Study on Tribological Properties of Polytetrafluoroethylene Drawn Uniaxially at Different Temperature

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Introduction

Polytetrafluoroethylene (PTFE) is one of the most remarkable synthetic polymers, combining a large range of useful chemical and physical properties and very low friction coefficient. Pioneering studies of the tribological properties of PTFE were done by Tabor long ago. The wear behavior of PTFE has drawn considerable interest during the past years, however, how to enhance the wear resistance of PTFE is still a problem, which has been puzzling the scientists all these years. Most of the work has been carried out on the effect of fillers on the tribological properties of PTFE. But less attention has been paid to the effect of the structure of PTFE itself on the tribological properties, especially, the relationship between the structure for PTFE drawn at relatively high temperature and the tribological properties.

It is well known that polymer microstructure has a great influence on the friction coefficient and on the wear rate. Many researchers have found that the tribological properties of drawn polymers are different from those of undrawn polymers, such as polyethylene, polycaproamide, and Nylon 6. Tanaka and Miyata have reported that the static friction of PTFE is sensitive to the direction of pre-rubbing of the friction surfaces and the static friction for sliding, parallel to the pre-rubbing direction, is much lower than that for sliding perpendicular to it. The mechanical properties and wear resistance of the compressed PTFE are higher than that of non-compressed PTFE. Li et al. have reported that the debris with long fibers is produced...
under higher temperature.\textsuperscript{[18]} Tanaka also has reported that the transfer film of PTFE is produced by the lateral connection of adjacent fibers.\textsuperscript{[19]} Moreover, the analytical results of scanning electron microscope (SEM) and SFM show that the fibril structure of PTFE is formed by drawing and sliding motion.\textsuperscript{[20,21]} It is well known that the wear resistance of PTFE fiber is several times higher than that of bulk PTFE. It is clear from the above review, that draw orientation and friction orientation are important in sliding process. However, published works provide only some limited results, presenting a systematic assessment of microstructure morphology on the wear behavior of polymers.

PTFE is highly crystalline and the melting point is generally at 327°C. At 375°C, it is in the semi-solid gel state and has extremely high melt viscosity. PTFE can have different physical state depending on the effects of temperature and molecular chains motion of PTFE is greatly influenced by temperatures. Therefore, the structures of PTFE drawn at different temperatures are different, which affects the tribological properties of PTFE.

This article tries to contribute in a preliminary manner to an understanding of the influence of drawing on tribological properties and further to establish the correlations between wear behavior and morphology of PTFE drawn uniaxially at 200, 327, and 375°C. The morphology of drawn samples and debris is characterized by the SEM, the DSC, and WAXD.

Experimental Part

Materials

The polymer used in this study is granular PTFE, which has a particle size of about 25 μm. The PTFE powder was charged into a die and pressurized up to 30 MPa at room temperature. The pressure was held for 2 min and was released to atmospheric pressure. The PTFE was sintered at 375°C for about 2 h in a circulating-air oven, and then cooled slowly to room temperature. The sintered PTFE was drawn at 200, 327, and 375°C, respectively on a stretching apparatus constructed in our laboratory. The elongated PTFE was cooled in air immediately to room temperature upon reaching the desired draw ratio. The actual elongation to calculate the draw ratio, was obtained by measuring the distance between two marked lines on the drawn PTFE, which had been removed from the drawing machine.

Friction and Wear Tests

The friction and wear tests were conducted on a pin-disc friction and wear tester. Stainless steel disc of 20 mm diameter was used. The polymer specimen pins were of the size of 2.0 × 1.4 × 2.5 mm³. Before each test, the surfaces of the discs were polished with metallographic abrasive paper to surface roughness of 0.09–0.11 μm Ra. Then the pins and the discs were ultrasonically cleaned in acetone and thoroughly dried. Sliding tests were performed under ambient conditions (temperature: 25°C, humidity: 50 ± 10%) at a speed of 0.42 m·s⁻¹, a normal load of 1.96 N, and the rotation radius of 8 mm. Sliding direction was along the drawn direction. The test durations ranged from 0 to 30 min.

Scanning Electron Microscope (SEM) Observation

The morphology of undrawn and drawn PTFE, was observed on JSM-5600LV SEM. Gold palladium alloy was sputtered on the samples for further observation.

Differential Scanning Calorimeter (DSC) and Wide Angle X-Ray Diffraction (WAXD) Analyses

The DSC was conducted on NETZSCH DSC204 instrument. The samples (3–5 mg) were stacked in aluminum pans with pierced lid, and experiments were performed under nitrogen atmosphere and heated from room temperature to 400°C at a rate of 10°C·min⁻¹. The structure of PTFE was determined with WAXD data, which was obtained by using Rigaku D/Max-rB diffractometer with a 18 kV rotating-anode generator and Cu Kα-target, operated at Voltage 40 kV and current 60 mA. The scan rate was 4°·min⁻¹, over the angular 2θ range from 5 to 60°.

Results and Discussion

Friction and Wear Properties

Figure 1 shows the relationship between the friction coefficient and sliding time for PTFE drawn at different temperatures. The friction coefficient of drawn samples is lower than that of undrawn PTFE (0.18). There is no significant difference in friction coefficient among drawn samples. But one sees that the friction coefficient for PTFE, drawn at 327°C, is a little lower than those of PTFE drawn at 200 and 375°C. Figure 2 presents the ratios of the wear rate of drawn
Scanning Electron Microscope (SEM) Analysis of Undrawn and Drawn Polytetrafluoroethylene (PTFE)

The morphologies of fractured surfaces of undrawn and drawn PTFE were observed by SEM. Figure 4 presents the morphologies of fractured surfaces of undrawn (Figure 4A) and drawn PTFE (Figure 4b–d), the cross-sections perpendicular to the draw direction; Figure 4B–D, fractured surfaces parallel to the draw direction), respectively. It is almost completely disoriented morphology for undrawn PTFE as shown in Figure 4A. With a draw ratio of 4, the structures change with the formation of new-ordered fiber structure for drawn samples. It can be concluded that the degree of fibrillation and orderliness of drawn PTFE is highly improved compared with undrawn PTFE.

It is well known that PTFE is highly crystalline and is composed of a ribbon-like crystalline structure folded compactly into a particle. Drawn at 200 °C, the motion of molecular chains is not complete and only the orientation of chain segment occurs, which leads to the curved ends of fibrils (Figure 4b) and the structure of lamellae interrupted by a few longitudinal gaps (Figure 4B). While for PTFE drawn at 375 °C the motion of molecular chains is almost complete, which would deprive PTFE of the morphology inherent to its particle and transform the particles into a polymeric mass, resulting in difficulty in pulling the fibril structure out of the particle. Meanwhile, the effect of relaxation is obvious in the drawing process. Therefore, the fractured surfaces are connected by something like non-crystalline substance (Figure 4d and D). Under these two conditions, the fibril crystal is formed a little difficultly, which leads to the lower degree of fibrillation and orderliness. However, drawn at the melting point of 327 °C, due to the effect of thermodynamic equilibrium of the melting
Figure 3. Scanning electron microscope (SEM) images of debris of undrawn and drawn PTFE (a and A, undrawn; b and B, drawn at 200 °C; c and C, drawn at 327 °C; d and D, drawn at 375 °C).
and crystallization, the ribbon-like structure is quite easily pulled out of the particle, which is beneficial for the formation of fibril crystal. The ends of fibrils are straight and much regular as shown in Figure 4c, and the whole surface parallel to the drawn direction consists of nearly perfectly aligned fibrils for PTFE drawn at 327 °C, as if they belong to a stalk of lamellae formed by drawing (Figure 4C). Thus the degree of the crystalline, fibrillation, and orderliness is higher than the other two drawn samples. The arrangement of microfibrils is tighter and the interaction between microfibrils is stronger. One sees in Figure 4C that there are less ruptured microfibrils and the lamellae structure, formed by fibrils is more obvious than Figure 4B and D. In comparison with Figure 3, it reveals that the degree of fibrillation for drawn samples corresponds to the variation of debris structure, i.e., if the degree of fibrillation of drawn sample is high, the degree of fibrillation of debris is also high.

It can be concluded from the above analysis that the degree of crystalline, fibrillation, and orderliness is different for samples drawn at different temperatures. Therefore, in the process of friction, the deformability and the micro fractured manner are different, which results in the variation of tribological properties. The degree of the crystalline, fibrillation, and orderliness is higher for PTFE drawn at 327 °C, which improves the deformability and reduces the size of the wear breakage unit. Thus the microfibrils are broken and the cotton-like debris composed of microfibrils is formed in the test process. While for the samples drawn at 200 and 375 °C, the degree of the crystalline, fibrillation, and orderliness is lower than that of PTFE drawn at 327 °C, which lowered the deformability. The strip-shaped debris with ruptured microfibrils on the edge of the debris and the strap-like debris composed of bundle-like substance, aligned respectively in same direction as formed. Thus the
degree of fibrillation of debris is lower and the wear resistance is worse than that of PTFE drawn at 327 °C.

**Differential Scanning Calorimeter (DSC) and Wide Angle X-Ray Diffraction (WAXD) Analyses of Undrawn and Drawn Polytetrafluoroethylene (PTFE)**

In order to learn about the information of crystallinity of samples quantitatively and to obtain more information about the structure of drawn PTFE, the DSC and WAXD analyses were performed for undrawn and drawn PTFE.

Table 1 lists the crystallinity of samples. As seen from Table 1 that crystallinity of PTFE drawn at 327 and 200 °C is higher than that of undrawn PTFE, while PTFE drawn at 375 °C is lower than that of undrawn PTFE. It is in agreement with the above analytical results.

Figure 5 shows the WAXD scan obtained for samples. A careful analysis of the WAXD data was carried out for the assignments of various reflections. A noticeable worthy difference is seen in the variation of intensities of different peaks with undrawn and drawn PTFE. As seen from Figure 5 various peak positions are the same in all cases. However, the intensities of the reflections 100/110/200 and 210 planes (at 2θ of 18, 31, 36, and 49°, respectively) increase obviously, especially, for PTFE drawn at 327 °C and the peaks of reflections of 024/018 and amorphous halo (at 2θ of 41, 45, and 16°, respectively) almost disappear when PTFE is drawn, indicating that the rearrangement of crystal occurs due to drawing. At the same time the crystallization and rearrangement in the amorphous region also take place. These findings together with the morphologies of fractured surfaces, clearly confirm the formation of orderly structure by drawing and the sample drawn at 327 °C possesses more orderly structure than samples drawn at 200 and 375 °C. Accordingly, PTFE drawn at 327 °C exhibits better tribological properties.

Wear is a shear process either on the surface or in the bulk. The degree of the crystalline, fibrillation, and orderliness is improved by drawing and the orderliness of molecular arrangement along draw direction also increases, which leads to an increase of the intensity of covalent bond in drawn direction compared with undrawn PTFE. The shear resistance along the drawn direction is strengthened, which improves the wear resistance parallel to the draw direction. Consequently, the sample drawn at 327 °C with the higher degree of the crystalline, fibrillation, and orderliness obtained better wear resistance.

**Conclusion**

The tribological behavior of PTFE is improved by drawing. The debris morphologies of samples are obviously different. The differences in the friction and wear behaviors of undrawn and drawn PTFE, result from the change of structure by drawing. The degree of crystallinity, orderliness, and fibrillation for PTFE drawn at 327 °C is higher than those of PTFE drawn at 200 and 375 °C. Therefore, the intensity of covalent bond along draw direction is higher. The shear resistance and the deformability of the material are greatly improved and the size of the wear breakage unit decreases, which results in a good tribological property for PTFE drawn at 327 °C.

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**Table 1. The crystallinity of undrawn and drawn samples.**

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<tr>
<th>Sample</th>
<th>Crystallinity</th>
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<tbody>
<tr>
<td>Undrawn PTFE</td>
<td>51</td>
</tr>
<tr>
<td>Drawn at 200 °C</td>
<td>60</td>
</tr>
<tr>
<td>Drawn at 327 °C</td>
<td>78</td>
</tr>
<tr>
<td>Drawn at 375 °C</td>
<td>42</td>
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</tbody>
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