

Mechanism of Filler Action in Reducing the Wear of PTFE Polymer by Differential Scanning Calorimetry

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ABSTRACT: Two types of representative nanometer materials, i.e., fibroid nanometer attapulgite and approximate spherical ultrafine diamond, were selected as fillers of polytetrafluoroethylene (PTFE) to study the mechanism of the wear-reducing actions of the fillers in PTFE composites. The friction and wear tests were performed on a block-on-ring wear tester under dry sliding conditions. Differential scanning calorimetry (DSC) was used to investigate material microstructure and to examine modes of failure. No significant change in coefficient of friction was found, but the wear rate of PTFE composites was orders of magnitude less than that of pure PTFE. DSC analysis revealed that nanometer attapulgite and ultrafine diamond played a heterogeneous nucleation role in PTFE matrix

and consequently resulted in increasing the crystallinity of PTFE composites. Moreover, the PTFE composite with higher heat absorption capacity and crystallinity exhibited improved wear resistance. A propositional "sea-frusta" frictional model explained the wear mechanism of filler action in reducing the wear of PTFE polymer, i.e., fillers in the PTFE matrix effectively reduced the size of frictional broken units for PTFE composites and restrained the flowability of the units, as well as supporting the applied load. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3091–3097, 2007

Key words: filler; wear mechanism; wear; polytetrafluoroethylene (PTFE) polymer; differential scanning calorimetry (DSC)

INTRODUCTION

Polytetrafluoroethylene (PTFE) is a high-performance engineering plastics and widely used in industry due to its unique properties, such as the low coefficient of friction, high thermal stability, excellent chemical resistance, and biocompatibility.^{1,2} Unfortunately, PTFE exhibits poor wear and abrasion resistance under load, limiting its application in the tribological field. Accordingly, many methods are used to improve the wear resistance of PTFE, such as filling various suitable fibers (e.g., glass, carbon and aramid fibers) and adding multifarious inorganic powders (e.g., metal and its compounds, graphite, rare earth compounds) and organic macromolecular polymers (e.g., UHWPE, PI, PEEK, EP), except for surface treatments (e.g., alkali metals and plasma treatment).^{3–11}

Furthermore, because nanometer materials possess a surface effect, volume effect, and cooperative effect, in recent years, varieties of inorganic nanometer particles have been added to the PTFE polymer to enhance its tribological properties.^{12,13} It is expected that good tribological properties can be obtained for

the PTFE polymer filled with nanoscale fillers compared with that filled with microscale particles. Li et al.¹⁴ reported that filling nanometer ZnO to PTFE could greatly reduce the wear of this polymer and the best anti-wear property was obtained with the composite containing 15 vol % nanometer ZnO, but the friction coefficient of nanocomposite was higher than that of the unfilled PTFE. In investigating the tribological properties of PTFE composites filled with 40 nm Al₂O₃, Sawyer et al.¹⁵ found that the friction coefficient of the composite increased slightly compared with the unfilled sample and that the wear resistance increased monotonically with increasing filler concentration. Lai and et al.^{16,17} researched the friction and wear behaviors of PTFE composites filled with nanoattapulgite and ultrafine diamond under dry frictional conditions, and showed that the wear rate of PTFE could obviously decreased when addition of nanometer particles was < 5 wt %.

So far, all published reports have shown that almost any type of fillers or fibers can greatly reduce the wear of the PTFE composites. How do fillers act on PTFE polymer in reducing its wear? Some researchers studied the mechanism of filler action in reducing the wear of PTFE polymer.¹⁸ One mechanism of the wear-reducing actions of the fillers in PTFE composites is the preferential load support of fillers, proposed by

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Lancaster¹⁹ and further developed theoretically by Tanaka and Kawakami.²⁰ Another mechanism is filler intensifying adhesion between the transfer film and its counterpart surface, which was put forward by Briscoe and the standpoint is accepted by many researchers.^{21,22} Besides, Tanaka²³ considered that the wear rate of PTFE was reduced by the addition of filler because the filler obstructed large-scale destruction of its banded structure, resulting in formation of small discontinuous fragments.

Although many researchers have put forward a number of viewpoints about the mechanisms of fillers action in reducing the wear of PTFE, the origin of wear resistance improvement in PTFE polymer composites is still an open question. It is well known that the property of materials has a strong dependence on its structure, so it is reasonable to analyze the tribological properties of PTFE on the basis of its bulk structure. However, until now, not much information has been available on explanations of wear mechanisms of PTFE composites from its bulk structure.

The purpose of the present work is to study the wear mechanisms of PTFE composites from crystalline structure. Two types of representative nanometer material, i.e., fibroid nanometer attapulgite and approximate spherical ultrafine diamond, are used as fillers of PTFE. Differential scanning calorimetry (DSC) is used to investigate material crystalline structure and to examine modes of failure.

EXPERIMENTAL

Materials and samples

PTFE powder was supplied by Asahi Glass Fluoropolymers (Tokyo, Japan), obtained by dispersion aqueous polymerization. Fibroid nanometer attapulgite powder was purchased from Anhui Mingmei Minerals (Anhui Mingguang, China); the single crystal length was 100–1000 nm, and the width was 10–25 nm. Ultrafine diamond powder with an average size of 10-nm diameter was obtained from Tsinghua University (China). It was prepared by detonation of explosives with a negative oxygen balance. Before the preparation of samples, attapulgite powder and diamond powder were purified, respectively, with deionized water by ultrasonic stirring and centrifugal separation. The detailed operational process was as follows: 10 g of the purchased powder was added to 500 mL of deionized water and was vigorously stirred for 2 h at 80°C under ultrasonic effect. After this treatment, the suspension was centrifuged to remove impurities. Then the centrifuged suspension was dried in a vacuum oven at 105°C for 12 h. The purified product was ground and screened with a 200-mesh sieve.

First, the purified nanometer attapulgite powder and ultrafine diamond powder were thoroughly

mixed, respectively, with the PTFE powder in the appropriate content alcohol through mechanical adding ultrasonic way, and then the suspension solution was filtrated, and the filtrated sample was dried in a vacuum oven at 105°C for 12 h. Finally, the product was crushed and screened with a 200-mesh sieve. Second, these mixtures were molded into the blocks by compressing molding under a pressure of 50 MPa for 5 min. Finally, the PTFE composite blocks were sintered at 375 ± 5°C for 3 h in an oven, maintained for 4 h at 330°C, and finally cooled freely to room temperature.

Friction and wear tests

The friction and wear tests were conducted on a block-on-ring wear tester. The contact schematic diagram of the frictional pairs was described elsewhere.¹⁷ A steel ring (composition: C: 0.42–0.52; Si: 0.17–0.37; Mn: 0.5–0.8; P: ≤ 0.04; S: ≤ 0.04; Cr: ≤ 0.25; Ni: ≤ 0.25) was used as the counterpart. The polymer specimen blocks were 6 × 7 × 30 (mm). Sliding was performed under ambient conditions (temperature: 20 ± 3°C, humidity: 50 ± 10%) at a sliding speed of 0.42 m/s. The friction force torque was determined by a torque-measuring system. Each friction and wear test was carried out for 120 min, and the values of the friction force torque were noted at an interval of 10 min. Before each test, the surfaces were polished with metallographic abrasive paper to Ra 0.2–0.4 μm for the specimens and Ra 0.09–0.11 μm for the counterfaces. Then, the blocks and the rings were cleaned ultrasonically in acetone and thoroughly dried. Also, three replicate friction and wear tests carried out to minimize data scattering, and the average of the three replicate test results was reported in this work. At the end of each test, the width of wear scar was measured with a measuring microscope, and the friction coefficient μ , wear volume V (mm³), and wear rate K (mm³/N · m) of the specimen were calculated from the following relationships:¹⁴

$$\mu = \frac{M}{R \cdot P} \quad (1)$$

$$V = \left[\frac{\pi}{180} R^2 \arcsin \frac{b}{2R} - \frac{b}{2} \sqrt{R^2 - \frac{b^2}{4}} \right] B \quad (2)$$

$$K = \frac{V}{P \cdot v \cdot t}, \quad (3)$$

where M is the friction force torque (N · mm), R the radius of the steel ring (mm), P the load (N), b the width of the wear scar (mm), B the width of specimen (mm), v the sliding speed of the steel ring (m/s), t the duration of friction (min).

DSC experiments

DSC was used for thermal analysis of PTFE, PTFE composites, and their debris to correlate material

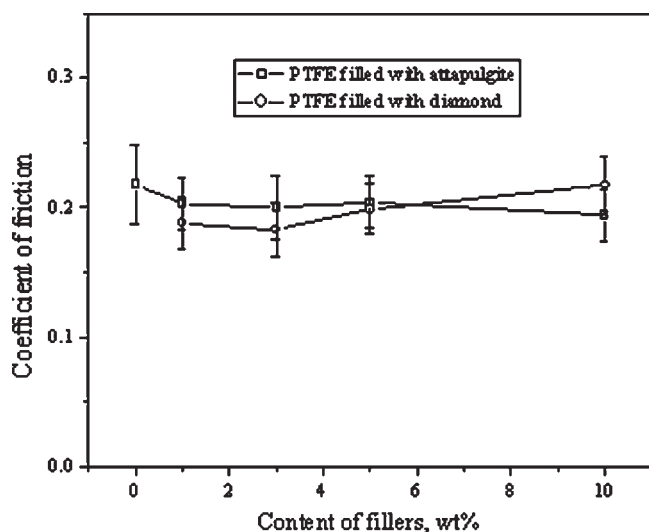


Figure 1 Effect of content of fillers on the coefficient of friction of PTFE and its composites filled with attapulgite and diamond, respectively. (Load: 200N.)

structure to the tribological performance. The samples of ~3–5 mg were placed in aluminum pans with a pierced lid. The tests were conducted under nitrogen atmosphere at a heating rate of 10°C/min up to 400°C, and maintained for 5 min at 400°C to eliminate the effect of the previous thermal history before crystallization; the melt was then dropped to 20°C at different cooling rates (5°, 10°, 15°, 20°C/min).

The crystallinity X_c (%) of the samples was then evaluated according to the following equation:

$$X_c = \Delta H_m / \Delta H_m^0 \times 100\%, \quad (4)$$

where ΔH_m is the measured heat of fusion and ΔH_m^0 is the heat of fusion of a perfect crystal of PTFE, which is assumed to be 82 J/g.²⁴

RESULTS AND DISCUSSION

Friction and wear properties

The effects of the content of fillers on the coefficient of friction and wear rate of PTFE and its composites filled with nanometer attapulgite and ultrafine diamond particles are given in Figures 1 and 2, respectively. In Figure 1 it can be seen that the friction coefficient of pure PTFE and its composites changes slightly with increasing content of filler; that is, the addition of fillers has very little effect on the friction coefficient of PTFE. This indicates that fibroid attapulgite or spherical diamond is not obviously effective for improving the friction-reducing ability of the composite. Figure 2 shows that the wear rate of PTFE composites decreases sharply when the content of fillers is <3 wt %, accompanied by a slight decrease as the content of fillers increases continuously.

When the content of the fillers is 10 wt %, the wear rate of the composite filled with attapulgite is $21.6 \times 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m}$; that filled with diamond is $9.4 \times 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m}$. Simultaneously, as can be seen by the naked eye, it is interesting to note that the filled-PTFE composite exhibits a considerably decreased wear rate as compared with the unfilled PTFE ($625.8 \times 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m}$). In a word, the addition of fillers with low content into PTFE is highly effective for improving the wear resistance of pure PTFE. These above results are consistent with which many investigators obtained.^{14,15}

Figures 3 and 4 show the effect of load on the friction coefficient and wear rate of pure PTFE and PTFE composites filled with 5 wt % nanometer attapulgite and ultrafine diamond, respectively. It can be seen in Figure 3 that the friction coefficient of PTFE composites is almost unchanged with increasing load. Figure 4 shows that the wear rate of pure PTFE increases gradually with increased load. When the Load is above 150N, the wear rate of PTFE increases obviously as load increases. In contrast, the wear rate of the composites increases with increasing load, but under any load the wear rate of PTFE composites filled with attapulgite and diamond is much lower than that of the unfilled PTFE. It can be concluded that the composites has higher PV value in contrast with pure PTFE. That is to say, the composites can support higher load than pure PTFE.

DSC analysis of bulk PTFE composites

A DSC study was conducted on bulk PTFE and its composites. Thermal traces of bulk PTFE and its composites filled with nanometer attapulgite and ultrafine diamond are shown in Figure 5(a,b), respectively. The heat of fusion, ΔH_m , corresponds to the area of the melting peak divided by the mass of the

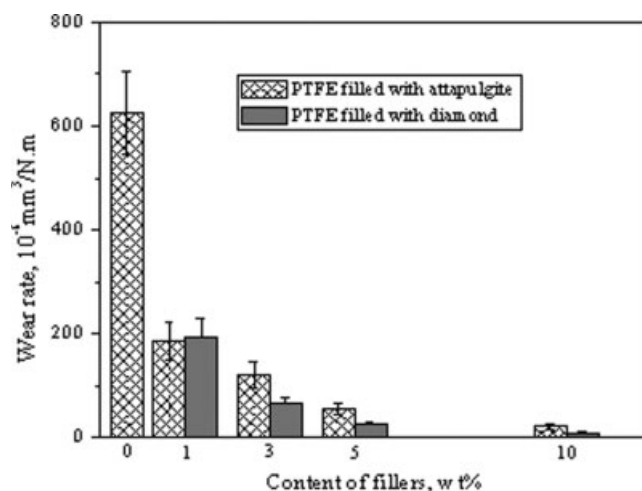


Figure 2 Effect of content of fillers on the wear rate of PTFE and its composites filled with attapulgite and diamond, respectively. (Load: 200N.)

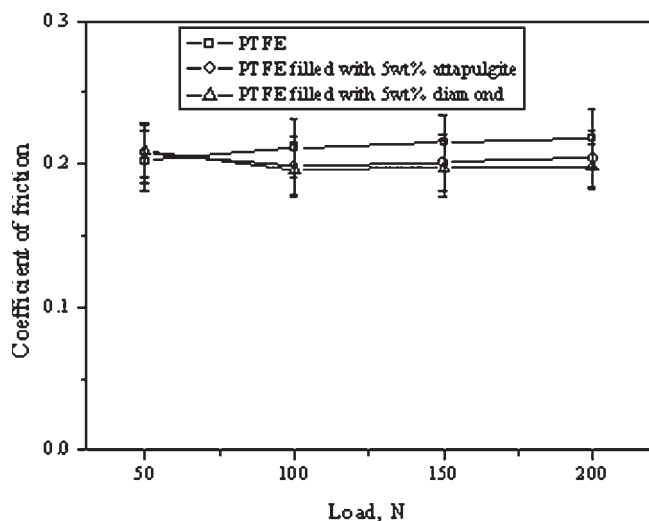


Figure 3 Effect of load on the coefficient of friction of PTFE and its composites.

sample to get an average heat of fusion for the samples and signifies the amount of heat absorbed per unit mass of the matrix during melting. A comparison between the thermal traces of pure PTFE and its composite materials shows no indication of any additional reaction between the filler and the matrix in the temperature range tested (from 20°C to 400°C) and no apparent variation in the position of the transition-melting peak. The results in Figure 5 show that ΔH_m values of the bulk PTFE composites are significantly greater than that of the bulk PTFE polymer. This indicates a higher heat absorbing capacity for the composites compared with the pure polymer. With increasing content of fillers, the heat absorbing capacity of the PTFE composites also increases. Table I summarizes the results of the DSC analysis on PTFE and PTFE-based composites. The crystallinity of PTFE based composites, whether filled with nano-

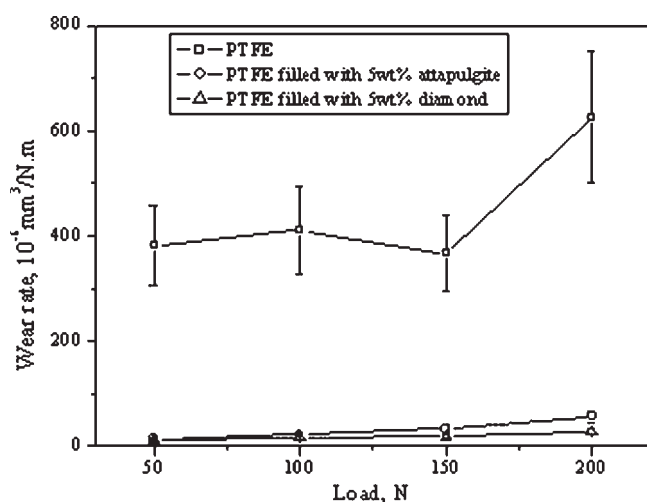


Figure 4 Effect of load on the wear rate of PTFE and its composites.

meter attapulgite or with ultrafine diamond, increases with increased filler content. However, it is not a monotonic increase with filler content. It is important to note that the crystallinity of the composites is ~ 10 – 20% higher than that of pure PTFE. These behaviors can be due to effects by the presence of filler materials within the PTFE matrix. These effects can be twofold. First, the matrix may form a strong bond with the filler materials increasing stability. Second, the presence of filler material leads to an increase in the degree of crystallinity of the matrix. Compared with the results in Figure 2, it can be deduced that the PTFE composite with higher heat absorption capacity and crystallinity exhibits improved wear resistance.

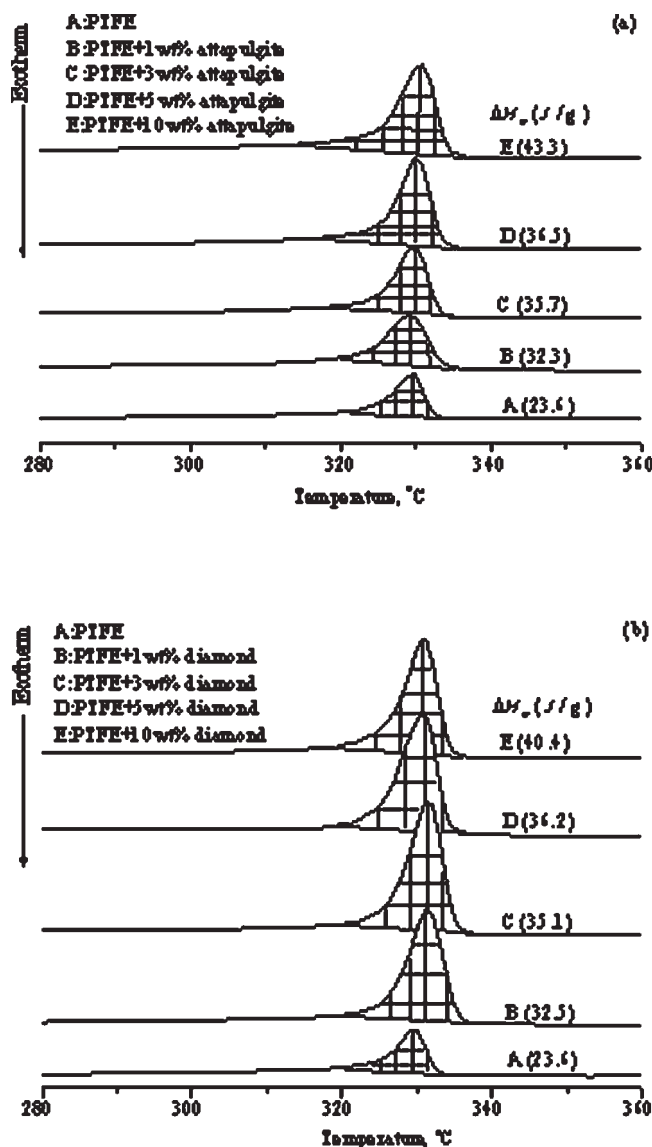


Figure 5 Thermal traces of PTFE and PTFE composites (a) filled with fibroid attapulgite, and (b) filled with spherical diamond using DSC. Operating conditions: heating rate 10°C/min, atmosphere nitrogen.

TABLE I
Results of DSC Analysis of PTFE and PTFE-Based Composites*

Content of filler	PTFE filled with attapulgite				PTFE filled with diamond			
	T_{pm}^a (°C)	T_{pc}^b (°C)	ΔH_m^c (J/g)	X_c^d (%)	T_{pm} (°C)	T_{pc} (°C)	ΔH_m (J/g)	X_c (%)
0	329.5	312.2	23.6	28.8	—	—	—	—
1	329.2	313.4	32.3	39.4	330.9	312.8	32.5	39.6
3	329.9	314.1	36.5	44.5	331.1	313.4	35.1	42.8
5	330.0	315.5	35.7	43.6	330.6	315.0	36.2	44.1
10	330.7	314.3	43.3	52.8	330.7	314.1	40.4	49.3

* Heating rate: 10°C/min; cooling rate: 10°C/min.

^a T_{pm} denotes the temperature corresponding to the peak of the melting curve.

^b T_{pc} denotes the temperature corresponding to the peak of the crystallization curve.

^c ΔH_m denotes heat of fusion.

^d X_c denotes degree of crystallinity.

Effect of nanometer filler on crystallization of PTFE

According to the Dobрева method, the cooling rate β and the undercooling ΔT_p are related as follows:²⁵

$$\log \beta = C - \frac{B}{2.3\Delta T_p^2} \tag{5}$$

The nucleation activity of fillers ϕ can be determined by the ratio:

$$\phi = \frac{B^*}{B}, \tag{6}$$

where B and B^* are the slopes of the $\log \beta$ vs $1/\Delta T_p^2$ dependence for both the homogeneous case and the heterogeneous case, respectively; C is constant; $\Delta T_p = T_{pm} - T_{pc}$, whereas T_{pc} denotes temperature corresponding to the peak of the crystallization curve, T_{pm} denotes the melting temperature of pure PTFE, which is 329.5°C (see Table I).

Figure 6(a,b) is plotted in terms of the non-isothermal crystallization data of pure PTFE and PTFE filled with nanometer attapulgite and ultrafine diamond, respectively. It was calculated in Eq. (5) that $\phi = 0.8 - 1$, which means that nanometer attapulgite and ultrafine diamond play a heterogeneous nucleation role during PTFE melting–crystallinity process. Accordingly, it can be concluded that the nucleation of fillers causes the crystallinity degree of PTFE.

Figure 7 is schematic diagram of crystallization process of PTFE and its composite. During the melting–crystallinity process, melting pure PTFE molecules entangles each other and forms many crystalline units. The individual units in the structure are the so-called crystalline blocks or bands, 10–100 μm in length and 0.2–1 μm in width. These units are composed of slices $\sim 200 \text{ \AA}$ thick, with each slice separated from its neighbor by a poorly crystalline or amorphous region.²⁶ The heterogeneous nucleation of fillers affects crystallization process of PTFE; it is reasonable to form smaller crystalline units for PTFE molecules in PTFE composites.

Wear mechanism

Debris is a product of frictional experiment, and analyzing debris is helpful to comprehend the friction

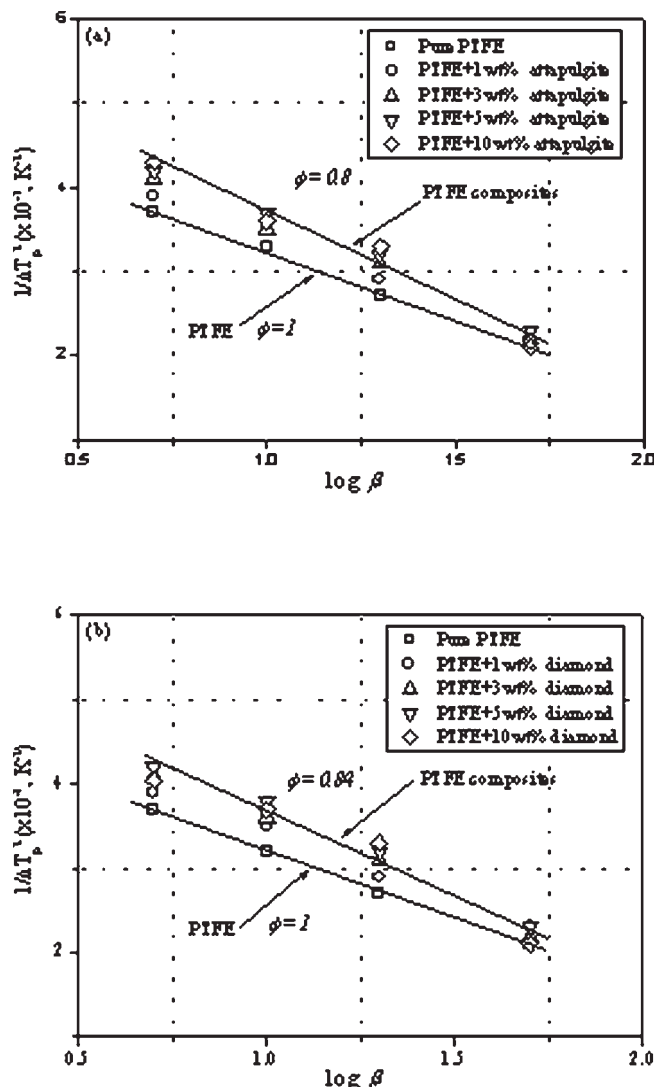


Figure 6 Rate dependence of the crystallization temperature of PTFE composites (a) filled with fibroid attapulgite, and (b) filled with spherical diamond in coordinates $1/\Delta T_p^2$ versus $\log \beta$.

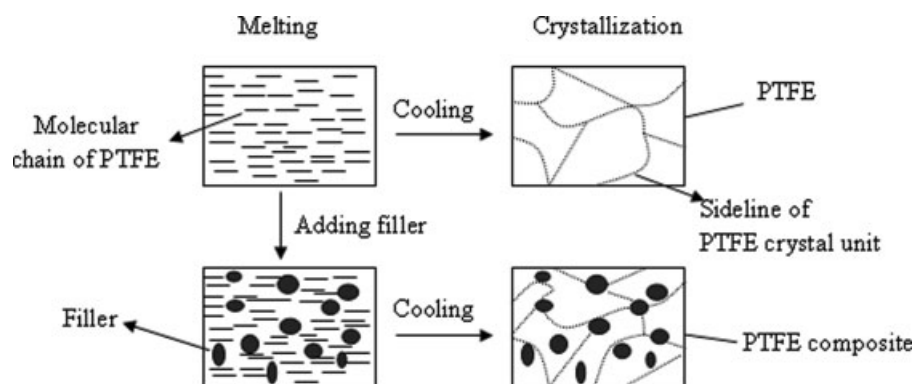


Figure 7 Schematic diagram of crystallization process of PTFE and its composite.

and wear mechanisms. To analyze the molecular weight of bulk PTFE and its debris, DSC continues to be used to measure the heat of crystallization (ΔH_c) of bulk PTFE and its debris. The results are given in Figure 8. The number average molecular weight, \bar{M}_n , is evaluated according to the empirically derived relationship between the number average molecular weight and the heat of crystallization²⁷

$$\bar{M}_n = 2.1 \times 10^{10} \Delta H_c^{-5.16} \quad (7)$$

and is estimated to be about 300×10^5 g/mol for pure PTFE, 3×10^5 g/mol for its debris. Li et al.²⁸ also reported that the molecular weight of debris is 2–3 orders of magnitude less than that of bulk PTFE. This indicates that the breakage of PTFE molecular chains took place under friction shear force during sliding. Furthermore, in our early research work, it knows from scanning electron microscopy (SEM) of debris that the debris of PTFE composite (500 μm) in size is much smaller than that of pure PTFE (2000 μm).¹⁶ This shows the fracture unit of pure PTFE is much bigger than that of PTFE composites under

frictional shear force. Hence, adding filler to PTFE can inhibit the breakage of PTFE molecular chains and effectively reduce the size of frictional broken units for PTFE composites.

Figure 9 is a sketch map of wear mechanism of filler action in reducing the wear of PTFE polymer. For pure PTFE material, it deforms easily under a normal load and frictional shear force causes PTFE to break away from friction system and forms debris. As a rule, it is well known that filler is superior to matrix PTFE polymer in the wear resistant, the existence of fillers prevents PTFE material from flowing away from friction system as well as carries the applied load. This sketch map is a so-called “sea-frusta” frictional model, where “sea” denotes the PTFE polymer and “frusta” denotes fillers in PTFE matrix.

CONCLUSION

The friction and wear behaviors of PTFE composites are correlated with material microstructures. DSC analysis shows that fibroid nanometer attapulgite and ultrafine diamond play a heterogeneous nucleation role in the PTFE matrix, which consequently leads to an increase in the degree of crystallinity of PTFE composites. Moreover, the PTFE composite with higher heat absorption capacity and crystallinity exhibits improved wear resistance. The wear mechanism of filler action in reducing the wear of

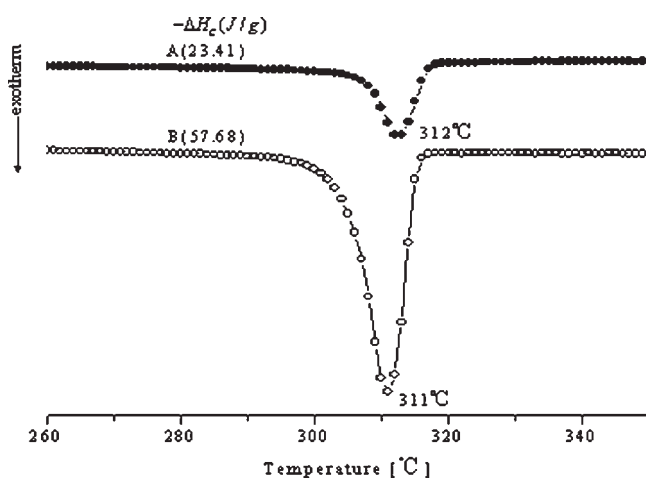


Figure 8 DSC traces. A, PTFE; B, debris of PTFE.

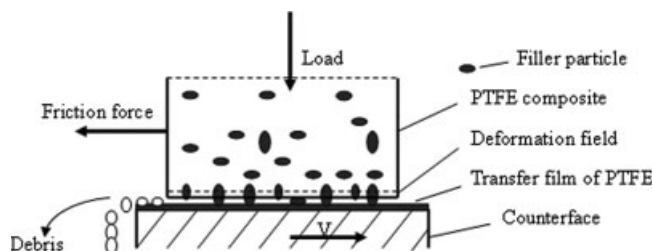


Figure 9 Sketch map of wear mechanism of filler action in reducing the wear of PTFE polymer.

PTFE polymer is that fillers effectively reduce the size of frictional broken units for PTFE composites and obstruct the flowability of these units, as well as supporting the applied load.

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