFE filaments reduced this friction coefficient to an average of μ = 0.13 and 10 vol.% aligned filaments yielded a friction coefficient of μ = 0.11. The friction coefficient of the 10 vol.% aligned ePTFE filaments versus sliding distance is shown in Fig. 3. The composite exhibits very short transient behavior and maintained a steady coefficient of friction for the entire experiment (over 2 million cycles). The sliding surfaces of the composites saw little change during testing, as shown in Fig. 4. PEEK filled with powdered PTFE had a friction coefficient of μ = 0.13 at similar loadings to the ePTFE filaments but did not see the same amount of improvement in wear rate as the aligned filament composites.

The wear rate of unfilled PEEK was found to be on the order of $K = 10 \times 10^{-6}$ mm^3/N m and in all samples was decreased with the introduction of PTFE filler material (Fig. 1b). PTFE powder filler (DuPont 7C) achieved a wear rate as low as

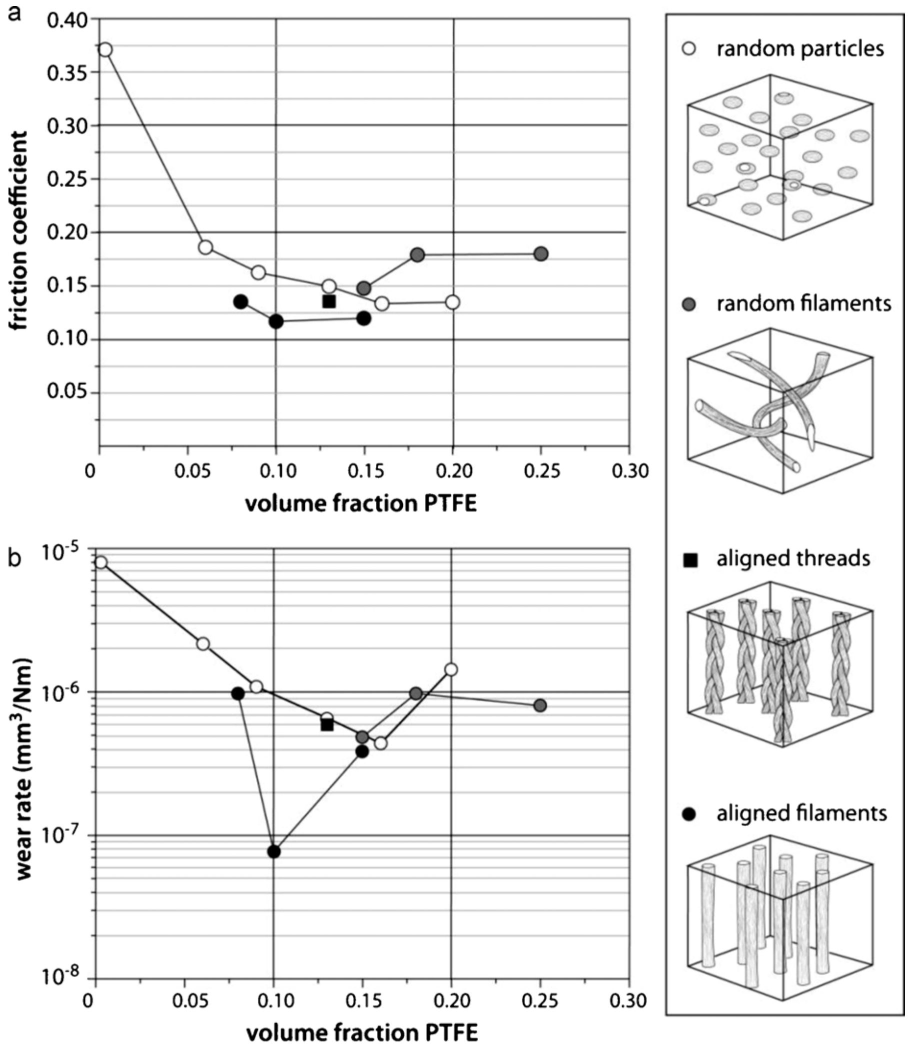

Fig. 2. (a) Friction coefficient versus PTFE filler loading. At low loadings of aligned ePTFE filaments, the friction coefficient was slightly less than that of the powder filled composites at similar loadings. (b) Steady state wear rates plotted against PTFE filler loading. Composites with expanded PTFE filaments aligned normal to the sliding direction demonstrated the best wear rates; the performance of randomly oriented filaments was similar to the powder PTFE filled PEEK composites.

$K = 0.45 \times 10^{-6}\,\mathrm{mm^3/N\,m}$ at a loading of 16 vol.%. Randomly oriented ePTFE filaments had wear rates higher than PTFE powder filled PEEK. Samples with aligned ePTFE performed markedly better: 10 vol.% aligned filaments, the wear rate was $K = 0.07 \times 10^{-6}\,\mathrm{mm^3/N\,m}$ and with 13 vol.% aligned threads $K = 0.5 \times 10^{-6}\,\mathrm{mm^3/N\,m}$.

The ultimate strength of the filaments can be found using the thread denier and tenacity. PlastomerTech provided 1800 denier thread with a tenacity of 3 g/denier, indicating that the thread should hold 5400 g (each filament should carry a third of this load). The theoretical strength of the filaments is approximately $\sigma_f = 700\,\mathrm{MPa}$.

$$\sigma_{\mathrm{f}} = \frac{F}{A} = \frac{4\,\mathrm{mg}}{\pi d^2} \tag{1}$$

Experimentally, the filaments held 1100 kg of load before failure. For all of our analysis the experimental ultimate strength was assumed to be $\sigma_f = 425\,\mathrm{MPa}$. By experimentally determining the critical length of fractured filaments, L_c, a force balance can be used to determine the interfacial shear stress, τ_s, between the ePTFE and the PEEK.

$$\sigma_{\mathrm{f}} \cdot \frac{\pi d^2}{4} = \tau_{\mathrm{s}} \cdot \pi d L_{\mathrm{c}} \;\therefore\; \tau_{\mathrm{s}} = \sigma_{\mathrm{f}} \cdot \frac{d}{4L_{\mathrm{c}}} \tag{2}$$

Table 1
Results of the fiber pull out tests. 18 fibers were included in each experiment, with 14 pulling out from the matrix. The most common length of pulled out fibers was 2.5 mm and no fibers longer than 5 mm were removed from the matrix.

Fiber length (mm)	Number of broken fibers
0–1.75	3
1.8–2.5	8
2.6–3.75	2
3.75–5	1

The critical length was determined from investigating the ends of the filaments after samples were fractured in tensile tests. The results of the test are shown in Table 1 and it was seen that the critical fiber length was on the order of 2.5 mm. Along with the measured filament diameter of 180 μm, the interfacial shear strength is approximately 7.7 MPa.

The aligned filaments had the clearest benefit to the tribological performance of the composites, and like previous studies have also found that the optimal arrangement of fibers is normal to the sliding direction [4,6]. The molecular alignment of the PTFE chains within the filaments gives rise to the tenacity of these ePTFE fibers. Conceptually, the design approach is to regulate the expression of PTFE to the transfer film by constraining the mobility and preventing gross particle or filament transfer. Previously,

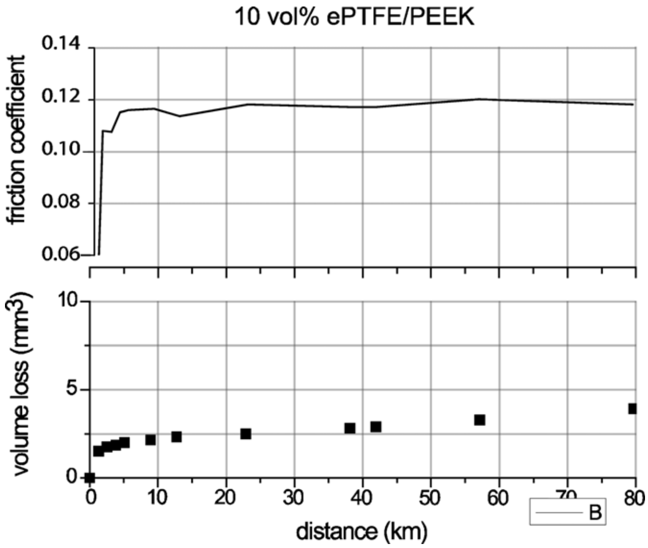

Fig. 3. Friction coefficient versus sliding distance for a 10 vol.% ePTFE/PEEK composite that is under 250 N of load with a reciprocating stroke length of 25.4 mm. The composite maintained a stable friction coefficient below $\mu = 0.125$ for the duration of the test. A plot of wear volume versus sliding distance reveals that the majority of material removed occurs in the first 10% of sliding.

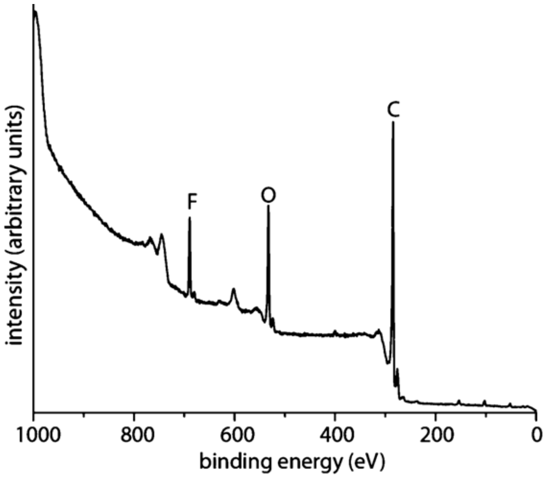

Fig. 5. XPS survey of the transfer film created by the 10 vol.% ePTFE/PEEK sample. The upper 2–5 nm of transfer film is composed of predominantly carbon (285 eV), oxygen (530 eV), and fluorine (685 eV).

it was found that thinner transfer films resulted in lower wear rates (i.e. the thinner the transfer films the more wear resistant the composites) [14,24]. Regulation of the debris morphology and transfer film development has been a goal of nanocomposites studies within tribology. Here, the regulation comes not from particle matrix interactions; rather, from the constraint and difficulty in removing aligned polymer chains from aligned wells of lubricous material.

The composition of the top few nanometers of the transfer film produced by the 10 vol.% sample is shown in Fig. 5. The top layers are primarily composed of carbon and oxygen, with small traces of fluorine. Surface profilometry and focused ion beam analysis revealed a film thickness of less than one micrometer. The average film thickness for the 10 vol.% film was 880 nm. Previous studies observed a brown transfer film associated with wear resistant PTFE composites; all of the wear

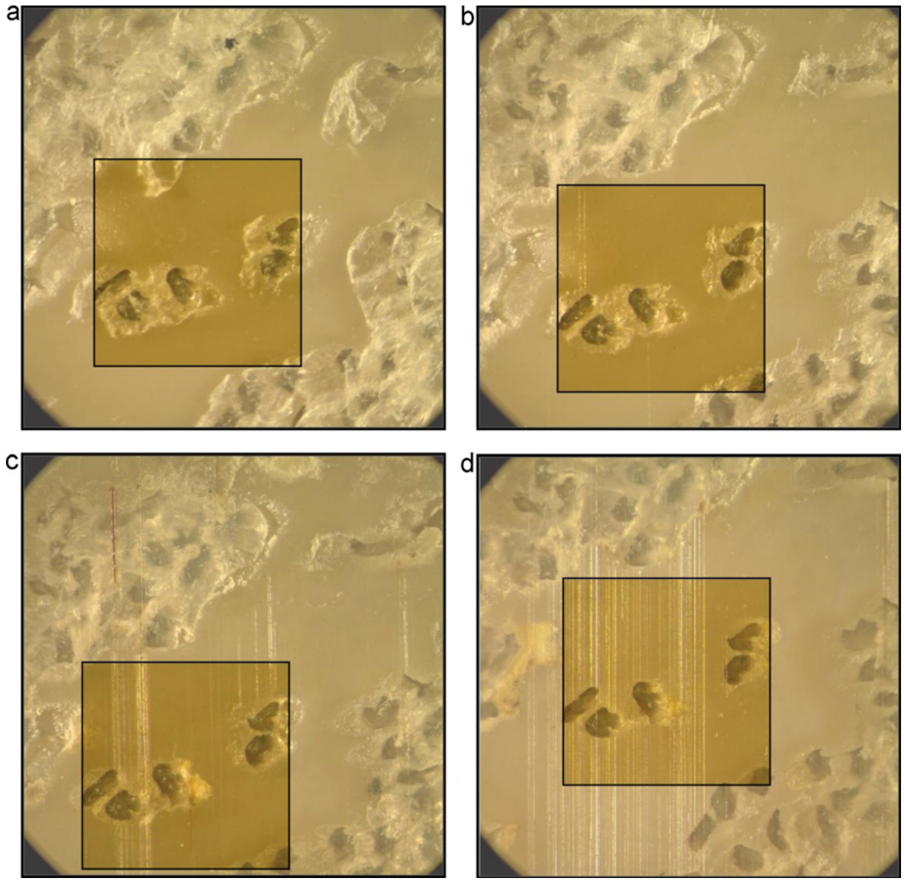

Fig. 4. Microscope image of the 10 vol.% sample (a) before testing, (b) after 5 km, (c) after 23 km and (d) after 57 km. Little change is seen on the sliding surface of the material.

resistant composites in this study also produced brown transfer films.

Consistent with prior studies, the friction coefficient and wear resistance were both optimal at the same sample configuration and loading. The wear resistance is much more sensitive than the friction coefficient, which was acceptably low for all of the samples. Overall, these composites were similar to some of the best performing PEEK/PTFE composites. The ability to garner such dramatic improvements in properties from PTFE chain alignment provides unique routes to regulate, design, and prescribe the PTFE transfer film development.

5. Conclusions

This paper explores the effectiveness of the inclusion of PTFE filaments in PEEK. The wear rates obtained from the ePTFE filled composites were better than conventional powder filled PTFE–PEEK composites. Further, ePTFE–PEEK composites saw little change to the sliding surface. The friction coefficients of the aligned expanded PTFE–PEEK composites were lower than the other composites tested, and were steady throughout testing.

- The inclusion of PTFE in PEEK dramatically reduces both the friction coefficient and the wear rate of the virgin materials.
- Inclusion of ePTFE filaments aligned perpendicular to the sliding surface enabled reduction of wear rate by an order of magnitude as compared to particle filled composites. A wear rate of as $K = 7 \times 10^{-8}$ mm^3/N m was achieved with 10 vol.% ePTFE/PEEK.
- The low wear of the ePTFE/PEEK samples were achieved by developing thin transfer films that utilize the highly oriented ePTFE as a lubricant reservoir. The transfer films were brown in color, thin, and contained carbon, oxygen, and fluorine at the surface.
- Expanded PTFE fibers of 5 mm or longer have sufficient surface area in contact with the PEEK to reinforce the matrix and resist being pulled out.

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