lubricants

MDPI

Review

A Review of Transfer Films and Their Role in Ultra-Low-Wear Sliding of Polymers

Jiaxin Ye [1,2], David L. Burris [2] and Ting Xie [1,*]

[1] Institute of Tribology, Hefei University of Technology, 230009 Hefei, China; [redacted]@hfut.edu.cn
[2] Department of Mechanical Engineering, University of Delaware, Newark, DE 19716, USA; [redacted]@udel.edu
* Correspondence: [redacted]@hfut.edu.cn; Tel.: [redacted]

Academic Editors: Werner Oesterle and Ga Zhang
Received: 16 January 2016; Accepted: 16 February 2016; Published: 26 February 2016

Abstract: In dry sliding conditions, polytetrafluoroethylene (PTFE) composites can form thin, uniform, and protective transfer films on hard, metallic counterfaces that may play a significant role in friction and wear control. Qualitative characterizations of transfer film morphology, composition, and adhesion to the counterface suggest they are all good predictors of friction and, particularly, wear performance. However, a lack of quantitative transfer film characterization methods and uncertainty regarding specific mechanisms of friction and wear control make definitive conclusions about causal relationships between transfer film and tribological properties difficult. This paper reviews the state of the art in the solid lubricant transfer film literature and highlights recent advances in quantitative characterization thereof.

Keywords: PTFE composite; transfer film; morphology; adhesion; friction and wear

1. Introduction

Polytetrafluoroethylene (PTFE) and its composites are attractive for use in tribological applications due to low friction coefficients [1,2], high melt temperature, and chemical inertness of the parent polymer. These materials are often mated against a metallic counterface to form friction pairs, such as guides, bushings, seals, and valve seats, to name a few. An important advantage of the PTFE composite–metal counterface sliding system is its ability to provide low friction and low wear in dry sliding conditions. The self-lubricating properties of this system are thought to be largely attributable to its ability to deposit a thin and protective layer of polymer onto the counterface, the so-called transfer film [3]. Contrary to the conventional wisdom that PTFE resists adhesion, Tabor *et al.* showed that PTFE readily transfers to surfaces it contacts [4,5]. Low friction, it turns out, is due to easy shear between PTFE lamellae or fibrils, not poor adhesion to the opposing surface, as originally thought [4]. Unfortunately, however, the same attributes that yield low friction also enable subsurface cracks to easily propagate, which results in large, plate-like debris, poorly adhered transfer films, and unacceptably high wear rates (K~10^{-3} mm^3/Nm) at speeds greater than ~10 mm/s [4,6].

Incorporation of micro-scaled fillers has been shown to reduce wear rates of PTFE typically by ~100× with >20 wt % filler loading [3,6–11]. Early on, the wear-mitigating effect of these particles was attributed to preferential support of the normal load by the filler and disruption of subsurface crack propagation [6,12]. In each case, significant wear reductions accompanied smaller wear debris and thinner, more complete, and seemingly adherent transfer films. Improved transfer films are believed to cause reduced wear by shielding the composite from the hard counterface asperities [8]. However, it has also been argued that improved transfer films are the consequence of reduced debris size [9,13].

The cause-effect relationship between wear rate, debris size, and transfer film quality remains an open question and is likely system-specific.

Large, hard fillers tend to abrade the transfer films and roughen the surface, which limits overall potential for friction and wear reduction [8]. Smaller fillers on the other hand have the potential to reduce wear, while polishing the transfer films and the counterface. Tanaka and Kawakami were the first to study sub-micron filler particles in PTFE; they performed poorly relative to the microparticles in the field and the authors concluded that nanoscale fillers were too small to disrupt large-scale destruction of the banded structure [14]. It was not appreciated at the time, however, that the combination of large loadings (20 wt %) and small particles (300 nm) are likely to lead to agglomeration, ineffective sintering, and a substantially weakened polymer composite. Interest in PTFE nanocomposites returned decades later after several studies independently demonstrated similar wear reductions of 100× with smaller loadings (5–10 wt %) of nanoscale zinc, carbon nanotubes, and alumina [15–17]. In each study, the authors reported transfer films that were thinner, more uniform, more complete, and less obviously damaged by sliding than those previously observed for PTFE-based materials.

In 2006, Burris and Sawyer discovered a unique alpha-phase alumina nanoparticle that reduced PTFE wear by 1000× with as little as 0.5 wt % filler [18]; this was the first demonstration of ultra-low-wear of PTFE ($K < 5 \times 10^{-7}$ mm^3/Nm) with less than 5% fillers. This particular system soon became the subject of many follow up studies [19–34]. More recently, Kandanur *et al.* found other nanofillers (graphene, carbon, *etc.*) that can also reduce wear of PTFE up to four to five orders of magnitude at a fraction of the loadings [34,35]. The extreme wear reductions and the scarcity of fillers in these systems suggested a mechanism other than those previously envisioned. As in previous studies, the reduction in wear rate was accompanied by decreased debris size and improved transfer film attributes, like thickness and uniformity.

2. Transfer Films and Their Link to Low Wear

Despite the clear protective role of the transfer film and the close observed relationship between transfer film characteristics and wear rate, it remains unclear if improved transfer films are the cause or the consequence of reduced wear rates. Briscoe first suggested transfer film adhesion is the dominant wear-reducing factor in polymer composites and is caused by filler-induced polymer degradation [8]. Bahadur and Gong concluded that filler chemistry was critical because decomposition enabled the filler to form a link between the transfer film and the counterface [3]. Schwartz and Bahadur attempted to make the first direct measurements of transfer film bond strength by gluing a copper tab to the transfer film formed by a PPS nanocomposite against steel. The peel strength increased with increased wear resistance, which is consistent with the hypothesis that well-adhered transfer films help cause reduced wear [36].

The strong correlation between transfer film attributes and wear rate makes conclusions of causation tempting. Bahadur and Tabor [9] attempted to directly test this relationship by measuring the wear rate of PTFE against a bare counterface, a PTFE transfer film, and transfer films of low wear PTFE composites. They found that the wear rate of PTFE was virtually independent of the condition of the transfer film upon which it slid. Furthermore, they interrupted the experiments and found that in every case, the pre-deposited transfer film was almost immediately removed by the passing pin. The apparent persistence of transfer films, they determined, reflects the immediate replenishment by new debris. They determined that the high-quality transfer films that accompany low-wear bond primarily through mechanical interlocking of small debris and concluded that high-quality films must be the consequence of low wear and not the cause.

Although Bahadur and Tabor found no evidence that transfer films persist during sliding contact, Bahadur and Gong found that wear rate correlated strongly with evidence of chemical reactions in the transfer films [3]. They suggested that reactive fillers help increase transfer film adhesion and thereby reduce wear relative to inert fillers. Interestingly, alumina, an inert filler, has proven to be one of the most successful fillers for reducing PTFE wear to date [18]. This fact is especially interesting because

different types of alumina fillers have been shown to yield orders of magnitude variations in wear rates of identically-prepared PTFE nanocomposite [13,37].

3. The Effects of Filler Characteristics on Transfer Films and Wear Rates

Figure 1 illustrates the transfer film of a typical PTFE composite; in this case, the PTFE was filled with 15 wt % 76 μm particles of Ni. The optical image (Figure 1a) shows a thick, but coherent, film; profilometry (Figure 1b) highlights obvious heterogeneity in the thickness over the observation window. Two line scans demonstrate that the film is as thick as 10 μm and as thin as 2 μm. The measured wear rate of this system was K ~10^{-5} mm^3/Nm, which represents a 40× improvement over unfilled PTFE.

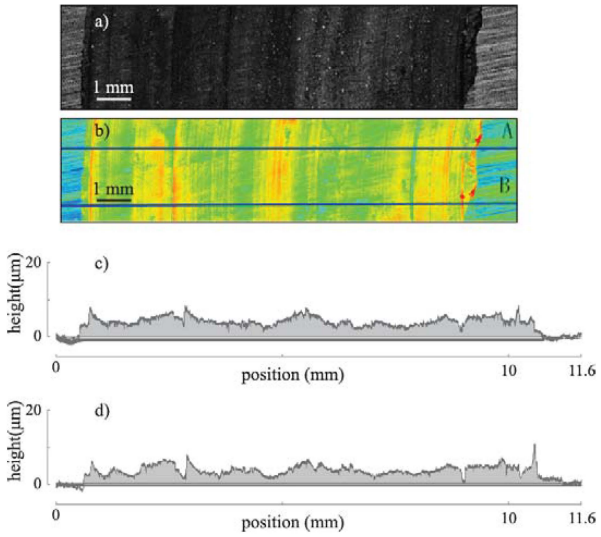

Figure 1. Morphology of the transfer film of a Ni/PTFE microcomposite (unpublished): (**a**) the optical image of the transfer film; (**b**) the height distribution mapping of the transfer film; (**c**) the cross-section profile of the transfer film along line A indicated in (**b**); and (**d**) the cross-section profile of the transfer film along line B indicated in (**b**).

The transfer film morphology of the Ni-PTFE microcomposite in Figure 1 is very different from those of the alumina–PTFE nanocomposites in Figure 2. The mixing, sintering, and testing procedures of these nanocomposite samples were identical; the only reported differences are the phase of the alumina and the size of the particle. The 44 nm $\Delta : \gamma$ phase alumina produced moderate wear rates on the order of 5×10^{-5} mm^3/Nm. The transfer film contains discernable patches of 100 μm length scale (Figure 2b). The fillers have clearly reduced debris size, improved the transfer film and reduced wear by comparison to unfilled PTFE whose transfer films contain platelets on the 1–5 mm size scale [6,31,32]. However, the 80 nm α phase alumina filled PTFE was more than 100× more wear resistant under the same conditions. The transfer film is clearly thinner (~1 μm) and more continuous (Figure 2c) [13,18].

In addition to producing thinner and more uniform transfer films, low-wear alumina–PTFE transfer films are obviously discolored [13,18,20,23–27,29,31,32,37–39], which suggests chemical reactions had taken place and possibly enhanced adhesion of the transfer film. In 2013, Ye and Burris used optical microscopy to determine the degree to which transfer films persist during sliding [20]. During run-in, wear rates were on the order of those of the $\Delta : \gamma$ composites, transfer films were relatively patchy and were removed and replaced each cycle as described by Bahadur and Tabor [9]. However, as Figure 3b illustrates, there is an abrupt (and repeatable) transition at which the wear rate decreases by orders of magnitude. At this point, the debris generation is no longer detectable and the transfer film becomes difficult to see optically. Atomic force microscopy revealed that nanoscale debris fragments were present and that continued sliding caused visual darkening as the fragments became denser across the surface.

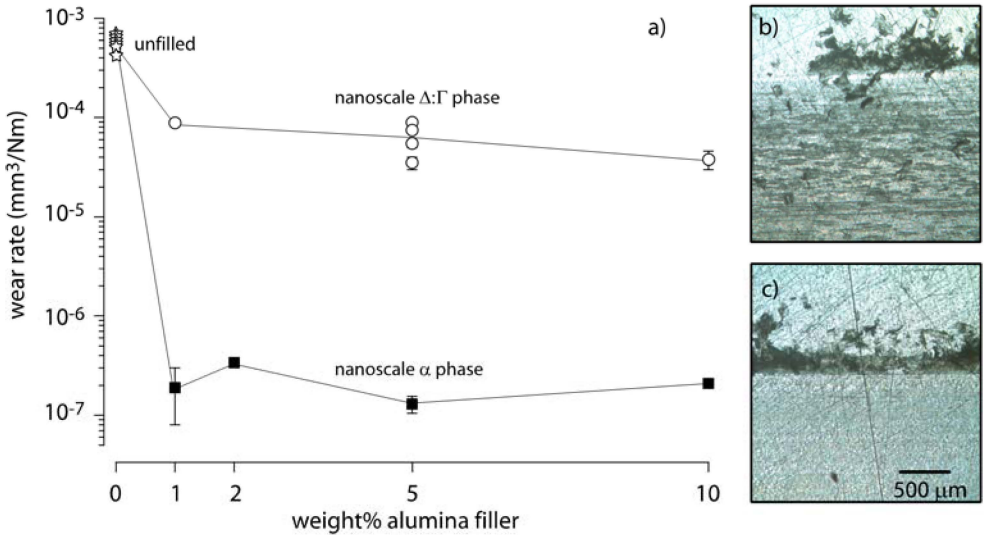

Figure 2. Two types of transfer films of PTFE composites. (**a**) Wear rates plotted *versus* alumina loadings of two types of filler phase and morphology; (**b**) transfer film of the moderate wear system (44 nm $\Delta : \gamma$ alumina); and (**c**) transfer film of the ultra-low-wear system (80 nm α alumina).

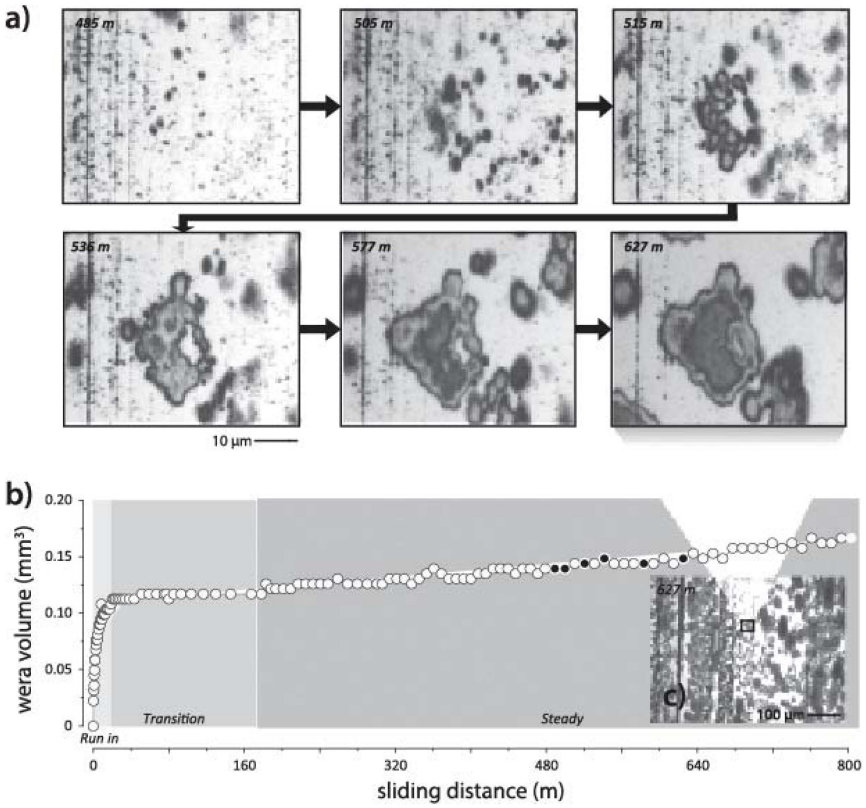

Figure 3. Images of transfer film development in an ultra-low-wear alumina–PTFE nanocomposite: (**a**) images illustrating the evolution of the steady state transfer film as a function of distance slid; (**b**) wear volume as a function of distance slid; and (**c**) steady-state transfer film morphology. Reprinted with permission from [20].

Following the transition period of virtually wear-free sliding, debris generation resumes, but the debris produced after the transition are markedly different than those produced before the transition.

The initiation and evolution of the steady state transfer film are illustrated in Figure 3a. Most of the visible debris at 485 m of sliding were sub-micron in the lateral dimension. As sliding progressed, there is clear evidence that these fragments persist, enlarge as they scavenge new material from the pin, merge together to form larger domains, and eventually develop a thickened and homogenized (Figure 3c) transfer film. These studies provide direct insight into the formation mechanisms of transfer films and demonstrate, despite prior evidence to the contrary [9], that adhesion and persistence do occur and are likely critical for achieving ultra-low-wear rates.

4. Quantifying Properties of Transfer Films

Transfer film quality has been difficult to quantify historically. Typically, the literature uses visual cues that include a convolution of thinness, coverage, and uniformity as indicators of quality and even adhesion. To date, however, our ability to answer basic questions about the cause-effect relationship between transfer film properties and wear rate is largely attributable to the difficulty in actually quantifying these transfer film attributes. Here, we outline recent advancements in efforts to quantify the relevant morphological, chemical, mechanical, and adhesive properties of transfer films and integrate those properties into our understanding of transfer film–wear causation.

4.1. Transfer Film Morphology

Early researchers of PTFE nanocomposite wear discovered that high-wear transfer films were always thick, patchy, and non-uniform and low-wear films were thin, continuous, and uniform [15–17]. Burris and Sawyer found that wear rates of PTFE and its composites tended to increase with the cube of the measured transfer film thickness over three orders of magnitude of change in wear rate [13]. Pitenis *et al.* found similar trend during *in vacuo* wear tests of PTFE composites [25]. Blanchet *et al.* [35] proposed that wear is likely related to the transfer film coverage of the wear track. Laux and Schwartz measured the thickness and coverage fraction of unfilled polyether ether ketone (PEEK) transfer films but found neither was a reliable predictor of wear rate [40]. Similarly, transfer film coverage did not correlate to the wear rate of the polyethylene terephthalate (PET) nanocomposites [41].

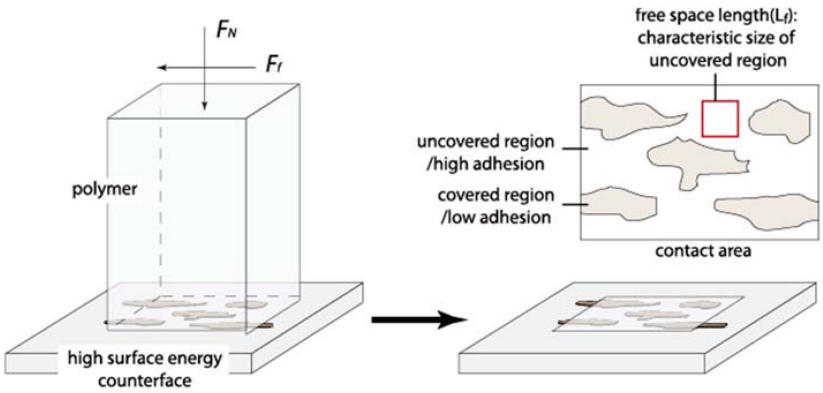

Figure 4. Free-space length model of transfer film. Reprinted with permission from [42].

Ye *et al.* [21] proposed that the polymer interacts more strongly with regions of exposed counterface and that the size of these uncovered regions should be a quantitative predictor of future debris size. Since the wear volume is proportional to the amount of debris and the cube of the debris size [43], the wear rate should be more sensitive to the characteristic size of the uncovered areas than the uncovered area fraction (Figure 4). The authors defined the free-space length as the characteristic size of the uncovered areas and developed a method to quantify this metric. The method is based on the iteration of a fixed-size overlaying box pixel-counting algorithm as explained in detail in [21]. The free-space length for representative images of the run-in, transition, and steady state transfer films of low-wear alumina–PTFE nanocomposites are represented by the length of the associated red boxes

in Figure 5a. As shown in Figure 5b, the free-space length appears to be a relatively good predictor of wear rate; the results also suggest there is a lower bound associated with full coverage and an upper bound associated with no coverage. The free-space length is also closely related to the visual cues that typically motivate adjectives like "uniform", "coherent", "continuous", and "complete" in the transfer film literature [15–17,37,44]. To date, however, there remain relatively few quantitative studies of transfer film morphology and the community has yet to agree on a single metric by which transfer film quality should be evaluated.

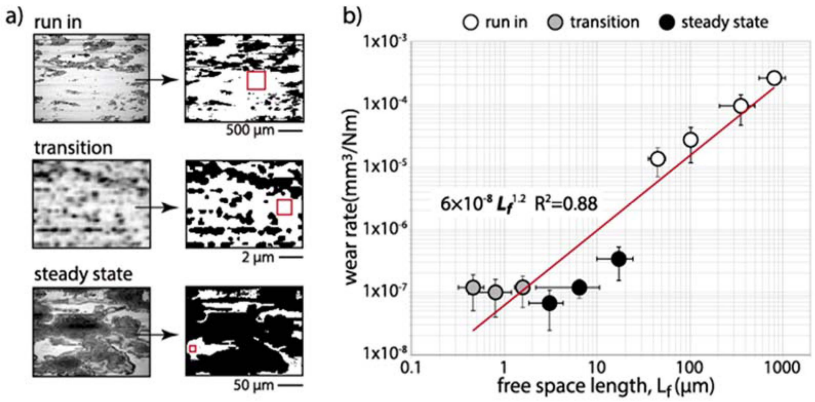

Figure 5. (**a**) Free-space lengths of representative transfer films of alpha alumina filled PTFE nanocomposite; and (**b**) free-space lengths plotted against the *in situ* wear rates of the composite. Reprinted with permission from [21].

4.2. Chemistry of the Transfer Film

It is reasonable to expect quantitative changes in transfer film morphology and wear resistance using fillers of different chemical reactivity like C and CuS [10]. It is less obvious why such differences would emerge between different alumina–PTFE nanocomposites (Figure 2). These particular systems do, however, present an interesting degree of control for elucidating the effect of transfer film chemistry since many of the other variables associated with different fillers can be eliminated.

Some of the earliest studies of these materials suggested that ultra-low-wear rates had chemical origins [45]. As wear rates decreased, transfer films not only become thinner and more coherent, but they became increasingly discolored. Burris *et al.* [46] found a new XPS peak at 288 eV in transfer films formed during ultra-low-wear sliding by PTFE and suggested that this "new tribochemical species" may help explain wear resistance of this system. Unfortunately, the XPS observation provided no direct insight into what the tribochemical species was or why it formed. Krick *et al.* [23] and Pitenis *et al.* [25] both found the removal of environmental moisture caused increased wear rates (from K~10^{-7} to K~10^{-5} mm^3/Nm), reduced transfer film quality, severe counterface abrasion, and loss of transfer film discoloration. The remarkable effects of water removal alone strongly suggested a wear reduction mechanism of tribochemical origins.

To help elucidate the effect of water vapor on the wear of PTFE nanocomposites, Onedera *et al.* [47,48] used computational tools to identify possible tribochemical reactions between PTFE and environmental moisture during sliding; based on the results, they proposed that PTFE end-chain carboxyl groups formed to help bond PTFE transfer films to the counterface. In 2015, Pitenis *et al.* [29] and Harris *et al.* [27] conducted spectroscopic studies on transfer film chemistry of the same low wear alumina PTFE nanocomposite. After one cycle, they found peaks typically associated with PTFE (Figure 6a). However, after periods long enough to cause discoloration of the transfer film, they found significant evidence of metal chelate salts of perfluorinated carboxylic acids (Figure 6b); the magnitude of the signal increased as the transfer film became increasingly discolored and as the wear rate decreased with increased sliding. They proposed that these metal chelate salts represent the bond between the polymer (perfluorinated

carboxylic acid) and the counterface (metal). Harris *et al.* [27] found evidence showing that PTFE chain ends not only chelate to the steel surface under the transfer film, but also to the surface of the alumina filler particles. Thus, tribochemistry in this system appears to stabilize the transfer film and the sliding surface of the solid lubricant, thus compartmentalizing damage and reducing wear [39].

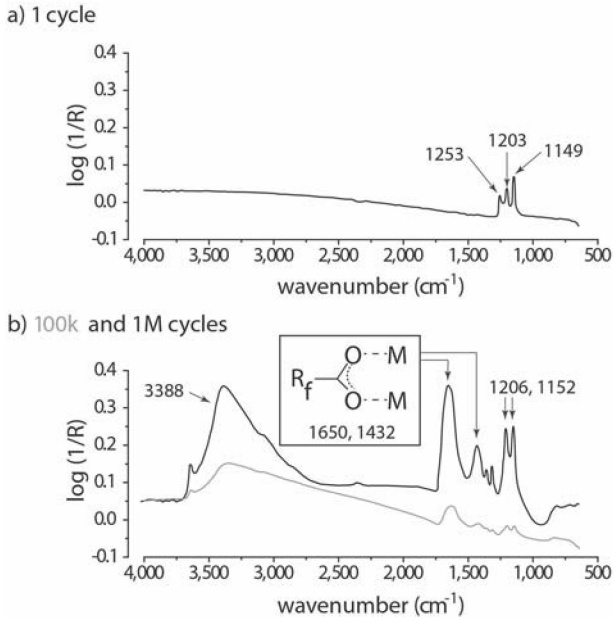

Figure 6. Infrared reflectance results from the metal surface after (**a**) one cycle of sliding; (**b**) 100 k (gray line) and 1 M (black line) cycles. Reprinted with permission from [27,29].

As a group with unprecedented expertise in tribology and fluoropolymer chemistry, Harris *et al.* [27] proposed a likely tribochemistry-based wear reduction mechanism in PTFE-related systems with the following essential steps: (1) PTFE chains break during sliding and form perfluoroalkyl radicals at new chain ends; (2) the perfluoroalkyl radicals react with atmospheric oxygen to form acyl fluoride end groups; (3) the acyl fluoride end groups hydrolyze in ambient humidity to form carboxylic acids; and (4) the perfluorinated carboxylic acids chelate to metals (Fe in the steel counterface and Al in the alumina fillers), thus stabilizing the transfer film and near surface of the pin. This hypothesis explains the observed environmental dependence of the PTFE nanocomposite's wear performance and represents a breakthrough in our understanding of ultra-low-wear PTFE.

Although chemistry certainly drives the wear reduction significantly in the low-wear PTFE composites, numerous evidence suggest it is the coupling of chemical and mechanical effects that enable the formation of a thin, continuous and adhesive transfer film that can survive millions of sliding cycles. Changes in load [49], velocity [6,49] and counterface roughness [13,28,32,50] can all change the system's wear performance by affecting the transfer film's mechanical and adhesive strength.

4.3. Mechanical Properties of the Transfer Film

Apart from transfer film morphology, improved mechanical properties of the transfer film have been suggested as an important contributor of wear reduction in PTFE and other polymer systems. Gong *et al.* [51] considered the transfer films as surface protective coatings and proposed that fillers reduce wear by mechanically strengthening the transfer film itself. Friedrich *et al.* [52,53] measured polymer transfer film hardness using microindentation, but the results were confounded by increasing contributions from the substrate with decreasing transfer film thickness. Randall *et al.* [54,55] used a nanoindenter and limited penetration depths to 10% film thickness in an effort to eliminate substrate effects. They found transfer films in the lowest wear system were ~30% harder and

stiffer than either counterpart material and suggested that this was the result of mechanical alloying. McCook *et al.* [56] conducted similar measurements on the wear surface of a PTFE-epoxy composite. Whereas the composite contained clear regions of high and low hardness from the epoxy and PTFE, respectively, the wear surface exhibited uniformly low hardness, suggesting that a running film of PTFE was preferentially drawn over the entire surface; these PTFE running films were thought to substantially decrease friction and wear by preventing adhesion between the epoxy phase and the counterbody. Xie *et al.* [57,58] measured two particle-filled PTFE microcomposite transfer films using nanoindentation and found the lower wear system has a slightly softer and more adhesive transfer film. The fact that transfer films can become harder or softer than either constituent reflects the complicated and yet uncertain role of transfer films in friction and wear control.

Krick *et al.* [24] used nanoindentation to study the mechanical properties of ultra-low-wear alumina–PTFE running films (on the composite's running surface). They found that running film hardness and modulus increase with increased sliding distance and decreased wear rates [24]. They suggested that changes in mechanical properties reflect filler accumulation and tribochemical degradation of PTFE, which is consistent with their more recent papers on the evolution of interface chemistry [27,29] and particle enrichment [30]. Ye [42] conducted similar measurements on transfer films from the same system. The transfer films had the same mechanical properties as the bulk composite during the run-in, but hardness and modulus both increased significantly following the transition to ultra-low-wear sliding, as shown in Figure 7a,b. Both figures share the same trend as the mechanical evolution of running films reported by Krick *et al.* [24]. Furthermore, there were strong correlations between transfer film mechanical properties and the system wear rater (Figure 7c,d), although the causal relationship remains uncertain; improved transfer film cohesive strength may simply be the consequence of the friction-induced polymer degradation and the accumulation of filler at the sliding interface [27,29,42].

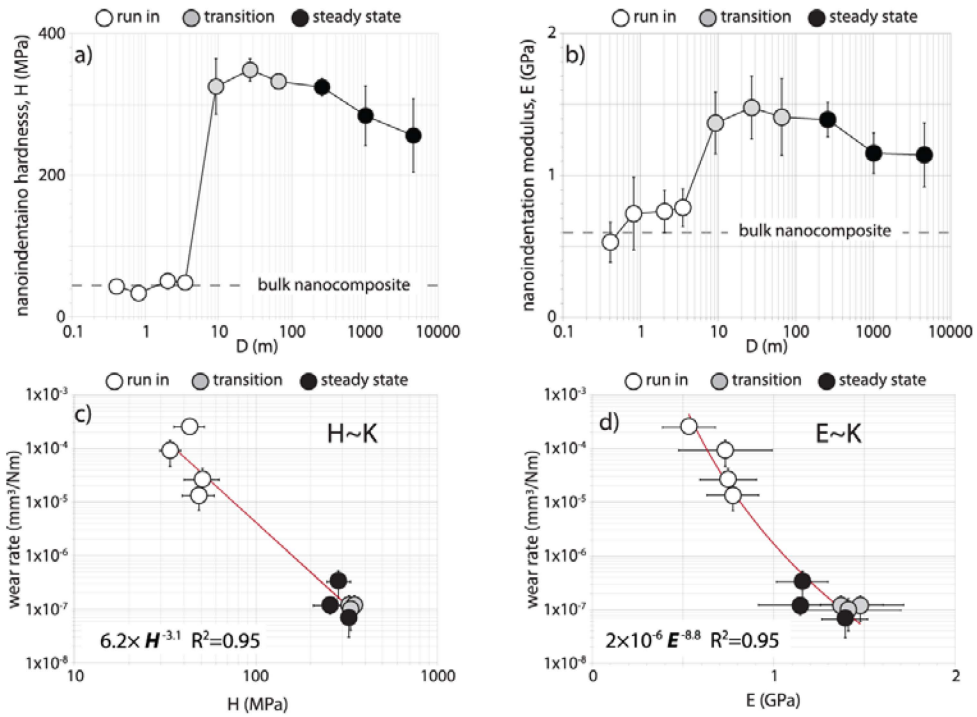

Figure 7. (**a**) Transfer film hardness *versus* sliding distance of transfer film development; (**b**) transfer film modulus *versus* sliding distance of transfer film development; (**c**) system wear rate *versus* transfer film hardness; and (**d**) system wear rate *versus* transfer film modulus. All error bars represent a 95% confidence interval. Reprinted with permission from [42].

4.4. Adhesion of the Transfer Film

The adhesion strength between transfer films and counterfaces is among the most frequently discussed mechanisms of wear reduction for polymeric solid lubricants [3,8–10,58–62]. Adhesion is often thought of in terms of bonding and may have physical or chemical origins [44,63–67]. Briscoe [8] first proposed that filler-induced polymer degradation helps improve transfer film adhesion. Bahadur and Tabor [9] suggested that transfer film adhesion was primarily due to mechanical interlocking of debris into the valleys of the rough surface. Bahadur and Gong [3] hypothesized that filler decomposition rather than polymer degradation improves the link between the transfer film and the counterface. Gong *et al.* [67] and Blanchet *et al.* [44] showed that fillers had no effect on the chemistry of the film-counterface interface of PTFE composites. More than two decades later, Harris *et al.* [27,29] revealed that strong adhesion in the ultra-low-wear alumina PTFE nanocomposite (Figure 6) system is likely to have chemical origins. This is the only system we know of that has demonstrated adherence and persistence over the course of a typical experiment [20].

Despite the ubiquity of adhesion in discussions of wear resistance, the magnitude of adhesive strength has proven difficult to measure. Schwartz and Bahadur [36] bonded copper tabs onto PPS nanocomposite transfer films and measured the peeling force as a function of filler loading. They found film wear rate decreased as adhesion strength increased. Unfortunately, it is difficult to completely rule out the potentially confounding effects of the bonding agent. In an effort to remove the bonded material from the measurement, Ye *et al.* [22] used thin film failure theory from Agrawal and Raj [68,69] to measure adhesive strength. Although this method eliminates the need for a second bonded interface, it provides the adhesive shear strength relative to the tensile strength of the film, which is unknown. The relative adhesive strength of the transfer film is plotted as a function of the sliding distance in Figure 8 for the ultra-low-wear alumina–PTFE system. It is interesting to note that a value of 1 represents the point at which the film–counterface interface has the same strength as the film material. In the run-in period of high wear rate, the interface bond is weaker than the film itself and delamination is the most likely failure mode; this is consistent with the fact that films were removed on each pass of the pin during this period. At steady state when wear rates are very low and transfer films very stable, the bonded interface is actually stronger than the film, which suggest that failure is most likely to occur within the film. This suggests that the film will persists indefinitely, which is consistent with direct observation [20]. This remarkable interface strength is very likely the result of the advantageous chemical processes described by Harris *et al.* [27].

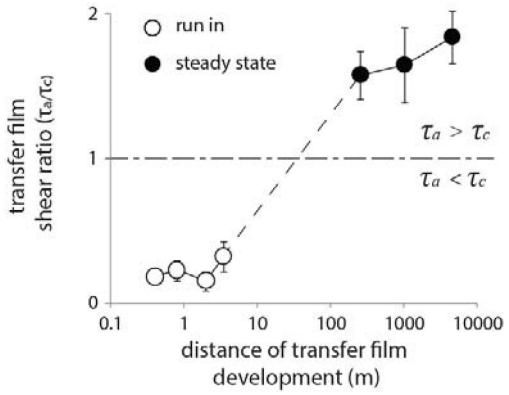

Figure 8. Transfer film strength ratio *versus* sliding distance of transfer film development. Reprinted with permission from [22].

The transfer film is essentially a tribological coating and, as a result, there is interest in directly assessing their tribological properties. Using bare steel balls against predeposited transfer films, Wang *et al.* [70–72] also found that PTFE composite transfer films were more wear resistant than those

of unfilled PTFE. Li *et al.* [49] conducted similar experiments with Si_3N_4 balls and found the wear life of transfer films was sensitive to the sliding conditions (load, velocity and counterface roughness, e.g.,) under which transfer films were originally formed. In 2015, Urueña *et al.* [73] used the same ball-on-flat configuration to test the wear resistance of the ultra-low-wear alumina–PTFE transfer films. They found the transfer film wear rate decreased with a decreased bulk wear rate during sliding, as would be expected. Surprisingly, however, wear rates of the transfer film were far greater (>100×) than the wear rate of the system during the formation of that film [73]; a simple control volume analysis requires that the wear rate of the transfer film can be no greater than the system wear rate, which implies that the transfer film had a different higher wear rate during control testing than it did during formation.

Burris *et al.* [37] measured the wear resistance of another ultra-low-wear PTFE composite transfer film and reported no signs of wear in post-test analysis after thousands of sliding cycles; in this case, however, films were self-mated. Thus, it appears that wear rates of transfer films depend strongly on the conditions used to make the measurement.

To better understand the potential effects of factors like contact pressure, shear stress, and friction coefficient on the wear rate of the film, Ye *et al.* [22] measured the wear rate of alumina–PTFE transfer film as a function of the spherical counterface material. As shown in Figure 9a, the wear rate of the same steady state film varied by five orders of magnitude by simply changing the counterface material. Interestingly, wear rate did not correlate to contact pressure, shear stress, or friction coefficient, but showed an abrupt transition from extremely high wear to extremely low wear at a critical surface energy. The transfer films only had exceptionally low wear rates when slid against PTFE and HDPE; this makes sense since PTFE is the mated material in the parent system.

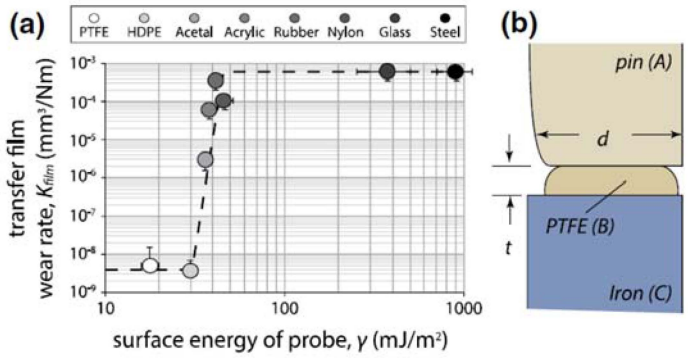

Figure 9. (**a**) Surface energies of the probes *versus* ultra-low-wear Al_2O_3/PTFE transfer film wear rates in microtribometry experiments. Error bars represent the 95% confidence interval; and (**b**) three-body wear model involving a pin (A), transfer film (B), and counterface (C). Reprinted with permission from [22].

The transfer film wear rate is plotted against the accumulated sliding distance used to create the film in Figure 10a using a low surface energy probe (HDPE) intended to simulate the parent conditions. During the run-in period, the transfer film wear rate greatly exceeded the parent system. Wear rate decreased with increased sliding distance, which agrees with the results from Urueña *et al.* [58]. In contrast to their results, however, the wear rates of steady-state films were well below those of the parent system. In general, the wear rate of the transfer film mirrored the wear rate of the parent system (Figure 10b).

Combining these results with adhesion strength measurements suggests that wear of these transfer film systems boils down to the location and relative strength of the weak interface. During run-in and in many other systems at steady state, the transfer film-counterface interface is weak and films are simply removed by the pin. As shown by Figure 8, some systems like the ultra-low-wear alumina–PTFE system at steady state develop sufficient bond strength that delamination becomes unfavorable. In this case, the weak interface must be (1) within the film; (2) between the film and the pin; or (3) within the

pin (Figure 9b). Sliding is permitted with a virtual absence of wear if the pin and transfer film are both strong relative to their interface; this was clearly the case when HDPE was tested against steady state transfer films of alumina–PTFE. Pins with higher surface energy significantly increased the strength of this interface until the film contained the weak interface; in this case progressive film wear on each pass led to relatively rapid failure. The transfer film tends to deposit its own transfer film for the same reason a transfer film formed in the first place.

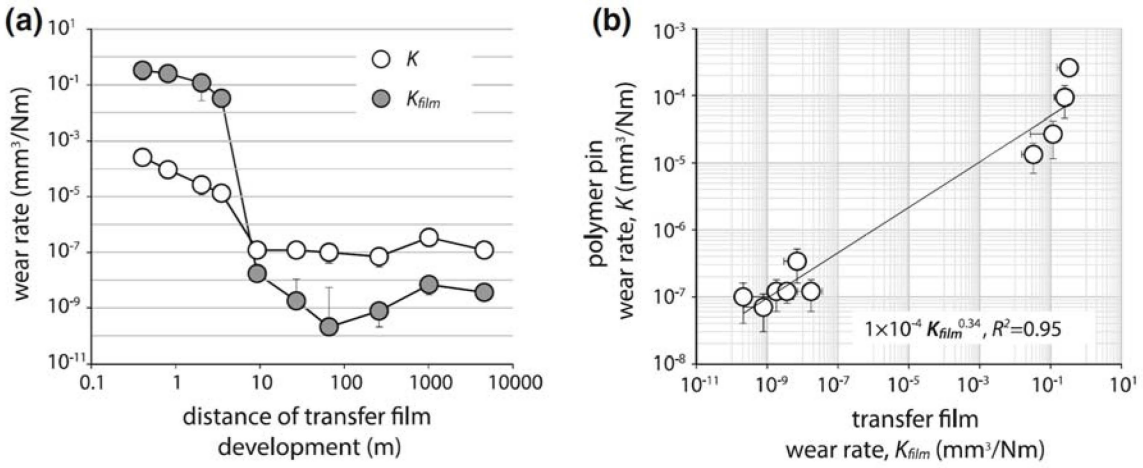

Figure 10. (**a**) Wear rates of the polymer pin (K) and the transfer film (K_{film}) *versus* distance of transfer film development in macrotribometry experiment; and (**b**) polymer pin wear rate *versus* transfer film wear rate. A least squares power law fit is shown for reference. All error bars represent a 95% confidence interval. Reprinted with permission from [22].

5. Summary

For many decades, observations of varied wear rates have corresponded to systematic changes in the appearances and physical characteristics of transfer films. The ubiquitous trend that reduced wear corresponds to improved transfer film quality has motivated strong suspicions that improved transfer films cause reduced wear by protecting the solid lubricant from the inherently damaging counterface.

The review of the literature shows that the answer to this chicken-and-egg question of causation depends on the system. For many systems, transfer films are worn away during sliding, which limits their ability to protect the solid lubricant against contact with the counterface. In these cases, the wear reduction mechanism may be due to more traditional reinforcement mechanisms such as mechanical reinforcement, preferential load support, crack arresting, and energy dissipation; transfer film quality appears to be improved when debris are smaller.

A particular alumina–PTFE system has demonstrated an unusual degree of wear reduction at remarkably low filler loadings. The transfer films of this unusual system are persistent, surviving for the entirety of a typical experiment. Recent studies using variable moisture environments have revealed a unique wear reduction mechanism of tribochemical origins. The chemical changes initiated via sliding create direct bonds between the polymer/filler and polymer/counterface, which stabilizes the near surface of each while bonding the transfer film to the counterface; ultra-low-wear sliding is permitted when the polymer and transfer film are sufficiently dissimilar to set up a weak sliding interface between them.

These ultra-low wear rates cannot persist without stable and persistent transfer films. This explains why wear rates increase when low-wear pins are tested against fresh counterfaces and why transfer film wear rates become unexpectedly high when tested against steel spheres; the high surface energy of the new counterface effectively scavenges the opposing surface, which disrupts the system. Bulk polymers

simply deposit a new transfer film and re-establish ultra-low-wear sliding; transfer films fail because they lack sufficient material to set up a new equilibrium.

Acknowledgments: The authors are very grateful for the financial supports from the National Natural Science Foundation of China (Grant No. 51275144 and 51505117) and the Air Force Office of Scientific Research (AFOSR YIP FA9550-10-1–0295) of USA.

Author Contributions: The authors contributed equally to the overall organization, the associated research, the writing and the editing of this review article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Friedrich, K.; Malzahn, J.C. Abrasive wear and fracture properties of short fiber/thermoplastic matrix composites. In *Wear of Materials*; ASME: New York, NY, USA, 1983; pp. 604–609.
2. Evans, D.C. The influence of abrasive fillers on the wear properties of polytetrafluoroethylene(PTFE)-based composites. In ASLE Proceedings—2nd International Conference on Solid Lubrication, Denver, CO, USA, 15–18 August 1978.
3. Bahadur, S.; Gong, D. The action of fillers in the modification of the tribological behavior of polymers. *Wear* **1992**, *158*, 41–59. [CrossRef]
4. Makinson, K.R.; Tabor, D. Friction and transfer of polytetrafluoroethylene. *Nature* **1964**, *201*, 464–466. [CrossRef]
5. Pooley, C.M.; Tabor, D. Transfer of PTFE and related polymers in a sliding experiment. *Nature* **1972**, *237*, 88–90. [CrossRef]
6. Blanchet, T.A.; Kennedy, F.E. Sliding wear mechanism of polytetrafluoroethylene (PTFE) and PTFE composites. *Wear* **1992**, *153*, 229–243. [CrossRef]
7. Lancaster, J.K. Polymer-based bearing materials: The role of fillers and fibre reinforcement. *Tribology* **1972**, *5*, 249–255. [CrossRef]
8. Briscoe, B. Wear of polymers: An essay on fundamental aspects. *Tribol. Int.* **1981**, *14*, 231–243. [CrossRef]
9. Bahadur, S.; Tabor, D. The wear of filled polytetrafluoroethylene. *Wear* **1984**, *98*, 1–13. [CrossRef]
10. Bahadur, S.; Gong, D.; Anderegg, J.W. The role of copper compounds as fillers in transfer film formation and wear of nylon. *Wear* **1992**, *154*, 207–223. [CrossRef]
11. Burroughs, B.R.; Kim, J.-H.; Blanchet, T.A. Boric acid self-lubrication of b2o3-filled polymer composites. *Tribol. Trans.* **1999**, *42*, 592–600. [CrossRef]
12. Blanchet, T.A. A model for polymer composite wear behavior including preferential load support and surface accumulation of filler particulates. *Tribol. Trans.* **1995**, *38*, 821–828. [CrossRef]
13. Burris, D.L.; Sawyer, W.G. Tribological sensitivity of PTFE/alumina nanocomposites to a range of traditional surface finishes. *Tribol. Trans.* **2005**, *48*, 147–153. [CrossRef]
14. Tanaka, K.; Kawakami, S. Effect of various fillers on the friction and wear of polytetrafluoroethylene-based composites. *Wear* **1982**, *79*, 221–234. [CrossRef]
15. Li, F.; Hu, K.-A.; Li, J.-A.; Zhao, B.-Y. The friction and wear characteristics of nanometer zno filled polytetrafluoroethylene. *Wear* **2001**, *249*, 877–882. [CrossRef]
16. Chen, W.X.; Li, F.; Han, G.; Xia, J.B.; Wang, L.Y.; Tu, J.P.; Xu, Z.D. Tribological behavior of carbon-nanotube-filled PTFE composites. *Tribol. Lett.* **2003**, *15*, 275–278. [CrossRef]
17. Sawyer, W.G.; Freudenberg, K.D.; Bhimaraj, P.; Schadler, L.S. A study on the friction and wear behavior of PTFE filled with alumina nanoparticles. *Wear* **2003**, *254*, 573–580. [CrossRef]
18. Burris, D.L.; Sawyer, W.G. Improved wear resistance in alumina-PTFE nanocomposites with irregular shaped nanoparticles. *Wear* **2006**, *260*, 915–918. [CrossRef]
19. Burris, D.L.; Zhao, S.; Duncan, R.; Lowitz, J.; Perry, S.S.; Schadler, L.S.; Sawyer, W.G. A route to wear resistant PTFE via trace loadings of functionalized nanofillers. *Wear* **2009**, *267*, 653–660. [CrossRef]
20. Ye, J.; Khare, H.S.; Burris, D.L. Transfer film evolution and its role in promoting ultra-low wear of a PTFE nanocomposite. *Wear* **2013**, *297*, 1095–1102. [CrossRef]
21. Ye, J.; Khare, H.S.; Burris, D.L. Quantitative characterization of solid lubricant transfer film quality. *Wear* **2014**, *316*, 133–143. [CrossRef]
22. Ye, J.; Moore, A.C.; Burris, D.L. Transfer film tenacity: A case study using ultra-low-wear alumina–PTFE. *Tribol. Lett.* **2015**, *59*, 1–11. [CrossRef]

23. Krick, B.A.; Ewin, J.J.; Blackman, G.S.; Junk, C.P.; Gregory Sawyer, W. Environmental dependence of ultra-low wear behavior of polytetrafluoroethylene (PTFE) and alumina composites suggests tribochemical mechanisms. *Tribol. Int.* **2012**, *51*, 42–46. [CrossRef]
24. Krick, B.A.; Ewin, J.J.; McCumiskey, E.J. Tribofilm formation and run-in behavior in ultra-low-wearing polytetrafluoroethylene (PTFE) and alumina nanocomposites. *Tribol. Trans.* **2014**, *57*, 1058–1065. [CrossRef]
25. Pitenis, A.A.; Ewin, J.J.; Harris, K.L.; Sawyer, W.G.; Krick, B.A. In vacuo tribological behavior of polytetrafluoroethylene (PTFE) and alumina nanocomposites: The importance of water for ultralow wear. *Tribol. Lett.* **2014**, *53*, 189–197. [CrossRef]
26. Sawyer, W.G.; Argibay, N.; Burris, D.L.; Krick, B.A. Mechanistic studies in friction and wear of bulk materials. *Annu. Rev. Mater. Res.* **2014**, *44*, 395–427. [CrossRef]
27. Harris, K.L.; Pitenis, A.A.; Sawyer, W.G.; Krick, B.A.; Blackman, G.S.; Kasprzak, D.J.; Junk, C.P. PTFE tribology and the role of mechanochemistry in the development of protective surface films. *Macromolecules* **2015**, *48*, 3739–3745. [CrossRef]
28. Harris, K.L.; Curry, J.F.; Pitenis, A.A.; Rowe, K.G.; Sidebottom, M.A.; Sawyer, W.G.; Krick, B.A. Wear debris mobility, aligned surface roughness, and the low wear behavior of filled polytetrafluoroethylene. *Tribol. Lett.* **2015**, *60*, 1–8.
29. Pitenis, A.A.; Harris, K.L.; Junk, C.P.; Blackman, G.S.; Sawyer, W.G.; Krick, B.A. Ultralow wear PTFE and alumina composites: It is all about tribochemistry. *Tribol. Lett.* **2015**, *57*. [CrossRef]
30. Krick, B.A.; Pitenis, A.A.; Harris, K.L.; Junk, C.P.; Sawyer, W.G.; Brown, S.C.; Rosenfeld, H.D.; Kasprzak, D.J.; Johnson, R.S.; Chan, C.D.; *et al*. Ultralow wear fluoropolymer composites: Nanoscale functionality from microscale fillers. *Tribol. Int.* **2016**, *95*, 245–255. [CrossRef]
31. McElwain, S.E.; Blanchet, T.A.; Schadler, L.S.; Sawyer, W.G. Effect of particle size on the wear resistance of alumina-filled PTFE micro- and nanocomposites. *Tribol. Trans.* **2008**, *51*, 247–253. [CrossRef]
32. Blanchet, T.A.; Kandanur, S.S.; Schadler, L.S. Coupled effect of filler content and countersurface roughness on PTFE nanocomposite wear resistance. *Tribol. Lett.* **2009**, *40*, 11–21. [CrossRef]
33. Kandanur, S.S. The Role of Filler Size & Content and Countersurface Roughness in the Wear Resistance of Alumina-PTFE Nano-Composites. Ph.D. Thesis, Rensselaer Polytechnic Institute, New York, NY, USA, 2010.
34. Kandanur, S.S.; Schrameyer, M.A.; Jung, K.F.; Makowiec, M.E.; Bhargava, S.; Blanchet, T.A. Effect of activated carbon and various other nanoparticle fillers on PTFE wear. *Tribol. Trans.* **2014**, *57*, 821–830. [CrossRef]
35. Kandanur, S.S.; Rafiee, M.A.; Yavari, F.; Schrameyer, M.; Yu, Z.-Z.; Blanchet, T.A.; Koratkar, N. Suppression of wear in graphene polymer composites. *Carbon* **2012**, *50*, 3178–3183. [CrossRef]
36. Schwartz, C.J.; Bahadur, S. Studies on the tribological behavior and transfer film–counterface bond strength for polyphenylene sulfide filled with nanoscale alumina particles. *Wear* **2000**, *237*, 261–273. [CrossRef]
37. Burris, D.L.; Boesl, B.; Bourne, G.R.; Sawyer, W.G. Polymeric nanocomposites for tribological applications. *Macromol. Mater. Eng.* **2007**, *292*, 387–402. [CrossRef]
38. Burris, D.L. *Wear-Resistance Mechanisms in Polytetrafluoroethylene (PTFE) Based Tribological Nanocomposites*; University of Florida: Gainesville, FL, USA, 2006.
39. Khare, H.S.; Moore, A.C.; Haidar, D.R.; Gong, L.; Ye, J.; Rabolt, J.F.; Burris, D.L. Interrelated effects of temperature and environment on wear and tribochemistry of an ultralow wear PTFE composite. *J. Phys. Chem. C* **2015**, *119*, 16518–16527. [CrossRef]
40. Laux, K.A.; Schwartz, C.J. Effects of contact pressure, molecular weight, and supplier on the wear behavior and transfer film of polyetheretherketone (peek). *Wear* **2013**, *297*, 919–925. [CrossRef]
41. Bhimaraj, P.; Burris, D.; Sawyer, W.G.; Toney, C.G.; Siegel, R.W.; Schadler, L.S. Tribological investigation of the effects of particle size, loading and crystallinity on poly (ethylene) terephthalate nanocomposites. *Wear* **2008**, *264*, 632–637. [CrossRef]
42. Ye, J. Characterizing PTFE Transfer Film Properties to Elucidate Transfer Film's Role in Ultra-Low Wear Sliding of Polymer Nanocomposites. Ph.D. Thesis, University of Delaware, Newark, DE, USA, 2014.
43. Rabinowicz, E. *Friction and Wear of Materials*; Wiley: New York, NY, USA, 1995.
44. Blanchet, T.A.; Kennedy, F.E.; Jayne, D.T. Xps analysis of the effect of fillers on PTFE transfer film development in sliding contacts. *Tribol. Trans.* **1993**, *36*, 535–544. [CrossRef]
45. Jintang, G. Tribochemical effects in formation of polymer transfer film. *Wear* **2000**, *245*, 100–106. [CrossRef]

46. Burris, D.L.; Santos, K.; Lewis, S.L.; Liu, X.; Perry, S.S.; Blanchet, T.A.; Schadler, L.S.; Sawyer, W.G. Polytetrafluoroethylene matrix nanocomposites for tribological applications. *Tribol. Polym. Nanocompos.* **2008**, *55*, 403–438.
47. Onodera, T.; Kawasaki, K.; Nakakawaji, T.; Higuchi, Y.; Ozawa, N.; Kurihara, K.; Kubo, M. Chemical reaction mechanism of polytetrafluoroethylene on aluminum surface under friction condition. *J. Phys. Chem. C* **2014**, *118*, 5390–5396. [CrossRef]
48. Onodera, T.; Kawasaki, K.; Nakakawaji, T.; Higuchi, Y.; Ozawa, N.; Kurihara, K.; Kubo, M. Effect of tribochemical reaction on transfer-film formation by poly (tetrafluoroethylene). *J. Phys. Chem. C* **2014**, *118*, 11820–11826. [CrossRef]
49. Li, H.; Yin, Z.; Jiang, D.; Jin, L.; Cui, Y. A study of the tribological behavior of transfer films of PTFE composites formed under different loads, speeds and morphologies of the counterface. *Wear* **2015**, *328–329*, 17–27. [CrossRef]
50. Xie, T.; Yang, H.; Xu, Z.X.; Yang, H.P.; Cui, A.L. Influence of steel surface texture direction on the formation of friction transfer film of sio2/PTFE composites. *J. Hefei Univ. Technol.* **2014**, *37*, 513–515.
51. Deli, G.; Qunji, X.; Hongli, W. Physical models of adhesive wear of polytetrafluoroethylene and its composites. *Wear* **1991**, *147*, 9–24. [CrossRef]
52. Friedrich, K.; Flöck, J.; Váradi, K.; Néder, Z. Experimental and numerical evaluation of the mechanical properties of compacted wear debris layers formed between composite and steel surfaces in sliding contact. *Wear* **2001**, *251*, 1202–1212. [CrossRef]
53. Chang, L.; Zhang, Z.; Ye, L.; Friedrich, K. Tribological properties of epoxy nanocomposites: Iii. Characteristics of transfer films. *Wear* **2007**, *262*, 699–706. [CrossRef]
54. Randall, N.X.; Bozet, J.L. Nanoindentation and scanning force microscopy as a novel method for the characterization of tribological transfer films. *Wear* **1997**, *212*, 18–24. [CrossRef]
55. Randall, N.X.; Harris, A. Nanoindentation as a tool for characterising the mechanical properties of tribological transfer films. *Wear* **2000**, *245*, 196–203. [CrossRef]
56. McCook, N.L.; Burris, D.L.; Bourne, G.R.; Steffens, J.; Hanrahan, J.R.; Sawyer, W.G. Wear resistant solid lubricant coating made from PTFE and epoxy. *Tribol. Lett.* **2005**, *18*, 119–124. [CrossRef]
57. Xie, T.; Zhou, Z.H.; Xu, Z.X.; Yu, J.W.; Jiao, M.H. *Characteristics of the Transfer Film and Tribological Properties of Oxide/PTFE Composites*; Trans Tech Publications Inc.: Pfaffikon, Switzerland, 2013; pp. 172–175.
58. Xu, Z.X. *Performances of Different Fillers in Polymer Composites during Frictional Transfer*; University of Technology: Hefei, China, 2012.
59. Bahadur, S. The development of transfer layers and their role in polymer tribology. *Wear* **2000**, *245*, 92–99. [CrossRef]
60. Bahadur, S.; Sunkara, C. Effect of transfer film structure, composition and bonding on the tribological behavior of polyphenylene sulfide filled with nano particles of tio2, zno, cuo and sic. *Wear* **2005**, *258*, 1411–1421. [CrossRef]
61. Xie, T.; Zhou, Z.H.; Xu, Z.X.; Yu, J.W.; Jiao, M.H. Characteristics of the transfer film and tribological properties of oxide/PTFE composites. *Adv. Mater. Res.* **2013**, *631–632*, 172–175. [CrossRef]
62. Xie, T.; Wan, Y.Y.; Miao, P.; Wen, D.D.; Jiao, M.H.; Yu, J.W.; Yin, Y.G. Dynamic transfer of PTFE three-layer composite materials during friction. *Lubr. Eng.* **2010**, *2*, 3.
63. Buckley, D.H.; Johnson, R.L. *Friction, Wear, and Decomposition Mechanisms for Various Polymer Compositions in Vacuum to 10–9 Millimeter of Mercury*; National Aeronautics and Space Administration: Washington, DC, USA, 1963; Volume 2073.
64. Pocock, G.; Cadman, P. The application of differential scanning calorimetry and electron spectroscopy to PTFE-metal reactions of interest in dry bearing technology. *Wear* **1976**, *37*, 129–141. [CrossRef]
65. Cadman, P.; Gossedge, G.M. The chemical nature of metal-polytetrafluoroethylene tribological interactions as studied by x-ray photoelectron spectroscopy. *Wear* **1979**, *54*, 211–215. [CrossRef]
66. Jintang, G.; Hongxin, D. Molecule structure variations in friction of stainless steel/PTFE and its composite. *J. Appl. Polym. Sci.* **1988**, *36*, 73–85. [CrossRef]
67. Deli, G.; Qunji, X.; Hongli, W. Esca study on tribochemical characteristics of filled PTFE. *Wear* **1991**, *148*, 161–169. [CrossRef]
68. Agrawal, D.C.; Raj, R. Measurement of the ultimate shear strength of a metal-ceramic interface. *Acta Metall.* **1989**, *37*, 1265–1270. [CrossRef]

69. Agrawal, D.C.; Raj, R. Ultimate shear strengths of copper-silica and nickel-silica interfaces. *Mater. Sci. Eng. A* **1990**, *126*, 125–131. [CrossRef]
70. Wang, Y.; Yan, F. Tribological properties of transfer films of PTFE-based composites. *Wear* **2006**, *261*, 1359–1366. [CrossRef]
71. Wang, Y.; Yan, F. A study on tribological behaviour of transfer films of PTFE/bronze composites. *Wear* **2007**, *262*, 876–882. [CrossRef]
72. Wang, Y.; Wang, H.; Yan, F. Investigation of transfer film of PTFE/bronze composites on 2024al surface. *Surf. Interface Anal.* **2009**, *41*, 753–758. [CrossRef]
73. Urueña, J.M.; Pitenis, A.A.; Harris, K.L.; Sawyer, W.G. Evolution and wear of fluoropolymer transfer films. *Tribol. Lett.* **2015**, *57*. [CrossRef]

© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons by Attribution (CC-BY) license (http://creativecommons.org/licenses/by/4.0/).