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Evaluation of the Tribological Properties of Carbon Fiber Reinforced Poly(vinylidene fluoride) Composites

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The current study examines the tribological performance of poly(vinylidene fluoride) (PVDF) and carbon fiber reinforced poly(vinylidene fluoride) (CF/PVDF) under dry sliding condition. Different contents of carbon fibers were employed as reinforcement. All filled and unfilled polyimide composites were tested against CGr15 ball and representative testing was performed. The effects of carbon fiber content on tribological properties of the composites were investigated. The worn surface morphologies of neat PVDF and its composites were examined by scanning electron microscopy (SEM) and the wear mechanisms were discussed. Moreover, all filled PVDFs have superior tribological characteristics to unfilled PVDFs. The optimum wear reduction was obtained when the content of carbon fiber is 20 vol.%.

Keywords poly(vinylidene fluoride) (PVDF), SEM, tribological, wear reduction

1. Introduction

Polymer matrix composites have shown the ability to balance traditional polymer properties such as low part weight and ease of processability with the strength and stiffness of reinforcing agents. Fiber reinforced thermoplastic composites have become an area of increased interest due to their shorter cycle times and greater potential recyclability compared to thermosetting polymers (Ref 1). Additionally, thermoplastic polymers have long elongations to break which can be particularly beneficial in unidirectional fiber composites (Ref 2). Fluoropolymers can be found in applications where abrasion, chemical resistance, as well as thermal stability are required. One of the most important fluoropolymers used today is poly(vinylidene difluoride) (PVDF) (Ref 3) which is used in a number of applications, where chemical resistance, mechanical strength and wear resistance are required (Ref 4). To date, there have only been a few studies that have investigated routes to reinforce fluoropolymers with carbon fibers. The development of composites based on thermoplastic fluoropolymers is a field that has generated thus far little attention within academia; however, industry seeks materials solutions for applications which require superior wear resistance and high mechanical strength. Carbon fiber reinforced PVDF represents a material that could be used in applications where chemical resistance and toughness are both required, such as in the oil and gas industry, where currently conventional monolithic materials are used in deep sea applications but will reach their limit if deeper reservoirs are to be exploited.

Fillers, in the form of particulates and fibers, are often added to polymeric materials to improve their stiffness and strength. This second phase filler material will influence the wear resistance of the composite material. There are many references that illustrate the influence of fillers and fiber reinforcement on the abrasive wear resistance of polymeric composites (Ref 5, 6). Fiber reinforcements, e.g. carbon, glass and aramid fibers, are the main candidates and have been widely employed. Many investigations have shown that the incorporation of fiber reinforcement improved the wear resistance and reduced the coefficient of friction due to the difference of tribological conditions (Ref 7-12). Attempts to understand the modifications in the tribological behavior of the polymers with the addition of fillers or fibers reinforcements have been made by many researchers (Ref 10, 13). Except for a few exceptions (Ref 14), the wear resistance was improved with lower fiber content generally, e.g. GF or CF filled PEN, PEEK, PA, and so on (Ref 15, 16). This was attributed to a reduced ability of ploughing, tearing and other non-adhesive components of wear by the fibers, provided good interfacial adhesion between the matrix and the fiber reinforcement existed (Ref 14). Carbon fiber reinforcement dominates in high-performance applications due to its outstanding mechanical properties combined with low weight.

The research on the friction and wear of thermoplastic PVDF and its composite is few. The purposes of the present paper are to clarify the tribological behavior of neat PVDF and carbon fiber reinforced PVDF composites sliding against CGr15 ball under dry sliding condition, so as to provide some practical guidance for the use of this kind of composites under dry sliding condition. The effects of filler content on the tribological properties were also comparatively discussed and the wear mechanisms of the composites were discussed based on the SEM examination of the worn surfaces.

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2. Experimental

2.1 Materials and Specimens

The reinforcements were polyacrylonitrile (PAN)-based unmodified and unsized high strength (HS) carbon fibers (supplied by Shanghai sxcarbon Technology Co., Ltd., China) with the following specified properties: tensile strength 2500 MPa; elastic modulus 200 GPa; density 1760 kg/m^3; diameter 7 μm; and length 75 μm. PVDF (Kynar 711) were kindly supplied by Arkema (Serquigny, France). Various matrix formulations with increasing carbon content were prepared by solution precipitation. The PVDF (homopolymer and carbon fiber involved) formulations were dissolved in dimethyl formamide (DMF, general purpose grade, VWR, Poole, UK) to make a 10 wt.% solution. A non-solvent of 80/20 (wt. ratio) DMF/water was added dropwise to induce precipitation. The precipitant was filtered, rinsed with ethanol, and then dried under vacuum at 100 °C. The product formed from solvent precipitation was a fine powder. Samples with the following compositions were prepared: pure PVDF, 10 vol.% CF/PVDF, 20 vol.% CF/PVDF and 30 vol.% CF/PVDF. The properties of PVDF composites prepared here were better than the composites prepared by melt compounding PVDF and carbon fiber.

2.2 Friction and Wear Tests

Friction and wear tests were done using a ball-on-block reciprocating UMT-2MT tribometer at room temperature with a relative humidity of 30-45%. The specimens were polished using a fine grade SiC emery paper and cleaned ultrasonically with acetone and dried before testing. The surface roughness is 0.6 μm. The reciprocating friction stroke was 5 mm and tests were conducted at a normal spring-driven load. Five tests were conducted under each test condition and the average values of measured friction coefficient, wear volume were used for further analysis. The test duration is 1800 s.

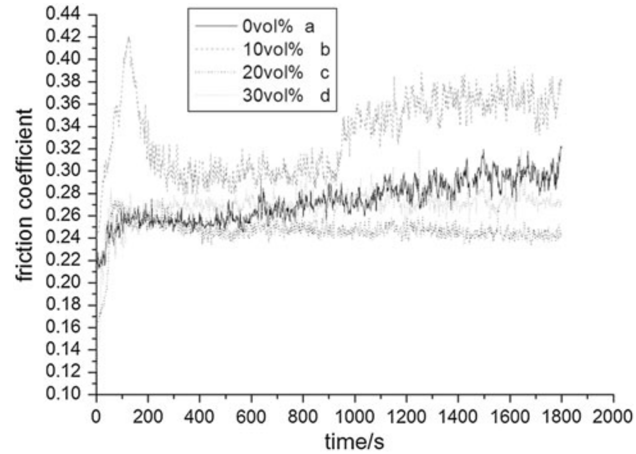

Fig. 1 Friction coefficient vs. sliding time at 9 N normal load and 4 Hz reciprocating sliding frequency

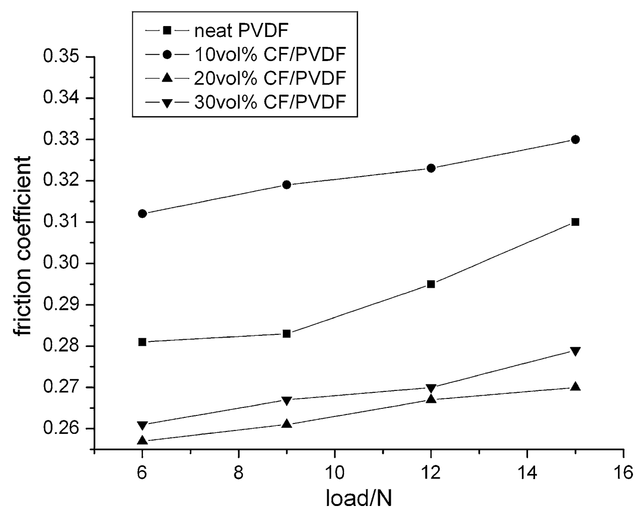

Fig. 2 Variations of friction coefficient with load (reciprocating sliding frequency: 4 Hz)

3. Results and Discussion

3.1 Measured Friction Coefficient

Figure 1 presents the typical evolutions of the friction coefficient of neat PVDF and CF/PVDF composite as a function of time at the reciprocating sliding frequency 4 Hz under 9 N applied load. In this study, the mean value of friction coefficients of the last 1600 s sliding time was taken for evaluating the friction coefficient of the PVDF and carbon fiber filled PVDF composite. It can be seen that the friction coefficient of neat PVDF increases quickly during the whole process. While that of 20 and 30 vol.% CF/PVDF significantly follows a parabolic pattern, the friction coefficients increase with respect to time and arrive at a relatively stable value at last. For 10 vol.% CF/PVDF, the friction coefficient increases during early testing and then decreases to a steady state, thereafter suddenly increases. After that, it stays at a constant level for the remaining period of the test.

The variations of friction coefficient of neat PVDF and CF/PVDF composite are shown in Fig. 2 and 3. It is seen in Fig. 2 that friction coefficients of all filled PVDF composites and neat PVDF increase as the load increases from 6 to 15 N under the same reciprocating sliding frequency 4 Hz. And the friction coefficient increases as the reciprocating sliding frequency increases from 1 to 12 Hz under the same load 9 N (Fig. 3). The composite exhibits better friction behavior since the reinforcing carbon fibers can reduce effectively the adhesion force and the plough. Moreover, 20 vol.% carbon fiber reinforced PVDF composite exhibits the lowest friction coefficient (0.255-0.275). The addition of the carbon fibers strengthened the combination of the interface between the fibers and the PVDF matrix and increased the elastic modulus of the PVDF composites. This would be the reason why the friction coefficient of the CF/PVDF was reduced. As a hard phase in the soft polymer matrix, carbon fibers can reduce the true contact area with the counterbody under certain load (Ref 17). As a result, it exhibits an important influence on reducing the plough and the adhesion between the relative sliding parts. The carbon fibers influence the tribological behavior of CF/PVDF in two aspects: first, it could lead to fractures in the interface of the two constituents; moreover, it could reduce the plough and the adhesion between the two sliding bodies. These two roles simultaneously influence the friction and wear behavior

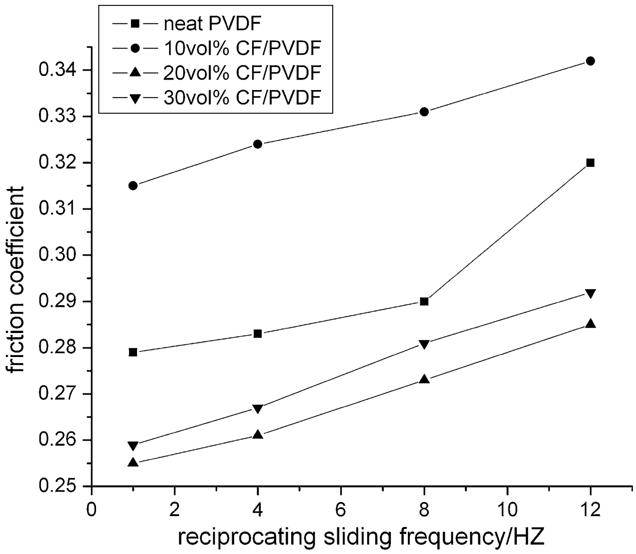

Fig. 3 Variations of friction coefficient with reciprocating sliding frequency (load: 9 N)

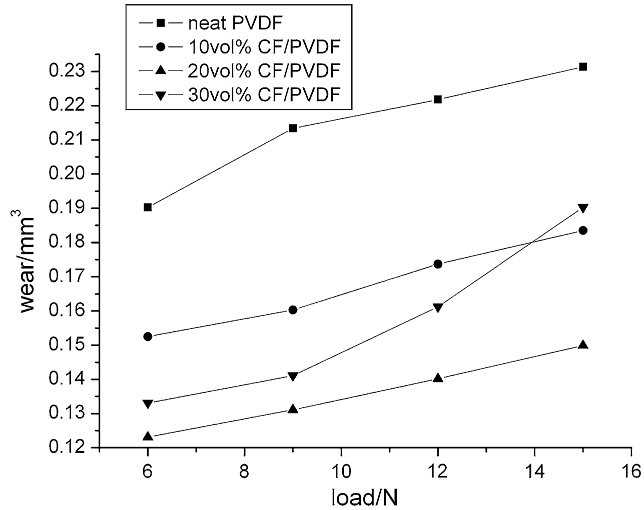

Fig. 4 Variations of wear loss with load (reciprocating sliding frequency: 4 Hz)

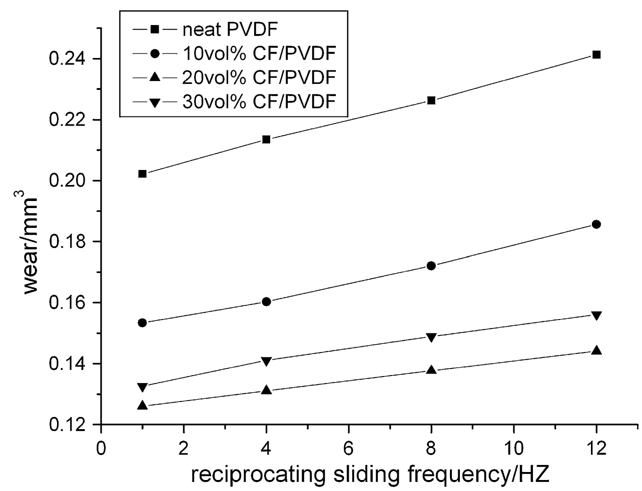

Fig. 5 Variations of wear loss with reciprocating sliding frequency (load: 9 N)

according to the sliding conditions. Interfacial fractures will appear on worn surface of CF/PVDF. Filled with lower content carbon fibers, the composite exhibits higher friction coefficient (0.313-0.334) compared with pure PVDF, so the higher friction coefficients in these cases appear to be derived from the activation of fracture in the interface of reinforcing fibers and PVDF matrix as interfacial energy dissipation mechanism during the sliding process (Ref 18). While for PVDF composite filled with higher carbon fiber content (30 vol.%), the lower coefficients of the friction compared with pure PVDF may result from the role CF played. For CF is a graphitized carbon with the hexagonal planes of its crystals aligned perpendicular to the fiber axis. The lubricating function of graphitized carbon is thought to be responsible for the reduction of friction coefficient as its composites slide against steel (Ref 19-21). It is a well documented fact that the CF can decompose into graphite crystals, which have very good lubricating properties. The graphite debris forms a thin lubricating film on the counterface, thereby reducing the abrasion process drastically. While the pure graphite filled PVDF composite does not have a good wear resistance for its poor mechanical property. When too many carbon fibers are added, the pull-out of carbon fiber will make the surface of sample rough, so the friction coefficient will be higher compared to that of 20 vol.% CF reinforcement.

3.2 Wear of the Neat PVDF and the CF PVDF Composites

Figure 4 shows the volumetric wear of unfilled PVDF the CF/PVDF composite as a function of the load applied. In general, the volumetric wear for unfilled and all filled PVDF composites increased with increasing applied load, but they exhibit different relationships between volumetric wear and load. The volumetric wear of the neat PVDF and PVDF composites filled with 10 or 20 vol.% of filler carbon fibers showed little increase with load while that of the PVDF composites filled with more filler fibers (30 vol.%) showed a sudden increase between loads of 9 and 15 N. Moreover, it can be seen from Fig. 4 that the addition of carbon fibers can improve the wear resistance of the PVDF composites and 20 vol.% carbon fiber reinforced PVDF composite exhibits the lowest volumetric wear. The unfilled PVDF composite showed, in general, the highest volumetric wear of all the specimens tested under the same sliding condition. Additionally, the high percentage (30 vol.%) of fillers in composite degraded the wear resistance of the CF/PVDF because the fillers themselves caused stress concentrations in the matrix. Furthermore, the detachment of fillers causes the adjacent matrix to be poorly supported and hence is subjected to greater stress and thus more susceptible to fracture.

Figure 5 also shows clearly that in most test conditions, 20 vol.% carbon fiber reinforced PVDF composite exhibits the lowest volumetric wear, while neat PVDF shows the highest. The increase of reciprocating sliding frequency provokes evident varieties of volumetric wear.

The dependence of the volumetric wear on reciprocating sliding frequency can be attributed to the friction-induced heat effects. Most energy dissipated during sliding is transformed into heat and a high-temperature gradient develops in the normal direction to the surface (Ref 21). As a result of the low thermal conductivity of PVDF (1.3 BTU/h/ft^2/°F in), frictional heat being generated during sliding surely provoked an increase of the contact temperature and the increase of reciprocating sliding frequency can be quantitatively correlated to the increase of sliding temperature.

Some frictional work was required to drag or to dig the carbon fibers off the matrix since the carbon fibers were limited by the PVDF matrix. These help to reduce material adhesion to the disc surface and bulk temperature of the wear surface. So, the addition of some certain carbon fibers can improve the wear resistance of the PVDF composites. But when the carbon fiber content was over a certain one, the wear resistance was, in turn, reduced because the fibers would be easily cracked or even dragged due to the lower continuity of the PVDF matrix and poor harmonization of deformation of the fibers with the matrix under the alterative interaction of the asperities of the counterface during sliding. Moreover, stress concentration easily occurred at the interface due to inhomogeneous plastic deformation between reinforcement and matrix and provides preferential sites for stress concentration. The composite that contained a higher fiber fraction may produce more abrasion debris, which contributes negatively to the wear resistance. The higher the CF content, the more the stress concentration sites will be.

3.3 SEM Studies on Worn Surfaces

The worn surfaces of the neat PVDF and CF/PVDF composite under the same load and reciprocating sliding frequency are shown in Fig. 6. In the case of unfilled PVDF (Fig. 6a), microcracks and peeling of PVDF were observed. And microcracking of the matrix material was the main wear mechanism operative. The matrix material exhibited very poor wear resistance in wear tests as it was removed. Large sections of removal as seen here were not observed in the case of CF/PVDF composite, as seen in Fig. 6(b)-(d). As the likelihood of abrasion in this case decreased markedly, wear was also reduced compared to that of the unfilled PVDF. In other words, changes in the topographical features accounted for the wear reduction mechanism.

Some debris were attached in the form of flakes. This feature suggests that fatigue wear is the main wear mechanism of CF/PVDF composite. The worn surface of the 10 vol.% CF/PVDF sample is shown in Fig. 6(b). Microcracks were observed at the surface either at the fiber-matrix boundary or at weak spots in the matrix and eventually led to delamination of the matrix material. Low content of carbon fiber cannot support the load from the counterface sufficiently, which means that the matrix far away from the carbon fiber has the same wear mechanism with neat PVDF.

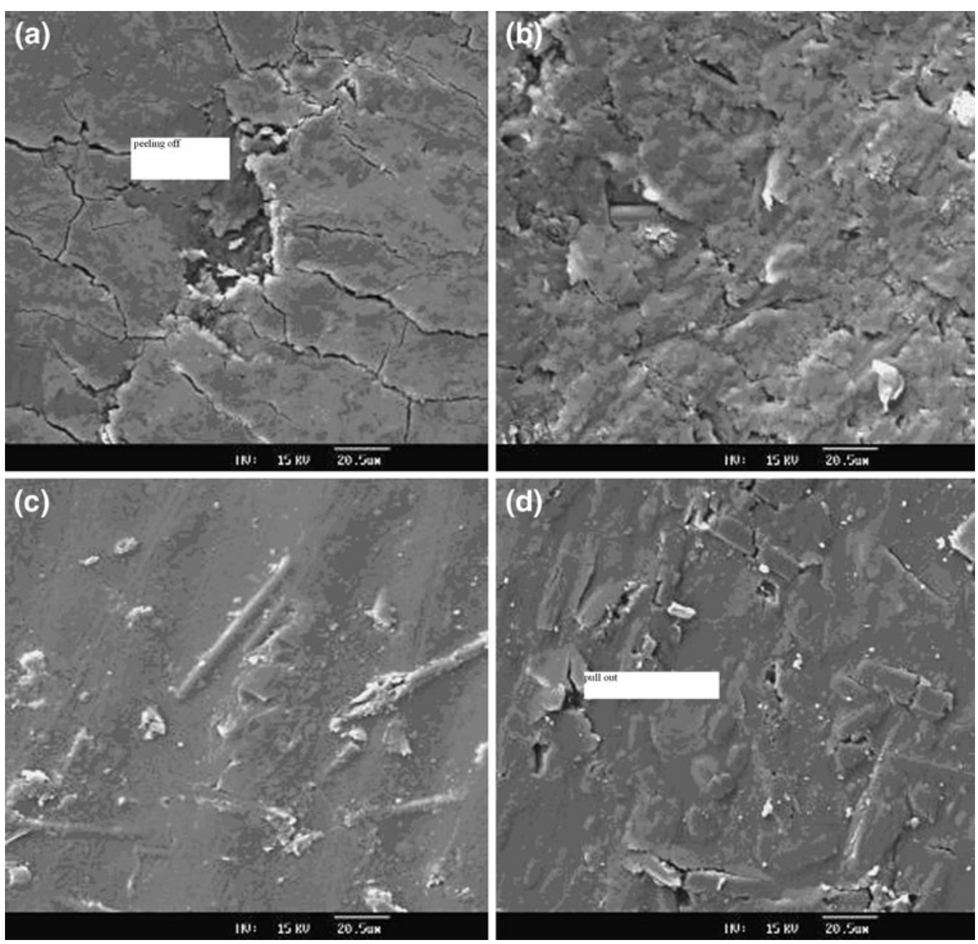

Fig. 6 SEM morphologies of the worn surface of (a) neat PVDF, (b) 10 vol.% CF/PVDF composite, (c) 20 vol.% CF/PVDF composite, and (d) 30% CF/PVDF

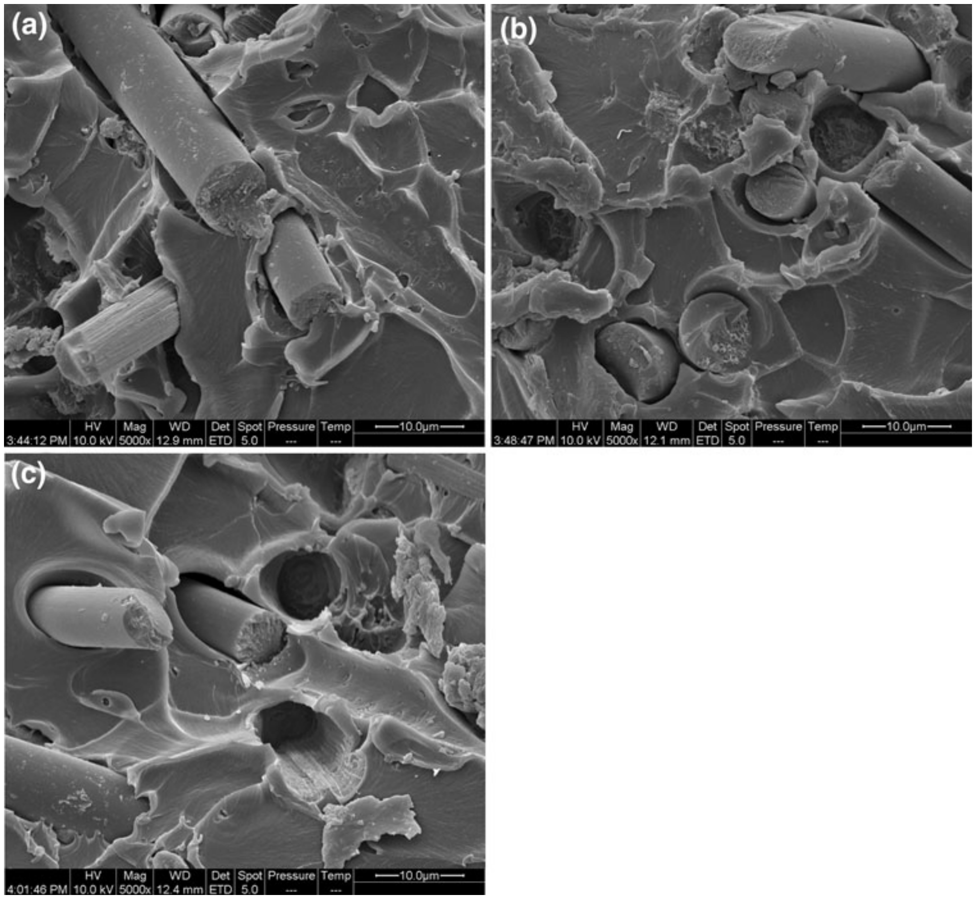

Fig. 7 Cross section SEM of (a) 10% CF/PVDF, (b) 20% CF/PVDF, and (c) 30% CF/PVDF

Figure 6(d) shows a large crack in the matrix, normal to the sliding direction, which formed after neighboring fillers had been detached. This would give rise to a high volume loss of matrix. Microcracking and subsequent spalling of material is an important wear mode for high content filled polymeric materials. The fiber tips were clearly observed, protruding out of the polymer surface. Evidently, this is so because CF has much better mechanical properties and wear resistance compared to matrix material. Probably, a crack follows the fiber-matrix interface and passes between the fibers at their closest distance. The crack propagates under the original surface matrix layer and causes fragments of the matrix to be broken off, leaving the fibers bare. The driving force for the crack comes from the friction forces being applied on the matrix surface. Where the fibers are close to each other, the matrix between the fibers are often fragmented and broken off when the crack propagates along the fiber surface. Plastic deformation occurred under sliding load together with some irregular-shape debris. Figure 6(d) also shows that large filler fibers were fractured into fragments and many small filler particles were detached from the matrix material leaving cavities in the matrix. These cavities were themselves stress concentrations and resulted in more cracks in the matrix and a higher volumetric wear. Large sections of matrix were removed causing even larger filler particles to be detached from the matrix. Thus, the fillers now do not support the load, resulting in a sudden increase in the volumetric wear.

While for the 20 vol.% CF/PVDF composite (Fig. 6c), the worn surface is relatively smooth and the peeling of matrix and carbon fibers is constrained due to the carbon fibers effectively supporting the load from the counterface. That is, the carbon fiber and matrix combine well. The cross-sectional micrographs of the composite are shown in Fig. 7. We can easily see the area between fiber and matrix. The fiber and matrix show the dispersion of the two phases. When the fiber content is high, the adhesion between fiber and matrix is poor. Then, the peeling of the fiber will be easy during the process of abrasion. In total, 10 vol.% CF is increasing COF, whereas 20/30 vol.% CF is reducing COF…but correspondingly (i) 10 vol.% is tending to increase wear, (ii) 20 vol.% shows least wear, and (iii) wear marginally increases with further 10 vol.% CF increase (in 30 vol.% CF). With 30 vol.%, the higher fracturing of CF is causing rough surfaces, which tends to increase COF, and consequently stress concentration and roughness lead to higher wear when compared to 20 vol.% CF.

4. Conclusions

1. The incorporation of carbon fiber into PVDF can effectively improve the friction and wear properties of the materials in sliding against stainless steel under dry sliding condition. When the carbon fiber content is 20 vol.%,

the optimum wear resistance property of composite is obtained.

2. The friction coefficient and volumetric wear of neat PVDF composites increase with the increase of the load and the sliding frequency.

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