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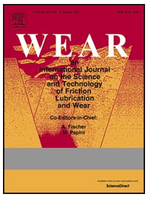

Wear resistance effects of alumina and carbon nanoscale fillers in PFA, FEP, and HDPE polymers

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ABSTRACT

Following numerous studies demonstrating the ability of nanostructured alpha-alumina filler to reduce the prohibitively high wear rate of polytetrafluoroethylene (PTFE) down to extremely small values ($\sim 10^{-7}$ mm^3/Nm) well below those of conventional PTFE micro-composites, alpha-alumina filler was also shown capable, in a couple recent studies, of imparting similar performance to another fluoropolymer, perfluoroalkoxy (PFA) copolymer, which otherwise was similarly lacking wear resistance in the unfilled state. In addition to duplicating such alpha-alumina performance in PFA, in this study such an extreme wear-reducing capability has also been demonstrated using nanocarbon powder, as an example representative of several other forms of nanoscale carbon filler that like alpha-alumina had been shown capable of providing extreme resistance to PTFE. Fluorinated ethylene propylene (FEP) copolymer, whose nanocomposites have not been tribologically explored previously, was thus more fully investigated here with not only alpha-alumina and nanocarbon, but also other nanotube (CNT) and mesoporous forms of nanoscale carbon fillers. In preliminary testing, only the alpha-alumina filler indicated an ability to impart its wear-reducing capability to FEP; a wear rate of $\sim 0.8 \times 10^{-6}$ mm^3/Nm was observed at 2 wt% alpha-alumina concentration. While this is an impressive reduction in wear rate, it is not quite as extreme a reduction as that observed in PTFE or PFA. The transport of the extreme wear resistance of nanocarbon powder in PTFE and PFA was even more partial and incomplete in FEP, with the $\sim 0.3 \times 10^{-3}$ mm^3/Nm unfilled FEP wear rate only reduced to $\sim 10^{-5}$ mm^3/Nm, while the CNT and mesoporous carbon fillers were even less effective. Correspondingly, ATR-FTIR spectra from FEP wear surfaces displayed sizable peaks evident of the chelation of chemical interactions known to be associated with wear resistance for PTFE and PFA matrices only in the most wear-resistant alpha-alumina case and to a lesser extent for the nanocarbon. Finally, it is demonstrated that such fillers demonstrate such strongly beneficial effects only in polymers that otherwise lack wear resistance, and may actually be deleterious for polymers such as high density polyethylene (HDPE) already having some inherent wear resistance in their unfilled state.

1. Introduction

As the fluoropolymer most utilized in tribological applications given its low-friction characteristics even during unlubricated dry sliding, the accompanying high rate of wear of polyetrafluoroethylene (PTFE) in such situations approaching 10^{-3} mm^3/Nm has long been addressed by inclusion of a broad range of filler particle materials that have conventionally been microscale and able to reduce wear by typically two and in some instances up to three orders-of-magnitude [1]. In likewise demonstrating wear resistance provided to PTFE by a range of filler materials, Tanaka and Kawakami [2] noted the two smallest filler materials in the study (MoS_2 and TiO_2 with size down to 0.3 μm) also provided the least increases in wear resistance, thus hypothesizing that fillers must have an adequate micro-scale size (several to 30 μm) to prevent the large-scale destruction of PTFE's banded structure that leads to debris formation and high wear rate when unfilled. This long-standing conventional wisdom that fillers of insufficient size may simply be transported within the large wear debris produced by PTFE rather than significantly interfering with that wear process, put forth years earlier by Ricklin [3] and shown to be followed in several examples of filler material tested at both micro- and nanoscale [4], was nonetheless eventually contradicted by the observation by Burris and Sawyer [5] of a

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nanoscale (80 nm) alumina filler instead reducing PTFE's wear rate even more effectively down towards 1.3×10^{-7} mm^3/Nm with 5 wt% content (already nearly this low with just a 1 wt% filler content), as compared to wear rates of more nearly $\sim 10^{-5}$ mm^3/Nm when such alumina had particle sizes of 0.5 μm or higher [6,7]. This extreme level of wear resistance effectiveness of alumina nanofiller in PTFE furthermore appeared to be limited to its alpha phase [5], and was subsequently shown to be capable of achieving such effectiveness even at trace loadings down to 0.5 vol%, and possibly even lower via added functionalization of such alpha-alumina filler surfaces [8]. When investigating ten other commercially-available example nanofiller materials the only other instance observing comparably extreme reductions of wear rate reduction down towards $\sim 10^{-7}$ mm^3/Nm was for carbon nanopowder particles, achieved by a modest filler content of 2 wt% with wear rate gradually dropping even further with increasing filler content [9]. In addition to alpha-phase alumina nanoparticles, extreme PTFE wear resistance that had only otherwise been found by nanocarbon particles has since been observed by other forms of carbon filler if having at least one dimension on the nanoscale, including carbon nanotubes [10], as well as thin graphene platelets [11] as also recently noted by Sun [12] too. Of the limited ability to enable $\sim 10^{-7}$ mm^3/Nm or lower wear rates in PTFE, which recently has additionally been reported using AlN and BeO nanofillers too [13], such ultralow PTFE nanocomposite wear has been most broadly demonstrated across multiple laboratories for the case of the alpha-alumina filler, for example [14–17].

With its smooth linear molecular profile and high extent to which it may crystallize, as well as its high molecular weight, the resulting extreme melt viscosity of PTFE is prohibitively high for conventional polymer melt processing and manufacturing techniques such as screw extrusion and injection molding, and thus more complex press-and-sinter powder metallurgy approaches must instead be taken. With only simple geometries typically pressed, the resulting bodies once sintered must then be further machined to final form. Copolymers of tetrafluoroethylene (TFE) with other fluorinated monomers including bulky side groups to disrupt the otherwise smooth linear PTFE molecular profile may enable more simple melt processing while also maintaining many of the low-friction and other desirable attributes of the PTFE fluoropolymer, with one commercially prominent example being perfluoroalkoxy (PFA) copolymer where some fraction of TFE monomer CF_2CF_2 are substituted instead with perfluoroalkylvinyl ether CF_2CFOR where perfluorinated alkyl R on side group C_nF_{2n+1} (such as propyl $n = 3$) to disrupt the otherwise smooth linear molecular profile when polymerizing TFE alone. With unfilled PFA displaying high sliding wear rates $>10^{-4}$ mm^3/Nm similar to unfilled PTFE, it has long been commercially available for tribological application in a composite form containing chopped glass or carbon fiber, with the ~2 order-of-magnitude reduction in wear rate typical of microfillers in PTFE also provided to PFA [18], as demonstrated again for such PFA microcomposites in sliding seal tests showing modest reductions in wear rate approaching down towards 10^{-6} mm^3/Nm. Sidebottom et al. [19] recently demonstrated the ability of nanoscale-structured alpha-phase alumina in an initial agglomerate filler form to further reduce PFA steady-state wear rates to extremely low levels well below 10^{-7} mm^3/Nm, like previously shown for PTFE, by filler contents as low as 5 wt% when instead processed by conventional extrusion melt processes. It was subsequently shown [20] that such levels of extremely reduced wear rate depend upon a modest amount of humidity in the surrounding air environment, with such ultralow wear behavior being largely lost if the environment was instead either dry or completely water-submersed.

Fluorinated ethylene propylene (FEP) copolymer is another prominent melt-processible copolymer of TFE substituted with some fraction of hexafluoropropylene CF_2CFCF_3 monomer. As with PFA, FEP has also been commercially available for tribological application containing chopped glass or carbon fiber, again with the typical ~2 order-of-magnitude microfiller reduction in wear rate as compared to unfilled fluoropolymer [18]. To date though, there have not yet been any reported studies of the potential to similarly transport more extremely increased wear resistance to conventionally melt-processed FEP fluoropolymer via alpha-phase alumina, or any other nanofiller material.

As such, the objectives of this study involve the alpha-alumina and carbon nanoscale fillers both already shown to uniquely provide extreme wear resistance to PTFE, namely: a cursory investigation into whether nanocarbon filler can also provide the extreme wear resistance in fluorinated PFA copolymer that has already been well established by alpha-alumina; a more extensive investigation into the as yet unexplored topic of FEP nanocomposite tribology and whether nanoscale alpha-alumina and/or nanocarbon can similarly provide extreme wear resistance as has been achieved by both in PTFE; what effects such nanofillers may have on the wear behavior of high-density polyethylene (HDPE) which though not a fluoropolymer shares a similarly linear smooth molecular profile as that of PTFE.

2. Experimental details

2.1. Materials and processing

The three polymer matrix materials studied were commercially available as: PFA "Hyflon P540" from Solvay Specialty Polymers in ~2 mm pellet form with 305 °C melt point; FEP "Neoflon NP-101" from Daikin Chemicals in ~2 mm pellet form with 255 °C melt point; and HDPE "Microthene FA70000" from LyondellBasell in ultra-fine ~20 μm powder particle form with 134 °C melt point.

Four nanoscale filler materials studied were commercially available as: alpha-phase alumina ("aluminum oxide APS powder 44653" from Alfa Aesar with 27–43 nm particle size); nanocarbon (carbon nanopowder "non-graphitic 633100" powder from Aldrich with <50 nm particle size); carbon nanotubes ("multiwalled carboxylic acid functionalized 755125" from Aldrich of ~9.5 nm diameter and ~1.5 μm length); mesoporous carbon (mesoporous nanopowder "graphitized 699624" from Aldrich with <500 nm size).

Polymer resin and filler powder quantities were measured out in relative amounts to produce batches with the various desired levels of filler content. Each batch mixture was dry-blended in bags by shaking. Thermo Haake PolyDrive twin-screw mixer was used to compound these mixtures, using a batch size of ~70 g for the fluoropolymer composites or a batch size of about half that mass for the HDPE composites to account for the lower density of HDPE. The PFA and FEP fluoropolymer composites were mixed at a 12 rpm screw speed for 8 min; at 325 °C for PFA and at 320 °C for FEP given its lower melt point. HDPE composites were mixed at 165 °C at an increased screw speed of 20 rpm for 10 min given its lower melt viscosity and low melt point. Molten composites were subsequently removed from the twin-screw mixer, with the mixer cavity thereafter disassembled and both screws removed to enable thorough cleaning so as to avoid any cross-contamination during processing of subsequent composites. Upon cooling of the melt-mixed composite material, it was cut into solid fragments that were placed within a cylindrical recess mold and pressed under ~25 MPa pressure for at least 1-h at 370, 300 and 180 °C for PFA, FEP and HDPE respectively. Thereafter, the pressure was released and the mold was allowed to cool slowly for approximately 6 h, after which the resultant cylindrical composite pucks were removed from the mold. From measurement of resultant puck thickness, diameter, and mass, the effective density of each puck's composite material could be approximated. Then from each pressed puck, pins of 4 mm × 4 mm square cross-section and length >10 mm were machined to provide wear test specimens with flat 4 mm × 4 mm contact surface at their end.

2.2. Wear testing

Dry sliding wear experiments of the composite materials in all cases were conducted in ambient air conditions at room temperature against 304 stainless steel counterfaces at 0.1 m/s speed with 50 N pin normal load creating a 3.125 MPa contact pressure. These conditions are comparable to those initiated by Sawyer et al. [21] in their earliest fluoropolymer nanocomposite wear investigations (0.05 m/s at 6.4 MPa against 300-series stainless steel) with most other groups subsequently undertaking such fluoropolymer nanocomposite wear research testing near this same range of conditions. The identically modest pressure x velocity product employed in this study is intended to be sufficient to generate readily measurable increases in polymer composite wear depth and corresponding volume and mass loss within increments of sliding duration that are not impractically long, yet not so high as to confound imposed test conditions with significant temperature rises and variations otherwise resulting from frictional heating. Sliding was halted periodically and mass loss with respect to the original composite mass was measured on an analytical balance with 0.1 mg precision, converting by density to produce a record of volume loss as a function of sliding distance. With primary interest focused on wear behavior, no measurements of friction were made in these studies.

The wear testing study in the case of PFA polymer was of limited scope, as the ability of nanoscale alpha-alumina to provide it with extremely high wear resistance has already been well documented [19, 20]. In addition to 5 wt% alpha-alumina to assure its effectiveness reported in the literature in PFA could be repeated here, the nanocarbon powder was investigated as a single representative carbon nanofiller within PFA assessing whether its ability to provide extreme wear resistance to PTFE would also be operative in PFA. The nanocarbon content of this composite was 3 wt%, in order to have a volume fraction comparable to that of the denser alpha-alumina, with both these contents previously shown to provide extremely low wear rates of $\sim 10^{-7}$ mm^3/Nm or lower to PTFE [6,9]. Unfilled PFA was also tested as the control for comparison. In this limited-scope testing for the PFA materials, sliding was performed on a unidirectionally rotating two-pin-on-disk tester having only a single test station (Fig. 1a), rather than a multi-station wear tester with its greater testing throughput reserved for the more expanded-scope testing of FEP and HDPE composites (to be described below). Each stainless steel disk counterface was square (50 mm × 50 mm) with its surface isotropically lapped by circular motion against 400 grit SiC abrasive paper resulting in a mean value of R_a roughness of 0.0639 μm (±0.0035 μm std dev, n = 20 measurements). The disk counterface was rotated about an axis normal to and going through the center of its surface at 52 rpm, with the center of each of the two pins located 18.4 mm off the disk's rotational axis and opposite that axis from each other, creating a 36.8 mm mean diameter of wear track upon the stainless steel disk within which both pins slide 180^o around the track from each other at a speed of 0.1 m/s. The two pins are held 36.8 mm apart within a common fixture, which is pneumatically loaded with 100 N total normal force against the stainless steel disk, split to provide the 50 N load and 3.125 MPa contact pressure on each pin.

As the FEP polymer in comparison has remained relatively unexplored in terms of possible wear resistance effects of nanofillers, its wear study was more exhaustive and included three forms of nanoscale carbon (nanocarbon powder, nanotube, and mesoporous) fillers, in addition to the alpha-alumina filler, as well as the unfilled FEP. Given the greater number of materials to be investigated, sliding tests were instead performed using a multi-station reciprocating pin-on-plate wear tester (Fig. 1b) as described in Ref. [7] with each pin loaded by approximately 50 N producing the corresponding 3.125 MPa pressure over its contact surface against its own mating 12.5 mm × 50 mm stainless steel 304 counterface, along which 40 mm long successive sliding strokes were repeatedly made in each direction at a speed of 0.1 m/s. These plate counterfaces were isotropically polished by circular motion through 3 μm diamond suspended in water against a cloth wheel resulting in a mean value of R_a roughness of 0.0246 μm (±0.0017 μm std dev, n = 20 measurements). The alpha-alumina, nanocarbon, and carbon nanotube (CNT) fillers were tested at a 2 wt% content at which each has been shown capable of bringing wear rate down at least to below 10^{-6} mm^3/Nm in PTFE [7,10] and even in the case of nanocarbon [9], while the mesoporous carbon filler was instead tested at the higher 5 wt% content required to similarly reduce wear rate down to at least 10^{-6} mm^3/Nm in PTFE [10].

When these fluoropolymer studies were extended to the non-fluorinated case of HDPE, the multi-station reciprocating wear tester and same sliding conditions were again employed. Beyond the unfilled and alpha-alumina filled cases, nanocarbon powder was again tested as representative of the carbon-based nanoscale fillers, as was also done for PFA polymer and its cursory testing. Nanocarbon filler was tested at several weight fractions up to 7.7 wt%, for which corresponding volume fraction 4 vol% considering the reduced polymer matrix density as compared to that of the fluoropolymer cases gives volume fractions in a comparable range as tested for the fluoropolymers, while the alpha-alumina was tested at weight fractions up towards 15 wt% to also reach such a 4 vol% filler volume fraction.

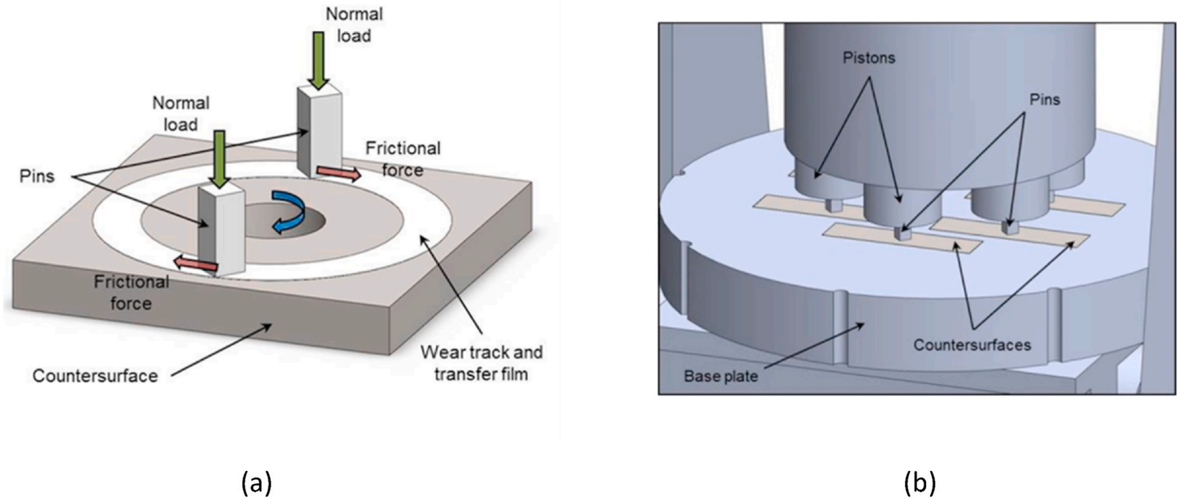


Fig. 1. Wear test geometries. (a) Single-station two-pin-on-disk used in limited-scope PFA testing with a pair of a composite's pins loaded against a common wear track upon unidirectionally rotated stainless steel countersurface, and (b) multi-station pin-on-plate used in expanded-scope FEP and HDPE testing with each composite pin loaded against a corresponding stainless steel countersurface within a baseplate providing all countersurfaces with same reciprocating motion left/right along their length.

2.3. Wear testing results

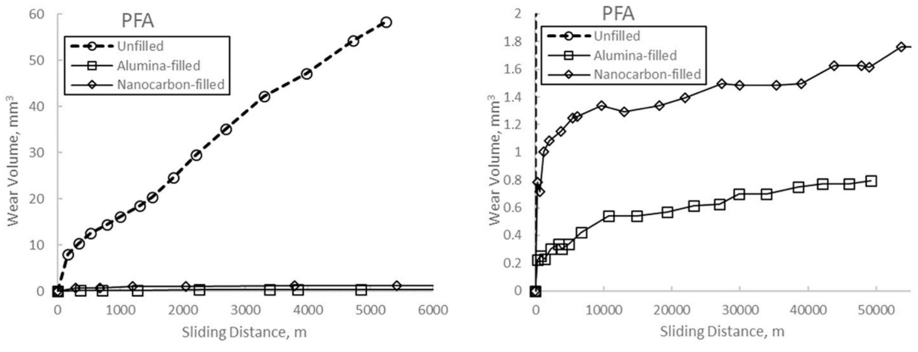
2.3.1. PFA

The wear volume from the two unfilled PFA pins supporting the total 100 N normal load in the two-pin-on-disk unidirectional sliding tests as a function of distance is shown in Fig. 2a. After a brief initial transient run-in period where the unfilled PFA loses nearly 10 mm^3 of its volume during the first ~150 m of sliding, thereafter steady-state wear conditions are adopted with further wear volume increasing linearly with sliding distance. Testing is halted for it not long beyond 5000 m of sliding where the wear volume is already approaching 60 mm^3 and a sloped linear steady-state wear behavior is easily identified. From the best-fit slope of this linear region, a steady-state wear rate of 1.03×10^{-4} mm^3/Nm is estimated for the unfilled PFA under these sliding conditions, quite comparable to the 1.4×10^{-4} mm^3/Nm steady-state value reported for unfilled PFA by Sidebottom et al. [19] under similar ambient air sliding conditions though at sliding speed and contact pressure values that are approximately two-fold lower and higher, respectively, than those employed here. Sidebottom et al. [19] similarly reported a brief run-in period as sliding commenced during which unfilled PFA exhibited a momentarily higher initial wear rate.

During this brief sliding distance within which the unfilled PFA pins completely wear out in Fig. 2a, the 5 wt% alpha-alumina and 3 wt% nanocarbon composites wear records both appear to be comparably flat and crowding the horizontal axis, representing not only the repeatability of the demonstration by Sidebottom et al. [19] of nanoscale alpha-alumina filler to extremely reduce the wear rate of PFA as it is broadly known already to do in PTFE, but also newly demonstrating the capability of nanocarbon filler to achieve the same in PFA as it had been previously shown to do in PTFE [9]. Fig. 2b focuses in on the much lower wear volumes these nanocomposites experience, out to extended distances of 50 km or beyond for which they may be slid without experiencing wear volumes or corresponding wear depths even approaching the ~1 mm order-of-magnitude. Both nanocomposites appear to experience an initial run-in period of greater wear before settling by 10 km sliding distance to a steady-state behavior of linear increase of volume loss with sliding distance. While the nanocarbon PFA composite may experience a run-in wear volume ~1.3 mm^3 (with corresponding wear depth of only 0.04 mm) in this instance that is more than twice as great as that from the alpha-alumina composite, their wear records thereafter are nearly parallel indicating comparable values of extremely reduced steady-state wear rate. These values were 0.77×10^{-7} mm^3/Nm and 1.00×10^{-7} mm^3/Nm, respectively, for the 5 wt% alpha-alumina and the 3 wt% nanocarbon PFA composites. Again, this performance was very comparable to that reported by Sidebottom et al. [19]; where for their 5 wt% alpha-alumina PFA nanocomposite an initial run-in transient was reported before settling to a lower steady-state wear rate of 0.68×10^{-7} mm^3/Nm. As seen in the photographs of the 50 mm × 50 mm stainless steel counterfaces still within their fixtures post-test in Fig. 3, the wear track from the unfilled PFA has considerable wear debris of its same white color discarded to both the inside and outside, while no such debris are seen in the case of the alumina-filled nanocomposite with only a lightly discolored thin transfer film within the wear track despite experiencing a nearly ten-fold greater sliding distance. Such a transfer film is also seen in the nanocarbon-filled PFA, with some very small amount of debris seen occasionally outside the wear track likely reflecting the approximately two-fold greater amount of initial run-in wear as compared to the alumina nanocomposite.

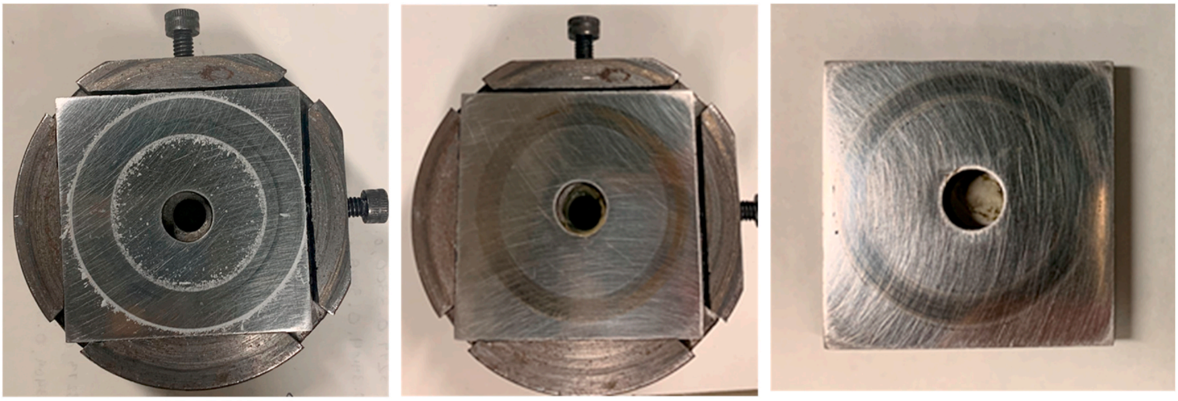
2.3.2. FEP

The wear volume from single pins of unfilled FEP and several FEP nanocomposites each supporting 50 N load during reciprocating sliding tests are shown as a function of distance in Fig. 4. FEP in its unfilled state appears to adopt nearly from the onset of sliding a linear and extremely steep loss of wear volume with increasing sliding distance, characterized by a steady-state wear rate of approximately $\sim 0.3 \times 10^{-3}$ mm^3/Nm, more similar to that of PTFE than the wear rate of unfilled PFA which while still large was just previously shown to be slightly lower, more near to 10^{-4} mm^3/Nm. As already long known for PTFE, and more recently known for PFA including the repeated demonstration in this study, nanoscale alpha-alumina filler's ability to drastically reduce fluoropolymer wear rate appears to translate to FEP as well, with the 2 wt% alpha-alumina composite's wear record remaining nearly flat, crowding the horizontal axis of Fig. 4. The low 0.8×10^{-6} mm^3/Nm steady-state wear rate measured in this alumina-filled FEP test is not quite as reduced though as the $\sim 10^{-7}$ mm^3/Nm extreme levels the alpha-alumina nanofiller is readily able to achieve in PTFE and PFA matrices. In contrast, the 2 wt% nanocarbon filler, also known to similarly produce extreme wear resistance in PTFE [9] and as well as in PFA shown above like alpha-alumina, fails to achieve the same in FEP. Its steady-state wear $\sim 10^{-5}$ mm^3/Nm, while somewhat reduced, is modest and more akin to what one would expect instead of a microfiller in the case of PTFE, and is seen to be adopted only after a run-in transient period of ~10 km sliding distance during which more rapid wear first liberates over 30 mm^3 of debris, consuming an approximate ~2 mm wear depth. The 2 wt% carbon nanotube CNT filler shown to achieve steady-state wear rate $< 10^{-6}$ mm^3/Nm in PTFE instead experience a run-in transient comparable to that of nanocarbon in FEP, with steady-state wear rate thereafter approximately 3×10^{-5} mm^3/Nm reduced even less than those modest reductions achieved by nanocarbon. The mesoporous carbon nanopowder filler, despite the higher 5 wt% content, provided very little benefit to FEP, with a steep and rapid linear loss of wear volume from the onset of sliding at a wear rate $\sim 0.2 \times 10^{-3}$ mm^3/Nm only slightly reduced from that of unfilled FEP, through a wear volume beyond 50 mm^3 (or wear depth beyond 3 mm) without indication of any potential transition to a steady-state of lower wear rate.



(a) (b)

Fig. 2. Wear volume from a pair of PFA pins in two-pin-on-disc testing as a function of unidirectional sliding distance under 100 N total normal load supported by two pins when unfilled and with alpha-alumina (5 wt%) or nanocarbon (3 wt%) fillers. (a) Initial sliding, (b) extended sliding.



Unfilled   Alumina-filled   Nanocarbon-filled

Fig. 3. Photographs of wear tracks left on square (50 mm × 50 mm) disk counterfaces after sliding against pins of PFA unfilled and with alpha-alumina (5 wt%) or nanocarbon (3 wt%) fillers.

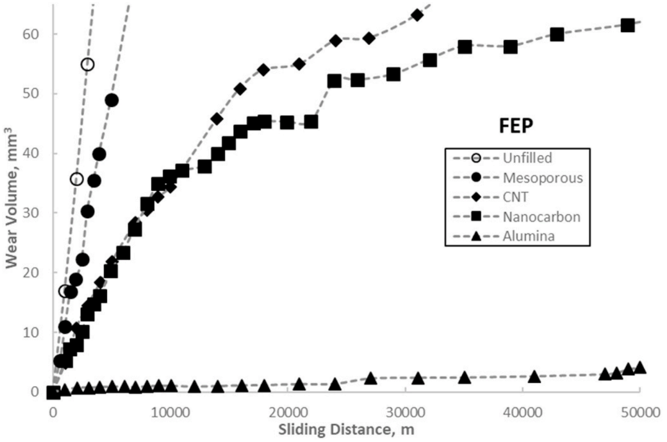
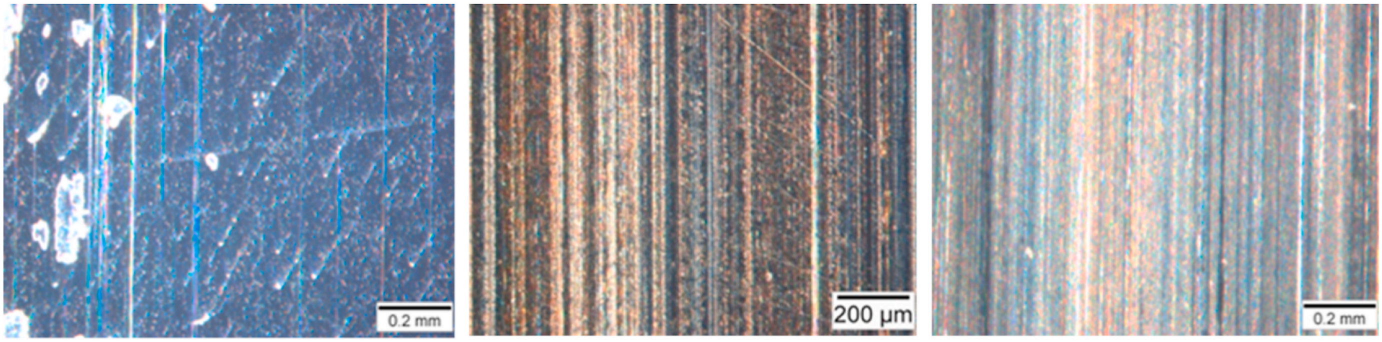


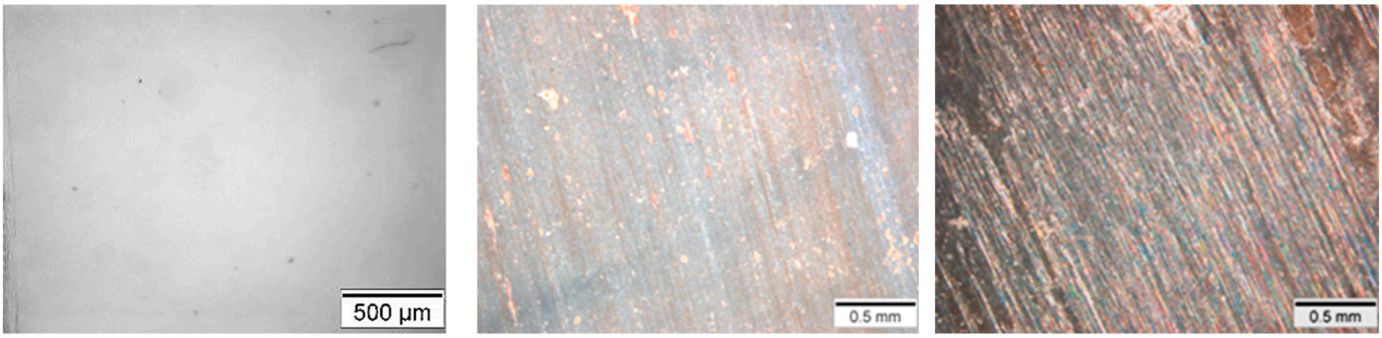
Fig. 4. Wear of FEP as a function of reciprocating sliding distance under 50 N total normal load when unfilled and filled with mesoporous carbon (5 wt%), carbon nanotube CNT (2 wt%), nanocarbon (2 wt%), and alpha-alumina (2 wt %) fillers.

As compared to unfilled FEP, further investigation will focus on nanocarbon filler and the apparent loss of its ability to provide extreme wear resistance in FEP that it had previously demonstrated in both PTFE and PFA, in contrast to alpha-alumina demonstrating maintenance of such ability to provide extreme wear resistance across all three of these fluoropolymers. Optical micrographs within the wear tracks on the stainless steel counterfaces produced by each of these three materials are preliminarily offered in Fig. 5, as well as optical micrographs of the pin surfaces themselves in Fig. 6. For the counterfaces, in the case of unfilled FEP in Fig. 5a there are several large plates of polymer material several hundreds of micrometers in-plane dimension that have been transferred to the counterface presumably by a delamination process akin to that described for unfilled PTFE [22] that upon continued sliding eventually detach and are discarded as severe-wear debris about the wear track edges. In contrast, for the alumina- and nanocarbon-filled cases there are no such large transferred plates to be seen, with instead the counterfaces lightly grooved from polishing by the nanofillers along the sliding direction with some light transfer film as evidenced by discoloration. Whereas the unfilled FEP pin surface in Fig. 6 does not display much evidence of even the direction of sliding, perhaps a result of the rate at which material is being worn and removed from its surface, striations on the alumina- and nanocarbon-filled pin surfaces mating with those on the counterface along the sliding direction are readily seen. While the nanocarbon filler material is black and in turn strongly blackens the entire pin and its sliding surface, the alumina filler material that was originally whitish within a translucent polymer can be seen as numerous particles and their larger agglomerations throughout the pin sliding surface, with adjoining streaked regions of light tannish brown discoloration. Since the dispersion of the filler particles was not characterized in this study following twin-screw melt mixing into the polymer matrix and molding, it remains unknown whether such agglomeration occurs within the mechanically-mixed region of the composite wear surface, or



Unfilled   Alumina-filled   Nanocarbon-filled

Fig. 5. Optical micrographs within wear tracks left on counterfaces after sliding against pins of FEP unfilled and with alpha-alumina (2 wt%) or nanocarbon (2 wt %) fillers.



Unfilled Alumina-filled Nanocarbon-filled

Fig. 6. Optical micrographs of FEP pin wear surfaces when unfilled and with alpha-alumina (2 wt%) or nanocarbon (2 wt%) fillers.

is already in place prior to wear testing having persisted through the melt-mixing process from an agglomerated state within the initial filler particle powder.

2.3.3. HDPE

In the reciprocating sliding tests of pins of HDPE and its nanocomposites each supporting a 50 N load, the most immediate observation from the wear records in Fig. 7 is that neither the alpha-alumina nor the nanocarbon filler act to significantly reduced the wear of unfilled HDPE. Over the 60–70 km range of distance the alpha-alumina nanofiller composites were slid, wear volumes were approximately twice that of the unfilled HDPE, with composites at all three filler contents tested producing wear records remaining close together within a narrow range despite composition varying from 0.32 to 4 vol%. In the case of nanocarbon filler, at the lowest 0.32 vol% content the composite wear record remained relatively unchanged from that of the unfilled HDPE, while at the higher filler contents up to 4 vol% wear volumes became considerably greater than that of the unfilled HDPE, as similarly observed for the three alpha-alumina nanocomposites tested. Of course, also notable of these wear records is how small a volume is worn from the unfilled HDPE despite many tens of kilometers of sliding distance, with a linear steady-state behavior adopted nearly from the initiation of sliding, already possessing an extremely low wear rate of approximately 3.6 × 10^{-7} mm^3/Nm. This level of HDPE wear resistance is actually not unexpected, as the ultra-high molecular weight form of such linear polyethylene in the unfilled state is well known as the polymer of choice for wear-resistant orthopedic joint replacement bearing surfaces, for example with Tetreault and Kennedy [23] measuring a wear rate of 4.0 × 10^{-7} mm^3/Nm for UHMWPE in dry oscillatory sliding against as-cast CoCr. Thus, while filler particles may prove highly beneficial in other cases such as PTFE, PFA and FEP where the wear resistance is otherwise exceedingly poor and a great margin is available for possible improvement by interrupting the rapid debris particle detachment mechanisms, in other polymers already possessing inherent wear resistance in the unfilled state such fillers may instead prove deleterious to that wear resistance. In fact, when studying the effect of 8 nm thickness graphene platelet nanofillers, gradual increases in volume fraction to 4%, a content shown capable of producing some considerable wear resistance to PTFE [11], instead caused gradually increasing rates of wear in HDPE, with further increases to 12 vol% or higher actually resulting in large-scale structural failures in HDPE with large chunks of pin breaking off under frictional sliding, likely the result of increasing probability of

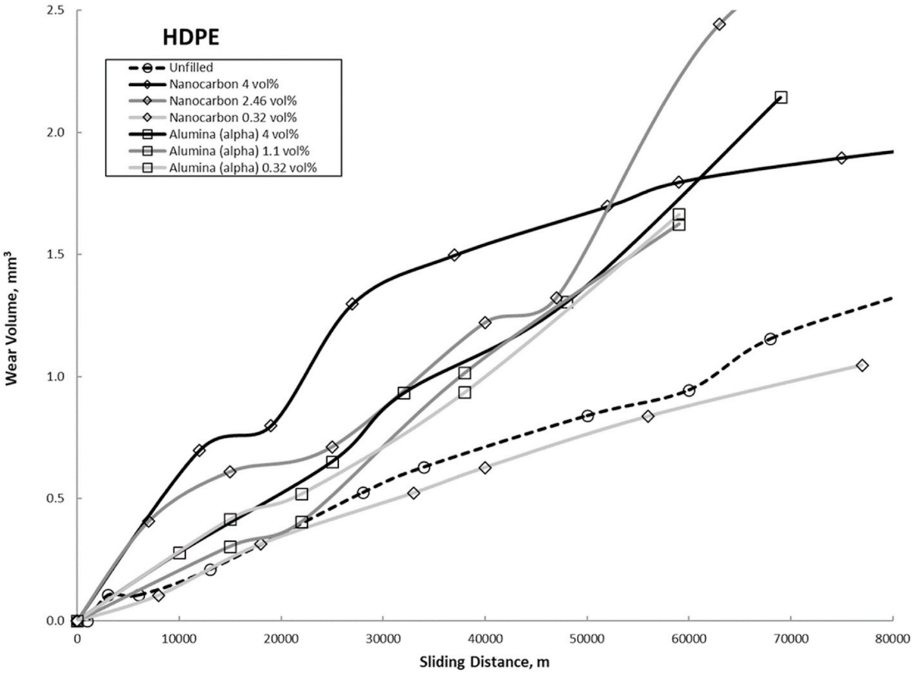


Fig. 7. Wear of HDPE as a function of reciprocating sliding distance under 50N total normal load when unfilled and with alpha-alumina or nanocarbon fillers at various contents.

weaker filler/filler interfaces within the composite.

3. Discussion: varying nanofiller effectiveness in FEP

Studying the behaviors of a wear-resistant 5 wt% alpha-alumina PTFE nanocomposite as a function of reciprocating sliding cycles, Pitenis [24] noted that while the low $<10^{-6}$ mm^3/Nm instantaneous wear rates reached upon 10^5 cycles remained as low as this value as sliding progressed through 10^6 cycles, they also noted that the ~200 nm thick transfer film at 10^5 cycles continued to grow with further sliding, reaching a ~1 μm thickness upon 10^6 cycles. Characterizing such transfer films by Fourier Transform Infrared (FTIR) spectroscopy in reflection mode from central regions of the stainless steel counterface wear track, in addition to the ~1150 cm^{-1} and ~1205 cm^{-1} peaks of PTFE within the nanocomposite it was noted that peaks near 1430 cm^{-1} and 1650 cm^{-1} also began to emerge within the transfer film, with intensities increasing as sliding progressed from 10^5 to 10^6 cycles. It is proposed that these new peaks are associated with chelation of the metal counterface with PTFE within the transfer film that had been partially transformed into perfluorinated carboxylic acids, via mechanical scission of PTFE chains under friction followed by reaction with humidity (H_2O) within the ambient surroundings and likely furthered by O_2 in the surroundings as well [25], and that such chemical bonding of transfer film to the metal counterface renders it more robust in maintaining a low-wear sliding interface of polymer composite instead against protective polymer transfer film. Krick [26] furthered such FTIR analysis by performing it on the wear-resistant alpha-alumina PTFE nanocomposite worn surfaces themselves, employing Attenuated Total Reflection (ATR) mode, and again noted appearance of such prominent 1430 cm^{-1} and 1650 cm^{-1} peaks there, indicating carboxylic acid end group formation of PTFE and chelation with metal, in the case of the nanocomposite wear surface with that metal instead within nanoscale fragmented alumina fillers, effectively crosslinking it into a robust low-wear sliding surface, being paired with the likewise robust transfer film. Such ATR characterization was subsequently adopted in our study of PTFE nanocomposites filled with nanocarbon, CNT, and graphene platelets [27], and as the wear rates monotonically decreased with increasing amounts of each of these effective nanofillers, the intensity of peaks associated with such carboxylation and metal chelation within these nanocomposite wear surfaces correspondingly increased. Likewise, at fixed filler content, the observation that wear rate of graphene-filled PTFE decreased with decreasing platelets thickness (and therefore increasing filler specific surface area) correspondingly displayed an increasing extent of carboxylation and metal chelation within the nanocomposite wear surface. Similarly, in the case of PFA where such extreme wear resistance is again achieved via alpha-alumina filler, such peaks associated with fluoropolymer chelation with metal (though slightly shifted to approximately 1434 cm^{-1} and 1665 cm^{-1}) are noted upon ATR of worn composite surfaces, while absent on such composite surfaces prior to sliding as well as on unfilled PFA surfaces either prior to or after wear [19].

Of the several fillers already known to provide extreme wear resistance to PTFE (including nanocarbon powder shown above also capable of such wear resistance in PFA) and tested further here, for FEP fluoropolymer it appeared only alpha-alumina was able to transfer any large degree of such wear rate reducing capability (0.8×10^{-6} mm^3/Nm), with nanocarbon powder providing just an intermediate reduction in steady-state wear rate (~10^{-5} mm^3/Nm) after an initial run-in period, Fig. 4. Upon ATR characterization of the various FEP composite surfaces prior to wear (Fig. 8), in addition to the two fluoropolymer peaks previously noted for PTFE (~1150 cm^{-1} and ~1205 cm^{-1}) a third one appears at ~993 cm^{-1} corresponding to FEP's additional trifluoromethyl side group, as previously noted for PFA where trifluoromethyl terminates PFA bulkier side group [19]. ATR of worn FEP composite surfaces reveals the strongest metal chelate peaks ~1430 cm^{-1} and 1650 cm^{-1} corresponding to the most wear-resistant alpha-alumina filled case (Fig. 8b), with nanocarbon-filled FEP of intermediate wear resistance still displaying such peaks though of lower intensity, while such peaks are absent from the less wear-resistant CNT and mesoporous carbon filler FEP composites. Thus it again appears in FEP that greater amounts of wear resistance are associated with fillers causing greater extents of chelation in composite sliding surfaces with the filler particles effectively serving as crosslink nodes connecting the polymer molecules into a network, and such chelation likely also more robustly bonding PTFE transfer films to the counterface.

Before attempting to construct any explanations at this time for why alpha-alumina filler appears able to translate its extreme wear-reducing chelation to FEP while other fillers that have demonstrated extreme wear-resistance and chelation in PTFE (including nanocarbon powder) are less capable of this translation, it is noted in these preliminary ongoing studies that such performance of alpha-alumina filler in FEP is actually somewhat variable. As shown in Fig. 9, if a pair of alumina-filled FEP pins fabricated from the same twin-screw mixed extrudate and molded puck is instead tested in unidirectional two-pin-on-disk sliding against disks of slightly increased roughness ($R_a = 0.0639$ μm), the measured 2.8×10^{-7} mm^3/Nm steady-state wear rate like the 8×10^{-7} mm^3/Nm value previously reported from Fig. 4 against a reciprocating plate of $R_a = 0.0246$ μm is again extremely reduced from the ~0.3×10^{-3} mm^3/Nm wear rate reported earlier for unfilled FEP. The more prominent difference in wear performance for this alumina-filled FEP under this unidirectional sliding against a slightly rougher counterface is instead the greater amount of wear that occurs during the initial transient run-in period before adoption of reduced steady-state wear rate, a ~3 mm^3 volume from a pin of 16 mm^2 contact surface corresponding to a ~0.5 mm wear depth during initial run-in. This transient run-in period is thought to be associated with the transformation of the composite as well as counterface surfaces from their initial as-prepared states towards that stabilized in steady-state, involving processes such as running film and transfer film formation on the composite and counterface surfaces, respectively, as well as topographic, compositional, and tribochemical changes to those surfaces. Thus it may be intuited that a counterface of slightly greater roughness as well as greater wear track length (115 mm circumference on the rotating disk as opposed to 40 mm stroke on reciprocating plate) might consume a greater initial run-in volume of composite before eventual attainment of steady-state conditions of comparable extents of extremely reduced wear rate. When investigating this same alpha-alumina filler under these same unidirectional and reciprocating sliding conditions bringing the steady-state wear rates of PTFE against 304 stainless steel comparably down towards levels approaching ~10^{-7} mm^3/Nm, Blanchet et al. [7] similarly found these steady-state wear rate values to be slightly higher in reciprocating as opposed to unidirectional sliding, as well as slightly higher against counterfaces of R_a roughness in the 0.06–0.08 μm as opposed to 0.015–0.03 μm range.

Though initially the alpha-alumina powder is whitish while the FEP pellets are translucent, upon twin-screw mixing of them in the extremely wear-resistant case reported above the compounded composite extrudate had become dark brown. However in a subsequent case despite seemingly employing the same filler, polymer, twin-screw mixer and mixing conditions, the new mixed extrudate instead only developed a slight tan discoloration (Fig. 10). Producing pin wear specimens from a molded puck of this newly mixed extrudate, in repeat unidirectional sliding no such transition to any extremely-reduced steady-state wear rate was observed this time (Fig. 9), as the rapid initial run-in wear instead continued through a pin wear volume of 6.6 mm^3 (shown) then on to 12.5 mm^3 by 1300m sliding distance at which point the sliding test was halted. The greater extent of chemical interaction between filler and polymer already taking place during this melt mixing process as reflected by the further discoloration in turn seems to correspond to attainment of the more extreme levels of wear resistance, as displayed in Fig. 9 with the ability to newly mold pucks from which pin sliding specimens display high wear resistance from the same prior more

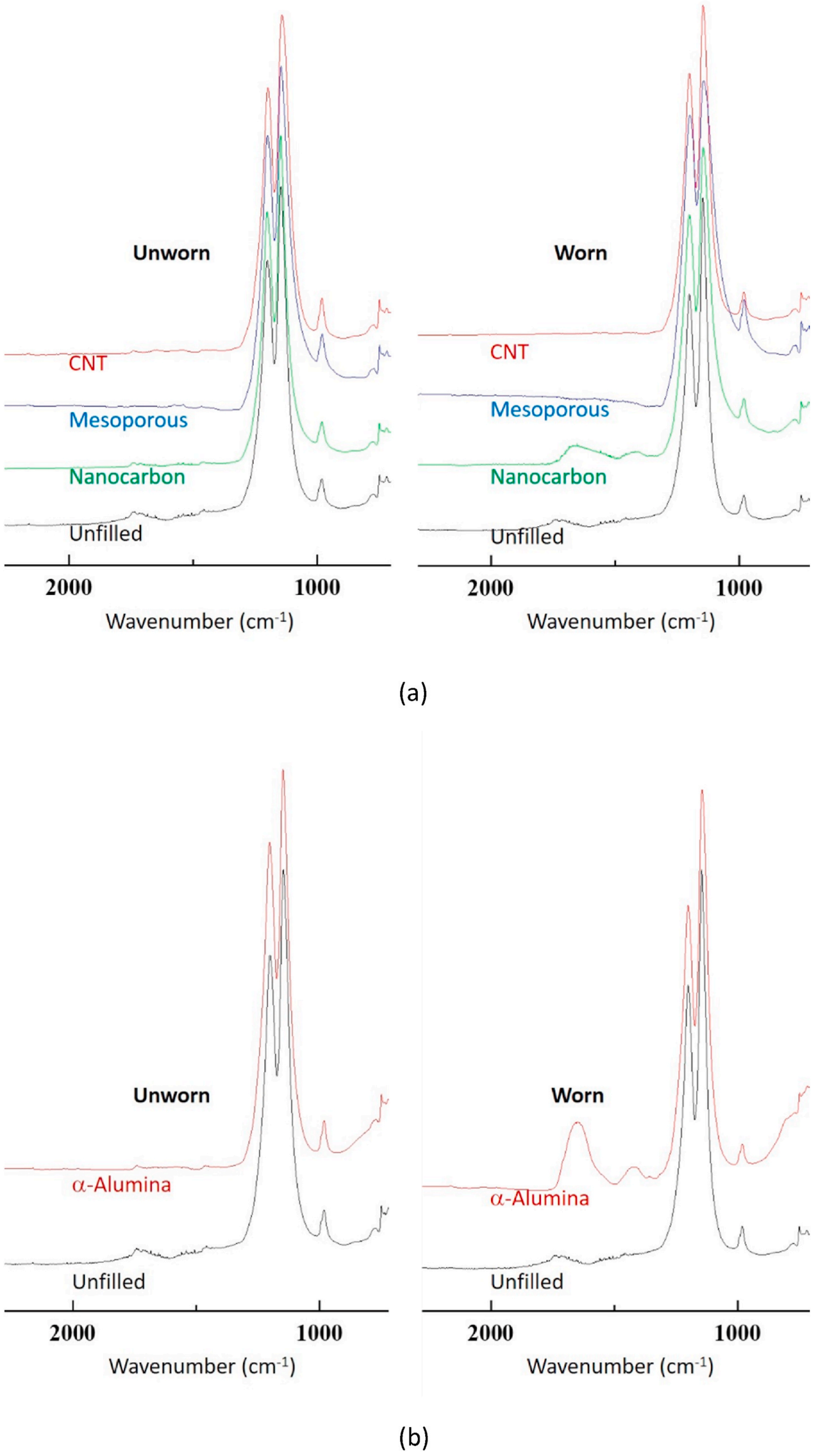


Fig. 8. ATR-FTIR spectra of filled FEP pin surfaces in both worn and unworn state, as compared to unfilled PTFE. (a) Mesoporous carbon (5 wt%), carbon nanotube CNT (2 wt%), nanocarbon (2 wt%) fillers, and (b) alpha-alumina (2 wt%) fillers. Only the alpha-alumina and the nanocarbon-filled FEP displaying considerable peaks at ~1430 cm^{-1} and 1650 cm^{-1} reflecting chelation chemical reactions.

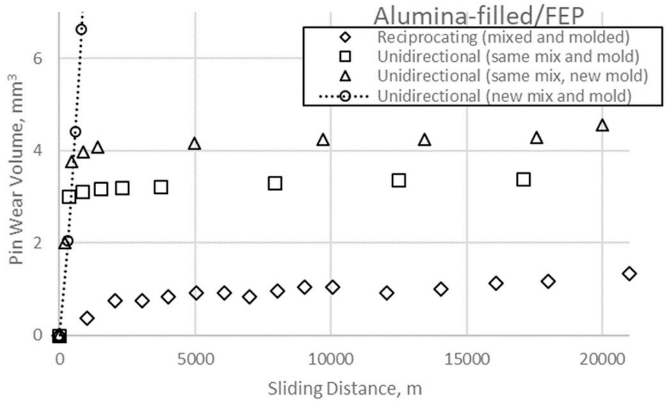


Fig. 9. Wear performance variability study of alpha-alumina filled FEP. Relative to performance in reciprocating pin-on-plate sliding originally reported in Fig. 4, wear volume per pin under 50N load in unidirectional two-pin-on-disk sliding against disk counterfaces also measured from various processed composite pins: from same twin-screw mixture and molded puck as original reciprocating test pin; from same mixture but newly molded puck; from newly mixed and molded batch.

discolored composite mixed extrudate. As shown in Fig. 9, for wear pins produced from a new molding of the same prior discolored extrudate mix, adoption of an extremely reduced state-state wear rate (in this case 3.0×10^{-7} mm^3/Nm) returned after an initial run-in wear volume of approximately 4 mm^2.

Thus for FEP and its potential for extreme nanocomposite wear resistance such as with this alumina filler, there appears to be some source of great variation, which may especially involve its melt mixing processes. Comparable variations in fluoropolymer composite wear resistance have previously been reported. For example, for such an alpha-alumina filler in the case of PTFE Krick et al. [28] showed a strong dependence of wear rate on environmental water and the relative humidity of the test environment, while for the alpha-alumina FEP composites reported here laboratory humidity levels during the blending preparation of the filler powder and polymer pellets and their subsequent melt mixing were neither controlled nor measured. Likewise, Burris et al. [29] showed while an alpha-alumina filled PTFE composite sintered at 360 °C displayed the well-known extreme wear resistance that this wear resistance was largely lost with wear rate increasing by two orders of magnitude upon a subsequent thermal cycle to 400 °C. Though target melt mixing temperatures are set to 320 °C for the FEP composites within the twin-screw, it appears small variations in temperature may hold importance, and actual variations in mixing temperature from batch-to-batch were not recorded. Clearly, the melt mix processing conditions are of focal interest in continued studies of tribological FEP composites.

4. Conclusions

1. The ability of alpha-alumina to transport its well-known extreme wear resistance in PTFE also to PFA fluoropolymer has been duplicated here, while furthermore the ability of nanocarbon powder to provide extreme wear resistance to PFA has been newly demonstrated with wear rate reduced to ~10^{-7} mm^3/Nm, as representative of numerous forms of nanoscale carbon fillers already known to also provide such extreme wear resistance to PTFE.
2. Newly investigating FEP, as compared to ~0.3×10^{-3} mm^3/Nm in its unfilled state, in preliminary wear studies only the alpha-alumina filler (2 wt%) evidenced an ability to largely transport any extreme wear resistance to this fluoropolymer achieving a 0.8×10^{-6} mm^3/Nm wear rate, while nanocarbon's effectiveness at such content was only a fraction of this ~10^{-5} mm^3/Nm, with other forms of nanoscale carbon filler even less effective at reducing unfilled FPE wear rate. Correspondingly ATR-FTIR of only the wear surfaces of the alpha-alumina and nanocarbon filled FEP displayed strong and intermediate extents, respectively, of chelation tribochemistry associated with nanocomposite wear resistance in PTFE and PFA.
3. Discoloration during twin-screw extruder melt-mixing of alpha-alumina filler into FEP shows some variation batch-to-batch, and in turn appears to be some variation of the achievement of wear resistance. Further studies are warranted investigating such discoloration, and the effects of possibly small differences in temperature profile that may be occurring during the melt-mixing as well as water exposure, for example in the form of ambient humidity.
4. As compared to such fluoropolymers that are so lacking of wear resistance, such nanofillers that are considered to be so beneficial in such case may instead be detrimental if compounded into polymers that in their unfilled state already possess an inherent level of wear resistance, as has been demonstrated here for HDPE.

Fig. 10. Batch-to-batch variations in discoloration upon twin-screw melt-mixing of alpha-alumina filler particles into FEP resin under seemingly identical conditions (320 °C, 12 rpm, 8 min). Only more heavily discolored composite to the left results in extreme wear resistance of Fig. 3.

Author statement

Mary E. Makowiec: Investigation; Formal Analysis. Grace L. Gionta: Investigation; Formal Analysis. Suvrat Bhargava: Investigation; Formal Analysis. Rahmi Ozisik: Supervision; Funding Acquisition; Resources; Writing – Review & Editing. Thierry A. Blanchet: Conceptualization; Supervision; Funding Acquisition; Project Administration; Writing – Original Draft; Writing – Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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