Tribological and Mechanical Properties of Carbon-Nanofiber-Filled Polytetrafluoroethylene Composites

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ABSTRACT: The effects of various filler concentrations (0.1, 0.5, 1, 1.5, 2, 2.5, and 3 wt %) on the tribological and mechanical properties of carbon-nanofiber (CNF)-filled polytetrafluoroethylene (PTFE) composites were studied. Moreover, the influence of various loads (50, 100, 150, and 200 N) and sliding velocities (0.692 and 1.39 m/s) on the friction and wear behaviors of the PTFE composites was investigated. The results showed that the friction coefficients of the PTFE composites decreased initially up to a 0.5 wt % filler concentration and then increased, whereas the antiwear properties of the PTFE composites increased by 1–2 orders of magnitude in comparison with those of pure PTFE. The composite with a 2 wt % filler concentration had the best antiwear properties under all friction conditions. The friction coefficients of the CNF/PTFE composites decreased with increases in the load and sliding velocity, whereas the wear volume loss of the PTFE composites increased. At the same time, the results also indicated that the mechanical properties of the PTFE composites increased first up to a 1 wt % filler concentration and then decreased as the filler concentration was increased above 1 wt %. In comparison with pure PTFE, the impact strength, tensile strength, and elongation to break of the PTFE composites increased by 40, 20, and 70%, respectively, at a 1 wt % filler concentration. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2430–2437, 2007

Key words: composites; mechanical properties; polytetrafluoroethylene (PTFE)

INTRODUCTION

Carbon fibers are widely used today as reinforcements for polymer matrices in many high-technology applications on account of their high specific tensile modulus and strength and excellent electrical and thermal properties. Carbon nanofibers (CNFs) are of great scientific interest because they retain the excellent properties of conventional carbon fibers and the properties of the material become increasingly size-dependent at low dimensions.[1] One of the advantages of CNFs is the improved processability and recyclability of thermoplastic nanocomposites. Polymer processing and recycling techniques are not expected to break down the filler; this issue is commonly encountered even in short-fiber-reinforced polymers. Furthermore, the small size of the CNFs ensures an excellent surface finish.

Polytetrafluoroethylene (PTFE) is used widely as an engineering plastic because of its outstanding thermal stability, good solvent resistance, and low friction coefficient. However, PTFE exhibits a high wear rate under normal friction conditions and poor mechanical properties. Thus, much effort has been continuously made to reduce the wear of PTFE and to improve the mechanical properties of PTFE by means of inorganic or organic compound inclusion.[2–6] Recently, nanometer particles, such as nanometer SiC, SiO_2, ZnO, and carbon nanotubes (CNTs), have been used as fillers of polymers to obtain good tribological properties.[7–10] Because CNFs are mechanically very strong and have a high aspect ratio,[11] CNFs are expected to significantly improve the tribological and mechanical properties of PTFE-based composites.

The purpose of this work was to study the tribological and mechanical properties of CNF/PTFE composites and gain some insight into the friction, wear, impact, and tensile mechanisms of CNF/PTFE composites. The worn surfaces, transfer films, impact-fractured surfaces, and tensile-fractured surfaces were also investigated. It is expected that this research could be helpful to the use of PTFE composites in practice.
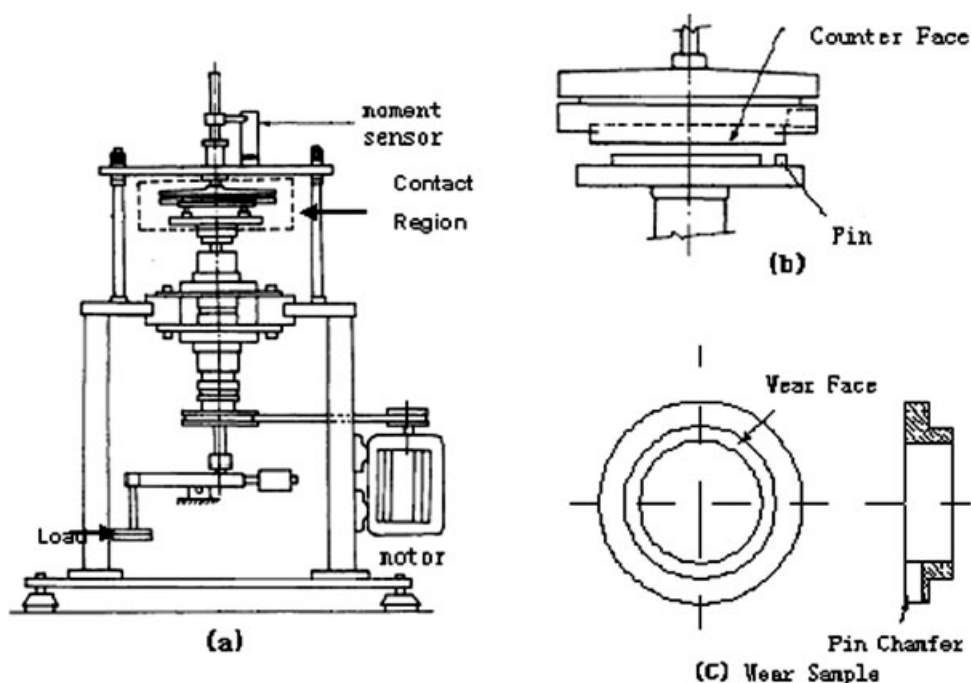
Figure 1 Configuration of the tester: (a) test machine, (b) contact region, and (c) sample.

EXPERIMENTAL

Materials

For the experiments, PTFE powder (a commercial product of Dupont, 7A-J) with an average of 25 μm was supplied by Shanghai Cheng Shun Goods and Material Co., Ltd. (Shanghai, China), and CNFs with an average diameter of 200 nm were supplied by the Key Laboratory for Mesoscopic Chemistry (Ministry of Education, College of Chemistry and Chemical Engineering, Nanjing University, People's Republic of China). CNFs were prepared from propylene over a Ni–Cu catalyst in a conventional horizontal tube furnace.

Preparation of the CNF/PTFE composites

The detailed process for preparing the composites was as follows. First, PTFE and CNF powder mixtures with mass fractions (mass of CNFs/mass of PTFE and CNFs) of 0.1, 0.5, 1, 1.5, 2, 2.5, and 3 were prepared and blended mechanically. Then, for the friction and wear tests, each mixture was molded into a ring-shaped block by compression molding. For the tensile tests, every mixture was molded into a narrow-waisted, dumbbell-shaped block. For the impact tests, each mixture was molded into a block ($120 \times 15 \times 5$ mm^3). All the compression was carried out under 70 MPa for 5 min. After that, the resulting PTFE composite block was sintered at 380°C for 4 h and cooled to the ambient temperature step by step. For the friction and wear tests, the sintered block was finally cut into a shape [shown in Fig. 1(c)] 26 mm in external diameter, 22 mm in inner diameter, and 2.5–3 mm in shoulder height.

Friction and wear tests

The friction and wear tests were conducted on a ring-on-ring friction and wear tester (Fig. 1). The counterface material was steel 45. Sliding was performed under dry friction and ambient conditions (temperature = 25°C, humidity = 50 ± 5%) at sliding velocities of 0.692 or 1.39 m/s and normal loads of 50, 100, 150, or 200 N. The test time was 30 min. The friction force was measured with a torque shaft provided with strain gauges, and the coefficient of friction was calculated from the friction force. Before each test, the surfaces of each specimen and counterpart ring were polished with 800-grit paper to a surface roughness of 0.2–0.4 μm and were cleaned with alcohol. At last, the wear volume loss was calculated from the loss of each specimen's weight.

In this work, three replicate friction and wear tests were carried out to minimize data scattering, and the average of the three replicate test results is reported.

Mechanical tests

The tensile tests were carried out on a model CMT5254 universal tester (Shanghai Sansi Technology Co., Ltd., Shanghai, China) at room temperature. The beam rate was 10 mm/min. The tensile tests were performed on a model XJJ-50 impact test machine (Shanghai Sansi Technology Co., Ltd., Shanghai,

TABLE I
Friction and Wear Results for Pure PTFE and Its Composites Filled with CNFs Sliding Against a Steel 45 Ring Under Dry Friction Conditions

Material	Friction coefficient	Wear volume loss (mm^3)
PTFE	0.202	453.38
PTFE + 0.1% CNFs	0.193	143.06
PTFE + 0.5% CNFs	0.192	41.26
PTFE + 1% CNFs	0.205	15.69
PTFE + 1.5% CNFs	0.231	10.87
PTFE + 2% CNFs	0.234	6.65
PTFE + 2.5% CNFs	0.245	8.32
PTFE + 3% CNFs	0.237	10.13

Sliding velocity = 1.39 m/s; load = 150 N; time = 30 min.

China). The impact strength, tensile strength, and elongation to break of the PTFE composites were tested according to Chinese National Standards GB1043-79, GB1040-79, and GB1040-79, respectively. All the values were averages of four measurements.

The worn surfaces, transfer films, impact-fractured surfaces, and tensile-fractured surfaces morphologies of pure PTFE and CNF/PTFE composites were examined with a Quanta 200 scanning electron microscope (FEI Co., Taiwan Branch, Hsinchu, Taiwan).

RESULTS AND DISCUSSION

Tribological properties of the CNF/PTFE composites

Effect of the filler concentration on the friction and wear properties of the PTFE composites

Table I shows the coefficients of friction and wear volume losses of pure PTFE and PTFE composites filled with various amounts of CNFs. The friction coeffi-

Figure 3 Relationship between the wear volume loss and sliding velocity of pure PTFE and CNF/PTFE composites (load = 150 N; time = 30 min).

cients of the CNF/PTFE composites decreased initially up to a 0.5 wt % filler concentration and then increased. During sliding, CNFs were released from the composite and transferred to the interface between the mating surfaces. The CNFs in the interface served as spacers, preventing direct contact between the two mating surfaces and thereby reducing the friction coefficient. The same result was also found by Chen et al.[10] when PTFE was filled with CNTs. The increase in the friction coefficient was due to the accumulation of fillers on the worn surfaces of the PTFE composites; this is similar to the work of many researchers.[2,12–14] However, the wear volume loss of the filled PTFE was sharply reduced by the filling of CNFs. In comparison with the wear volume loss of pure PTFE, that of the
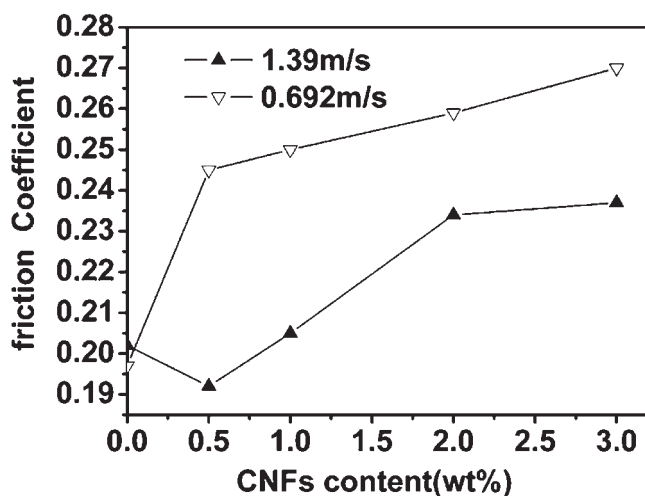

Figure 2 Relationship between the friction coefficient and the sliding velocity of pure PTFE and CNF/PTFE composites (load = 150 N; time = 30 min).
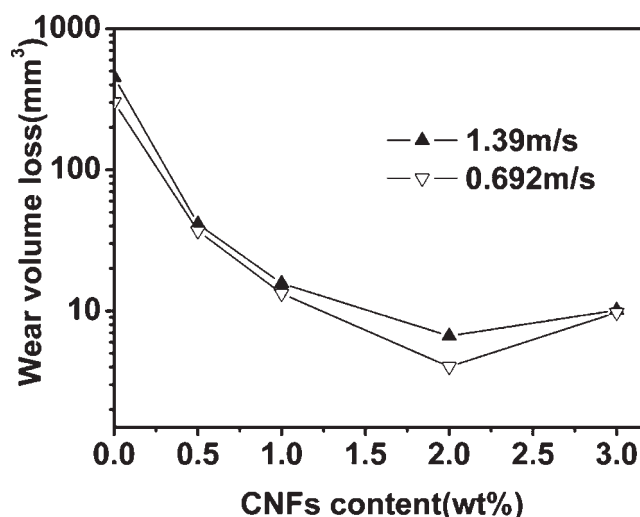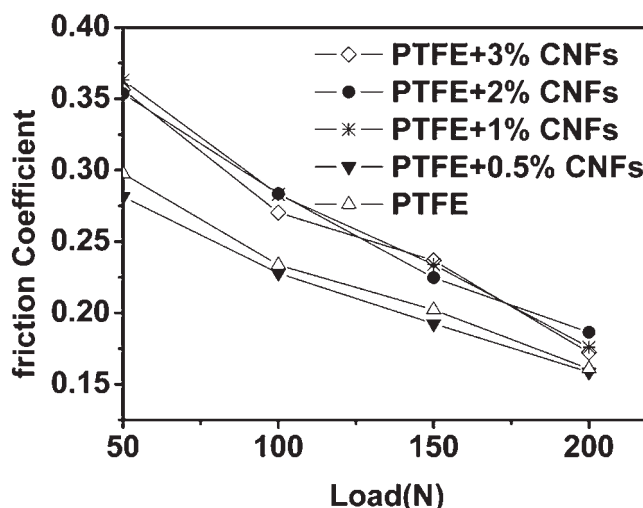

Figure 4 Friction coefficient/load relationship of pure PTFE and CNF/PTFE composites (sliding velocity = 1.39 m/s; time = 30 min).
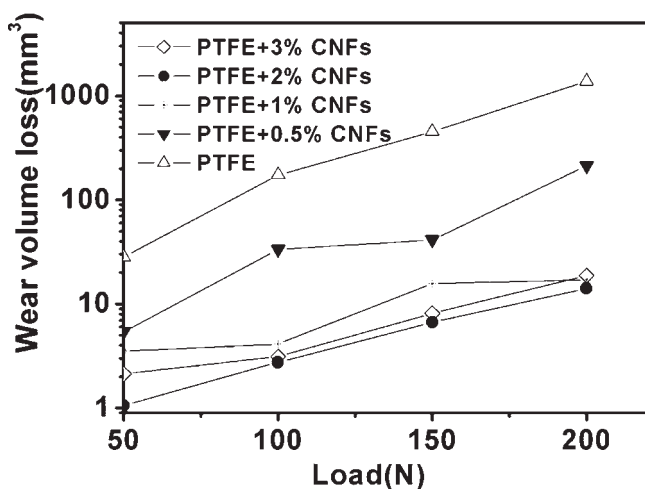
Figure 5 Wear volume loss/load relationship of pure PTFE and CNF/PTFE composites (sliding velocity = 1.39 m/s; time = 30 min).

PTFE composite filled with only 0.5 wt % CNFs decreased by 1 order of magnitude. With a further increase in the CNF content, the antiwear abilities of those composites were improved even more. The wear volume loss reached the lowest value when the composite contained 2 wt % CNFs, which was only about 1/70 of that of PTFE without CNFs. This indicated that the filler concentration played a key role in the wear properties of the PTFE-based composites.

Variation of the friction and wear properties of the CNF/PTFE composites with the sliding velocity

Variations in the friction coefficient and wear volume loss with the sliding velocity for various specimens under a load of 150 N are shown in Figures 2 and 3, respectively. Pure PTFE exhibited a much higher friction coefficient and wear volume loss at a high sliding velocity than at a low sliding velocity. This indicated that, with an increase in the sliding velocity, the film-drawing process at the sliding surface became great enough to cause failure in the PTFE subsurface, leading to the more severe wear process.[15] In contrast, the friction coefficients of the CNF/PTFE composites were lower at a high sliding velocity than at a low sliding velocity, whereas the wear volume loss of the filled PTFE composites became slightly higher. When the filler concentration was 3 wt %, the wear volume loss of the PTFE composite was nearly the same at low and high sliding velocities.

Effect of the load on the friction and wear properties of the PTFE composites

Variations of the friction coefficient and wear volume loss with the load for PTFE and its composites filled

with CNFs sliding against steel 45 under dry friction conditions are shown in Figures 4 and 5, respectively. Figure 4 shows that the friction coefficients of the CNF/PTFE composites decreased with increasing load under dry friction conditions. Under all loads, the friction coefficient of the PTFE composite containing 0.5 wt % CNFs was slightly lower than that of pure PTFE, whereas the friction coefficients of the PTFE composites filled with 1–3 wt % CNFs were higher than that of pure PTFE. The friction properties of the
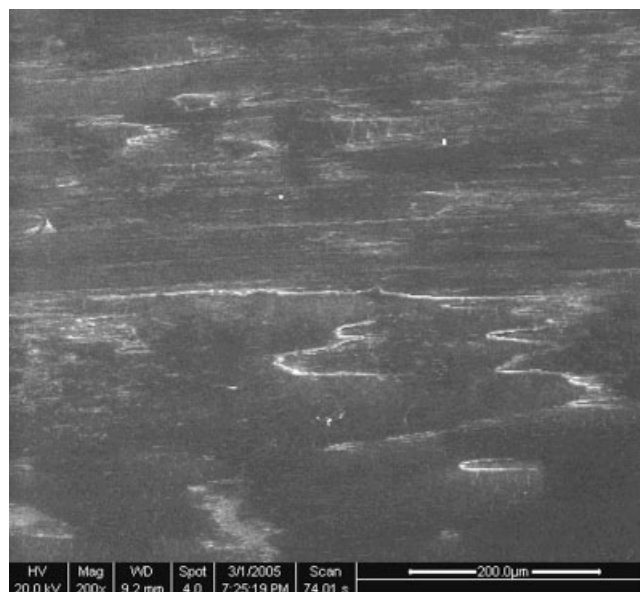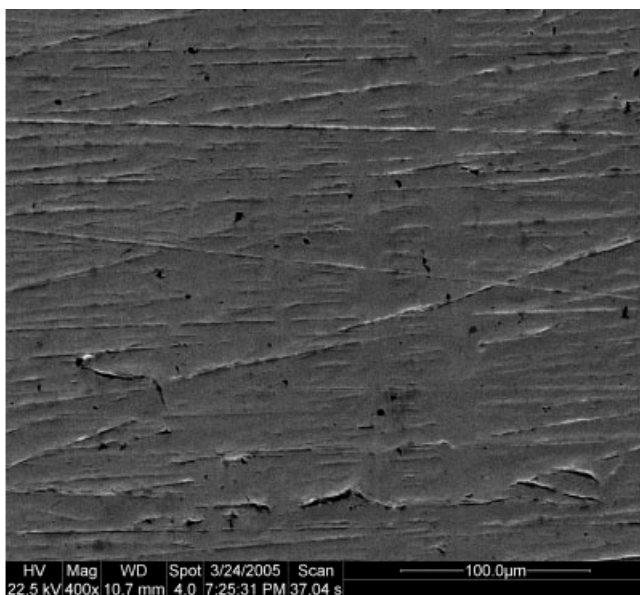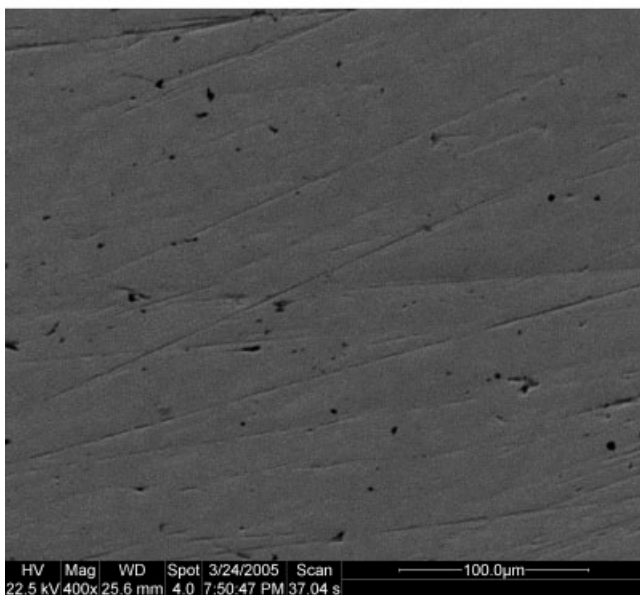

(a)
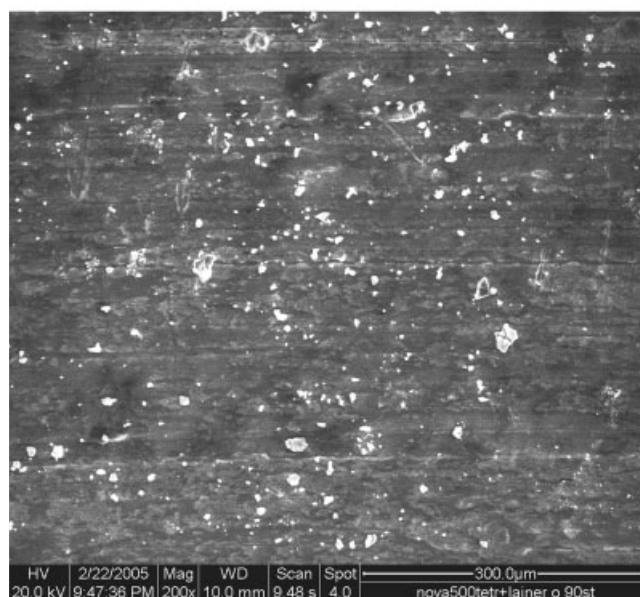
(b)

Figure 6 SEM micrographs (200×) of worn surfaces: (a) pure PTFE and (b) a 2 wt % CNF/PTFE composite (load = 150 N; sliding velocity = 1.39 m/s; time = 30 min).

(a)

(b)

Figure 7 SEM micrographs (400×) of transfer films: (a) pure PTFE and (b) a 2 wt % CNF/PTFE composite (load = 150 N; sliding velocity = 1.39 m/s; time = 30 m).

PTFE composites filled with 1–3 wt % CNFs were nearly the same. When the load was 200 N, pure PTFE was rapidly worn off, whereas the CNF/PTFE composites still maintained excellent friction properties. The results of Figure 5 show that the wear volume loss of pure PTFE increased sharply with increasing load. The wear volume loss of the CNF/PTFE composites also increased with the load, but the values were much lower than those of unfilled PTFE under every load. In this work, the best antiwear ability was obtained with the composite containing 2 wt % CNFs. Under 200 N,

the wear volume loss of the 2 wt % CNF/PTFE composite was only about 1/100 of that of pure PTFE.

Scanning electron microscopy (SEM) investigation of the worn surfaces

To understand the effect of CNFs on the friction and wear behaviors of the CNF/PTFE composites, the worn surfaces of pure PTFE and a 2 wt % CNF/PTFE composite were studied with SEM (Fig. 6). Some obvious plucked marks, which were caused by the destruction and transfer of the subsurface of pure PTFE, appeared on the worn surface of unfilled PTFE [Fig. 6(a)]. This indicated that adhesion was the dominant wear mechanism of unfilled PTFE. In contrast, fewer plucked marks but some narrow nicks appeared on the worn surface of the 2 wt % CNF/PTFE composite [Fig. 6(b)]; this meant that the filler in the composite could dramatically reduce the adhesive wear of PTFE.

SEM investigation of the transfer films

To compare the wear mechanism of pure PTFE with that of CNF/PTFE composites, Figure 7 shows the micrographs of their transfer films formed on the surfaces of steel 45 rings. Figure 7(a) shows that the transfer film of pure PTFE was rough and discontinuous and was easy to scale off during the friction process, so the protection from the transfer film was nonexistent. However, the transfer film of the 2 wt % CNF/PTFE composite appeared to be smooth and coherent [Fig. 7(b)]; this promised to provide excellent antiwear properties for the CNF/PTFE composite.[16] The results indicated that CNFs strengthened the bond between the transfer film and the counterpart surface, which was able to keep the softer composite material from being damaged.
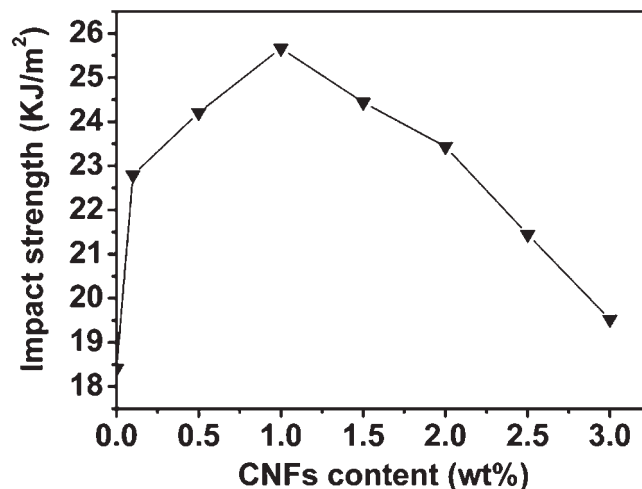

Figure 8 Impact strength/CNF filler content relationship of pure PTFE and CNF/PTFE composites.

Mechanical property examinations

Impact properties

The impact energies, measured at the ambient temperature, are shown in Figure 8. The impact strength of pure PTFE was only 18.4 kJ/m^2. An obvious toughening effect could be seen when PTFE was filled with CNFs. The impact strength of the CNF/PTFE composites increased with increasing filler concentration and reached a maximum value (25.7 kJ/m^2) at the filler concentration of 1 wt %, which was about 40% higher than that of pure PTFE. As the filler concentration increased above 1 wt %, the impact strength decreased.

SEM micrographs of the impact-fractured surfaces of pure PTFE and 1 wt % CNF filled PTFE are shown in Figure 9. Macroscopically, the fracture surface appeared smooth in pure PTFE [Fig. 9(a)] and rough in 1 wt % CNF filled PTFE [Fig. 9(b)]. However, an examination at a higher magnification revealed a striking variation in the fractured surface morphology. Figure 9(d) shows an impact-fractured surface of the PTFE composite containing 1 wt % CNFs. Many voids caused by debonding could be observed around the CNF domains. This was consistent with the cavitation mechanism of microsized rigid particles, as summarized by Gaymans et al.,[17] which consists of three
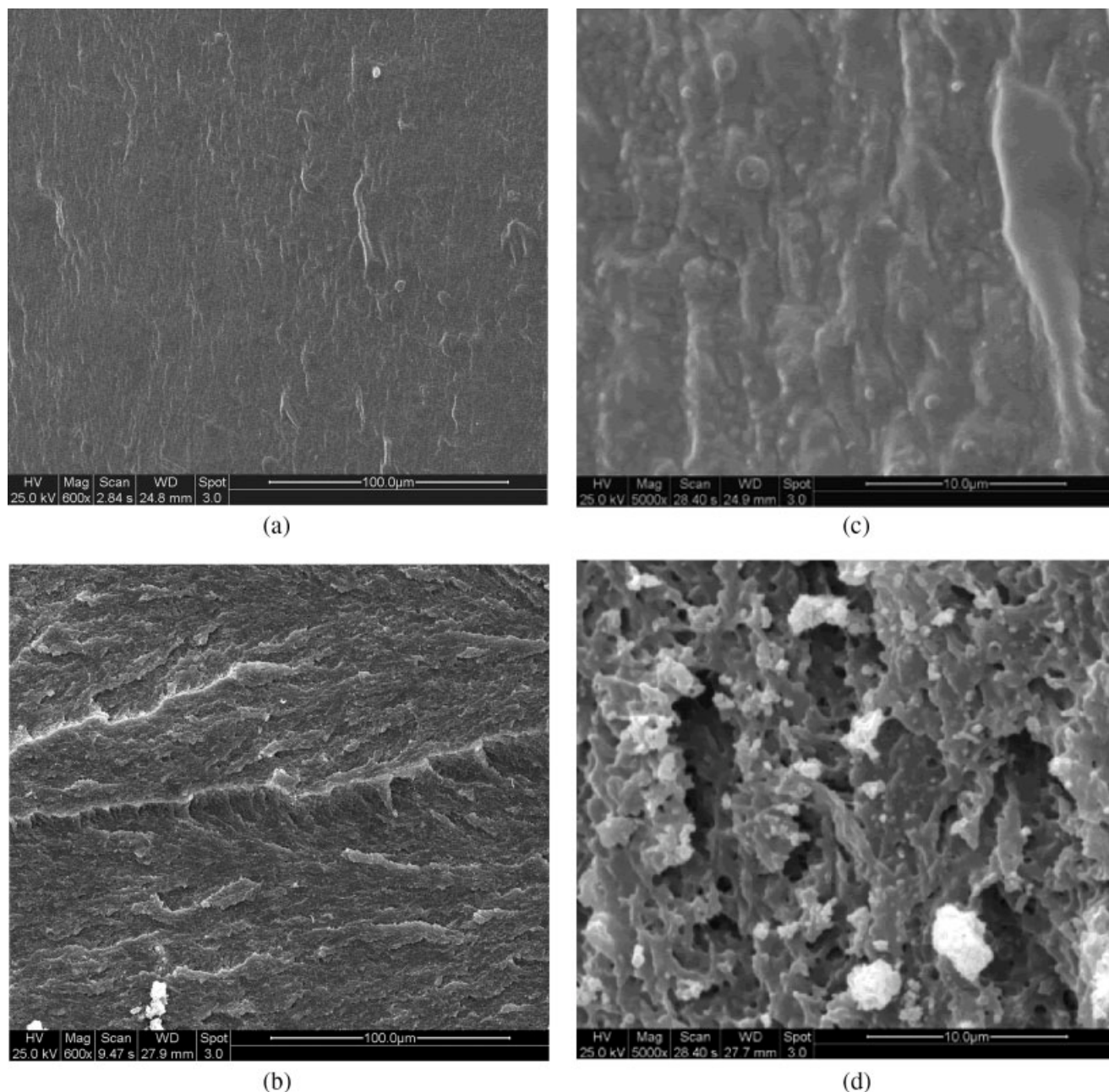

Figure 9 SEM micrographs of impact-fractured surfaces: (a,c) pure PTFE and (b,d) a 1 wt % CNF/PTFE composite. The original magnifications were (a,b) 600× and (c,d) 5000×.
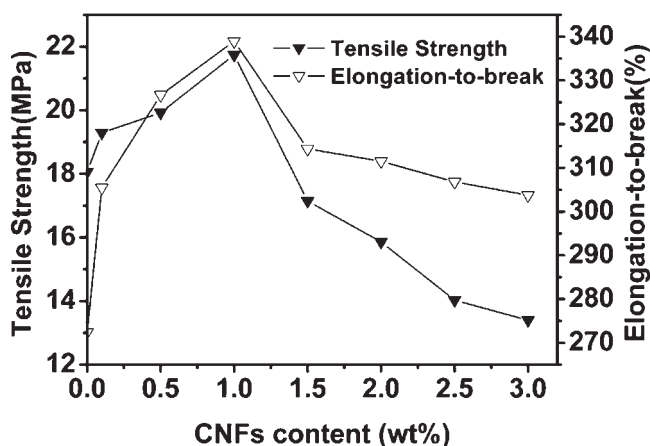
Figure 10 Tensile property/CNF filler content relationship of pure PTFE and CNF/PTFE composites.

stages: stress concentration, debonding, and shear yielding. CNFs served as stress concentrators because of their different elastic properties in comparison with PTFE. Debonding took place at the CNF–PTFE matrix interface because of an impact load, and voids surrounding CNFs promoted limited matrix shear yielding. Thus, more fracture work was dissipated, and the impact energy was improved.

Tensile properties

The tensile properties of pure PTFE and CNF/PTFE composites are shown in Figure 10, indicating that a reinforcing and toughing effect of the CNFs on the polymeric matrix was fully brought into play. As shown in this figure, the tensile strength of the CNF/PTFE composites increased first up to 1 wt % and then decreased as the filler concentration increased above 1 wt %. In comparison with pure PTFE, the tensile strength of the CNF/PTFE composites increased by 20% when the filler concentration was 1 wt %.

The increase in the tensile strength can be explained from two perspectives: nanoparticles and crosslinking. If a matrix is more crosslinked, we know its strength will be higher. On the other hand, if nanoparticles are infused into a polymer, they will form a relatively weak particle–polymer interface that will act as a crack dissemination mechanism during the very early stage of crack growth and eventually delay the formation of the dominant crack.

SEM micrographs of the postfractured specimens are shown in Figure 11. The crosslinked fibers are clearly visible for the 1 wt % CNF infused sample in Figure 11(b). On the other hand, no traces of crosslinking are visible in Figure 11(a). The decrease in the tensile strength of the CNF/PTFE composites above 1 wt % can be interpreted as a change in the dispersion status of the fillers. It is believed that a higher

filler loading is detrimental to its uniform dispersion in the polymer matrix.

Failure strain can be used to partially assess the rupture behavior of a composite material. The incorporation of fillers usually results in a decrease in this parameter, regardless of the interfacial adhesion.[18] It is true even in a system exhibiting an impressive impact toughness improvement with the addition of mineral fillers.[19] However, the plot shown in Figure 10 demonstrates that the values of the elongation to break of PTFE can be significantly increased with CNFs, imply-
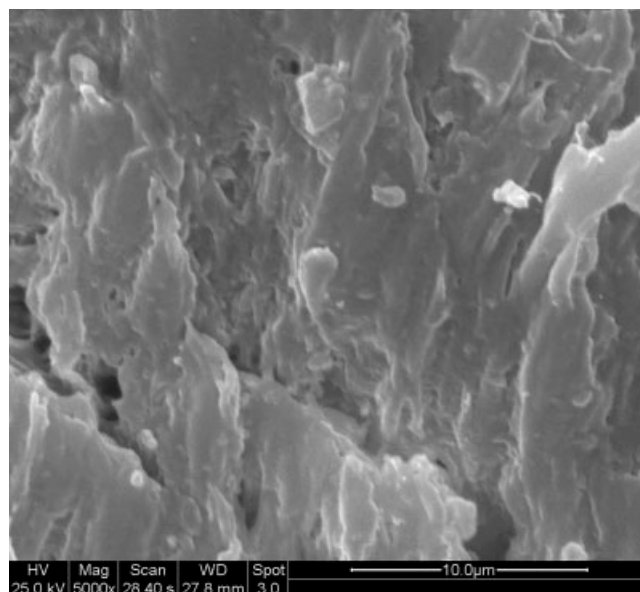
(a)
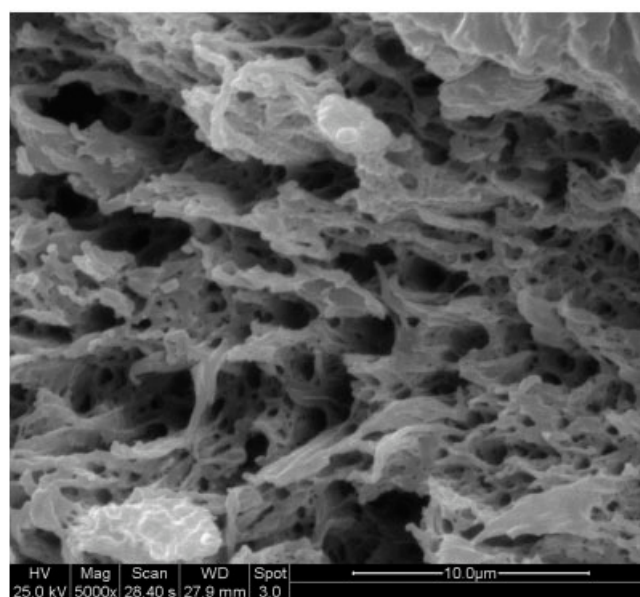
(b)

Figure 11 SEM micrographs (5000×) of (a) PTFE and (b) CNF/PTFE.

ing a failure mechanism different from those involved in conventional composites.

In comparison with pure PTFE, the elongation to break of the CNF/PTFE composite increased by 70% at the filler concentration of 1 wt %. The increase in the elongation to break could be attributed to interfacial viscoelastic deformation and matrix yielding. The further tendency of a decrease in the elongation to break above a filler concentration of 1 wt % suggests that matrix deformation is related not only to the interface feature but also to the dispersion state of the fillers.

CONCLUSIONS

CNFs were introduced as fillers in concentrations of 0.1–3 wt % in the preparation of CNF/PTFE composites. CNFs effectively reduced the adhesive wear of PTFE, thereby significantly improving the wear resistance of CNT/PTFE composites. The optimal concentration of CNFs in PTFE was only 2 wt %, which is much lower than that of conventional macroscopic carbon fibers. The wear volume loss of 2 wt % CNF filled PTFE was only about 1/100 of that of PTFE without CNFs under the friction conditions of 200 N and 1.4 m/s.

The friction coefficients of the CNF/PTFE composites decreased with an increase in the load and sliding velocity, whereas the wear volume loss of the PTFE composites increased with an increase in the load and sliding velocity. During the frictional process, a uniform and coherent transfer film of the CNF/PTFE composites appeared on the counterpart surface. This film promised good antiwear properties for the CNF/PTFE composites.

The impact strength of the CNF/PTFE composites increased with increasing filler concentration and reached a maximum value (25.7 kJ/m^2) at the filler concentration of 1 wt %, which was about 40% higher than that of pure PTFE. As the filler concentration increased above 1 wt %, the impact strength decreased. The increase in the impact strength was due to the debonding between CNFs and PTFE.

The tensile properties of the CNF/PTFE composites increased initially up to a 1 wt % filler concentration and then decreased. In comparison with pure PTFE, the tensile strength and elongation to break of the PTFE composites increased by 20 and 70%, respectively, at the filler concentration of 1 wt %. The increase in the tensile strength was believed to have been caused by enhanced crosslinking in the matrix.

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