An Investigation of Friction and Wear Behaviors of Polyimide/Attapulgite Hybrid Materials

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Introduction

As one of the most important super-engineering plastics, polyimide (PI) has been used in automotive, air, railway transport systems and micro-electronic applications for outstanding thermal, mechanical, anti-wear and electrical properties as well as resistance to solvent and radiation. In earlier studies on friction and wear of PI, many researchers have studied how factors such as type of atmosphere, temperature, contact stress, and PI molecular structure affect the friction and wear of PI. Fusaro et al. studied the friction and wear behaviors of PI films and bulk materials mainly in vacuum condition. They found that a polymer transfer film on the counter surface was developed, resulting in low friction and wear due to the plastification ability of the PI polymer surface. Cong et al. investigated the effect of temperature on friction and wear of PI. It was found that at continuously varied temperatures the friction factor of PI increased initially to a maximum value (0.66), then decreased to 0.16 gradually with increasing temperature. Under a given temperature, the friction factor of PI increased rapidly to a maximum value and thereafter decreased to a stable value with increasing sliding time. However, the wear rate of PI increased gradually with increasing temperature. In order to obtain perfect friction and wear properties, many researchers modified also PI using fillers such as graphite, MoS2, fluoride graphite, PTFE and fiber and so on. Samyn et al. investigated tribological behaviors of pure and graphite-filled PI under atmospheric conditions. The results showed that addition of 15 wt.-% graphite powder as internal solid lubricant strongly influences friction and wear.

However, with the booming of polymer nanocomposite in the recent years, many attempts were made to develop...
nanoparticulate filled polymer composites to improve the tribological performance of the materials.\textsuperscript{[7]} It is expected that good tribological properties can be obtained for the polymers filled with nanoscale fillers compared to that filled with microscale particles, owing to the effect of the unique nature of the ultrafine particulates on the bulk properties of polymer-based nanocomposites. The effects of inorganic nanometer particles, such as SiC, SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4} and ZrO\textsubscript{2}, on the tribological properties of some polymers have been studied.\textsuperscript{[8–11]} Cai et al.\textsuperscript{[12]} researched the tribological properties of polyimide/carbon nanotube (PI/CNT) nanocomposites. The bending strength and microhardness of the PT/CNT nanocomposites increased with increasing CNT content and reached stable values at a certain content of CNT. CNT could effectively enhance the friction-reduction and antiwear capacity of the nanocomposite. Cai et al.\textsuperscript{[13]} still investigated the tribological properties of Al\textsubscript{2}O\textsubscript{3}-PI nanocomposites. Results indicated that the PI-based nanocomposites with appropriate properties of nanometer Al\textsubscript{2}O\textsubscript{3} particles exhibited lower friction coefficient and wear volume loss than PI under the same testing conditions. The nanocomposite containing 3.0–4.0 wt.-% Al\textsubscript{2}O\textsubscript{3} registered the lowest wear volume loss under a relatively high load. However, in these literatures dealing with nanoparticle-filled polymer composites for tribological applications where composites are usually prepared by mechanical mixing, it is difficult to disperse these particles into indeed nanoparticles in the polymer matrix. Therefore in this paper we disperse suspended nanometer particle into poly(amic acid) (PAA) by the solution dispersion.

Attapulgite (AT), or palygorskite, is a family of fibrous hydrous magnesium silicates. The structure of AT was first proposed by Bradley, who described a theoretical half unit-cell formula Mg\textsubscript{2}Si\textsubscript{5}O\textsubscript{20}(OH\textsubscript{2})(OH\textsubscript{4})\textbullet 4H\textsubscript{2}O.\textsuperscript{[14]} The chemical structure of AT is given in Figure 1. The mineral finds important uses as an animal waste adsorbent, pesticide carrier, decolorizing agent, in the oil refining and pharmaceutical industries and catalyst and catalyst support.\textsuperscript{[15–17]} Due to its special layer-chain structure and low price, nowadays AT is receiving a great deal of attention. However, until now, much less information has been available on the friction and wear behaviors of PI-AT hybrid materials.

The purpose of this work is to study the friction and wear behaviors of the PI-AT hybrid materials films under dry frictional conditions. Some insights into the friction and wear mechanisms of the PI composites are given. It is expected that this study may be helpful for applications of AT.

**Experimental Part**

**Materials**

Nano-attapulgite powder was obtained from Anhui Mingmei Minerals Co., Ltd. (China); its single crystal length was 100–1 000 nm and width was 10–25 nm.\textsuperscript{[18]} Pyromellitic dianhydride (PMDA), 4, 4\textsuperscript{0}-oxydianiline (ODA) and N,N-dimethylacetamide (DMAc) were purchased from Shanghai chemistry agent Co., Ltd. (China) and used without further purification.

**Pretreatment of Attapulgite**

It is well known that AT clay has some other components beside AT, such as quartz and carbonate.\textsuperscript{[19]} These chemicals exist in the form of relatively large particles which are difficult to be dispersed in water or separated under shear into smaller dispersion units. These large particles in matrix will deteriorate the properties of PI, thus we tried to purify AT. The purifying process was as follows: 10 g of the purchased AT was added to 500 ml of deionized water and was vigorously stirred for 2 h at 80 °C. After this treatment, the AT suspension was centrifuged in order to remove impurities. Then the centrifuged suspension was dried in a vacuum oven at 105 °C for 12 h. The purified clay was ground and screened with 200-mesh sieve. Finally, two grams of the screened powder was added to 98 g DMAc. First the mixture was treated for 30 min using an ultrasonic bath and then vigorously stirred for 4 h at 80 °C. A stable suspension was obtained and kept until use.

**Synthesis of Poly(amic acid)**

Poly(amic acid) (PAA) was synthesized by adding 0.14 mol of ODA into a three-necked flask containing 500 g of DMAc under nitrogen purge in ice water. After ODA had completely dissolved in DMAc, 0.14 mol of PMDA, which was divided into three batches, was added to the flask batch-by-batch with a time interval of 30 min between the batches. After all the PMDA was dissolved, the mixture in the flask was stirred for 6 h at room temperature, and a viscous PAA solution was obtained. The PAA solution was kept in a freezer until use.
Preparation of PI/AT Hybrid Materials

The PI/AT hybrid materials were prepared by blending the required ratios of AT suspension with PAA solution. The blends were stirred for 4 h to achieve complete dispersion of AT into PAA. The PI/AT composite films for tensile test were prepared by casting PAA/AT on a glass plate. However the samples for friction and wear tests were prepared by spraying PAA/AT on a steel ring with 40 mm diameter. Onto the steel ring surface was sprayed a layer of sand before spraying PAA/AT. These samples were put in an air convection oven at 70 °C for 2 h before the imidization step. Imidization of PAA/AT was carried out by putting the samples in an air-circulation oven at 100 °C, 200 °C and 300 °C for 1 h, respectively.

Characterization

The morphologies of the hybrids were observed using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The samples for SEM observation were fractured in liquid nitrogen, and then were sputter-coated with a thin layer of gold palladium alloy prior to SEM examination. The samples for TEM study was first prepared by pouring PI/AT films into epoxy capsules and by curing the epoxy at room temperature. Then the cured epoxies containing PI/AT films were microtomed into thin slices in a direction normal to the plane of the films. Subsequently, a layer of carbon about 3 nm thick was deposited to these slices that being on copper nets for TEM observation. Tensile properties of the solution-cast films were tested with an Instron Mechanical Tester (model 5567). The crosshead speed was set as 0.5 mm min⁻¹ in all experiments. The specimens were prepared by being cut into strips 4 × 30 mm. An average of at least five individual determinations was used.

Friction and Wear Test

Dry sliding wear tests were conducted on a ball-on-disc friction and wear tester to evaluate the tribological properties of PI/AT films. A schematic diagram of the wear tester is described in Figure 2. A stainless steel ball was used as the counterpart, its diameter was 3 mm. Sliding was performed under ambient conditions (temperature: 20 ± 3 °C, relative humidity: 50 ± 10%) at a sliding speed of 0.84 m·s⁻¹ and a load of 2 N. Each friction and wear test was carried out for 10 min. The frictional force transferred to a sensor was recorded throughout the tests. The sensor produced an electric output that depended on the frictional force. The electric signal amplified by a multi-meter was stored in a computer via a general-purpose interface bus (GPIB). The wear volume V (mm³) and wear rate K (mm³·N⁻¹·m⁻¹) were calculated from the following relationships:

\[ V = \frac{2\pi l}{180} \left( \frac{\pi r^2 \sin \frac{d}{2} - d}{2} \right) \sqrt{r^2 - \left(\frac{d}{2}\right)^2} \]

\[ K = \frac{V}{P \cdot v \cdot t} \]

where \( r \) is the radius of the stainless steel ball (mm), \( d \) the width of the wear scar (mm), \( l \) the radius of wear scar ring (mm), \( P \) the load (N), \( v \) the sliding speed of the steel ring (m·s⁻¹), \( t \) the duration of sliding (min). Three replicate friction and wear tests were carried out so as to minimize data scattering, and the average of the three replicate test results was reported in this article.

After the wear tests, the worn surfaces of the hybrids and worn debris were examined by SEM in order to elucidate the friction and wear mechanisms. In order to increase the resolution for the SEM observation, the tested composite specimens were plated with gold coating to render them electric conductivity. Also, worn debris of pure PI and its composites was still analyzed by Fourier Transform infrared spectroscopy (FT-IR).

Results and Discussion

Microscopic Observations

Figure 3 shows SEM micrographs of the hybrids containing 0, 3 and 7 wt.-% of AT. Compared with the fractured surface of pure PI, it can be seen from Figure 3(b) and (c) that there are many tiny particles in that of the hybrid materials; these particles are dispersed uniformly into the PI matrix. However, it is obvious that aggregation of these particles occurred with increasing content of AT. It is impossible to observe the AT particle size in the PI matrix using an SEM, thus TEM was used furthermore to observe the dispersion of AT particles in the PI polymer. Figure 4 is a TEM photograph of the hybrid containing 5 wt.-% AT. It can be seen from Figure 4 that AT particles are about 10–100 nm in width and 100–1 000 nm in length. In addition, we know that fibrillar single crystal of AT is the smallest structure unit with a width of 10–25 nm and 100–1 000 nm in length.

This implied that it is more difficult to disperse AT particles into single crystal structure in polymer than in water. However, as we know, the size of so-called nanoparticles is less than 100 nm in one dimension. Accordingly, this explained that the PI nanocomposite could be prepared by the solution dispersion when the content of AT in PI matrix is below 5 wt.-%.
Friction and Wear Properties

Figure 5 and 6 show the recorded friction coefficients as a function of time and the average values as a function of AT filler content, respectively. The average friction coefficient ($\bar{\mu}$) for each test is calculated using Equation (1) and the variance ($\sigma^2$) is calculated using Equation (2). In both these equations $t$ is the total duration of the test in seconds.

$$\bar{\mu} = \frac{1}{T} \int \mu dt$$  \hspace{1cm} (1)

$$\sigma^2 = \frac{1}{T} \left[ \int \mu dt - \left( \frac{\int \mu dt}{T} \right)^2 \right]$$ \hspace{1cm} (2)

In Figure 5 and 6 it is clear that the friction coefficient of the PI hybrids decreases due to the presence of AT filler, but the decrease is small and it increases after 1 wt.-% of AT filler. Comparing pure PI and the PI hybrid materials, the addition of AT is favorable for lowering the friction coefficient when the AT content is less than 5 wt.-%.

In Figure 7 the calculated wear rate $k$ (mm$^3 \cdot N^{-1} \cdot m^{-1}$) versus filler content is plotted. The wear width at the end of the tests was used to calculate the wear rate of the PI hybrids. Form Figure 7 it can be seen that the wear rate of the PI hybrids first decreases considerably and then increases sharply with increasing AT content. The lowest wear rate in this study is for the PI hybrid with almost 3 wt.-% filler; the lowest wear rate is $k = 2.9 \times 10^{-5}$ mm$^3 \cdot N^{-1} \cdot m^{-1}$ which means that the wear resistant of the hybrid is over 6 times more than the traditional unfilled PI. Moreover, from Figure 6 it can be seen that the average friction coefficient for the sample is $\bar{\mu} = 0.26$. Accordingly, it can be deduced that an appropriate AT content in the PI matrix can effectively decrease the friction coefficient and wear rate of pure PI.

Mechanical Properties

In order to study the wear mechanisms of the PI hybrid materials, we first analyzed mechanical properties of the PI hybrids. Figure 8 shows the tensile strength and elongation at break of the PI/AT hybrid materials as a function of AT content. It can be seen from Figure 8 that the tensile strength increases with increasing AT content and reaches the highest value (103.5 MPa) at a content of 5 wt.-% AT, this is ca.
20% higher than that of the original PI (82.4 MPa). When the AT content is above 5 wt.-%, the tensile strength decreases sharply. The elongation at break of the composite shows the same variation tendency with increasing AT content, when the amount of added AT is 5 wt.-%, the elongation at break (10.5) of the hybrid is ca. 60% higher as compared to that of pure PI (6.5). From the above analysis it may be seen that the addition of AT to PI can improve both strength and toughness when the content of AT is less than 5 wt.-%. This suggests that there is a reinforcement effect attained by the dispersion of the AT clay into PI films. This effect could be due to nanometer lever dispersion of AT in the matrix. From Figure 4 it can be seen that dispersion of AT in PI films is at the nanometer level. However, on the contrary, when the addition of AT exceeds 5 wt.-%, AT destroys the mechanical properties of PI. This is attributed to agglomeration of AT in PI matrix, as can be seen in Figure 3(c). Comparing tribological properties and mechanical properties of the PI hybrids, it appears that the hybrids with the best mechanical properties do not correspond to those with the best friction and wear behaviors. Thus we further investigate the wear mechanisms of the PI/AT hybrid materials from worn surfaces and debris.

**SEM Analysis of Worn Surfaces**

The SEM micrographs of the worn surfaces of pure PI and its hybrid materials under experimental conditions are shown in Figure 9. It can be seen that the wear width of the hybrid containing 3 wt.-% AT (217 μm) is much smaller in comparison with that of pristine PI (388 μm). On the contrary, the wear width of the hybrid including 7 wt.-% AT (391 μm) is a little bigger than that of pure PI. This demonstrates that AT filled to PI polymer obviously can improve wear resistance of PI at a low content of AT. However, excessive AT in PI matrix will destroy the tribological properties of PI. In addition, we also can see in Figure 9 that the worn surface of pure PI is relatively smoother than the hybrids and shows signs of light adhesion and abrasive wear. However, the worn surface of the hybrids is rougher compared to neat PI and the scuffing, ploughing and plastic deformation on the worn surface of the hybrids is severer to some extent compared to PI matrix. It indicates that the type of wear changes from adhesive wear of pure PI into abrasive wear of the PI hybrids with AT. Moreover, there are fracture evidences on the worn surface of the hybrid containing 7 wt.-% AT. These behaviors could be attributed to a low content of AT which can be fully dispersed into nanometer particles and leads to strengthen interactive force between PI polymer and AT particles. Accordingly, the wear rate of the hybrids decreases greatly in contrast with that of pure PI. However, an excessive AT content in PI matrix will result in the aggregation of AT particles. This decreases the interactive forces between the PI polymer and the AT particles, so the wear of the hybrids obviously increases.
Analysis of Debris

Debris is a product of frictional experiments, and therefore its analysis is helpful for comprehending friction and wear mechanisms. In this work, SEM is also used for the analysis of debris. SEM micrographs of debris of pure PI and its hybrid materials are given in Figure 10. Figure 10 shows that both debris of pure PI and its hybrid materials consist of flakes. However, debris of the PI composite is considerably smaller than that of pure PI. With increasing AT content, the size of debris decreases from about 100 to 10 μm. From this it can be deduced that the incorporation of AT contributes to prevent the formation of bigger debris. However, from Figure 7 it may be seen that the hybrids with the smallest debris do not have the lowest wear rate. A comparison of Figure 9 and Figure 10 suggests that abrasive wear is a dominating wear form at high AT content.

An FT-IR spectrum is given in Figure 11. It can be seen that the peak position of debris of pure PI at 1 375 cm$^{-1}$ is apparently different from that of the PI matrix. This can indicate that the imide bond was broken during the frictional process and a carboxylic salt was formed. This process is as follows:

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This shows on the one hand that the chemical reaction of pure PI occurred during the friction process. On the other hand this behavior also discloses that the interactive force between pure PI and the counterpart steel ball is strong. Accordingly it can be deduced that the type of wear of pure PI is mainly adhesive wear. This analysis is consistent with above shown SEM analysis of worn surfaces. However, the peak positions of debris of the hybrid containing 3 wt.-% AT are almost the same as those of the PI matrix. This implies that the chemical reaction of the hybrids did not occur during the friction process and also reveals that the interactive force between the hybrids and the counterpart steel ball is weak and illustrates that the type of wear is not adhesive wear. From Figure 9(c) it can be seen that the type of wear of the PI hybrids is mostly abrasive wear.
Conclusion

(1) The particle size of AT in the hybrid containing 5 wt.-% AT is about 10–100 nm in diameter and 100–1 000 nm in length.

(2) The friction coefficient and wear rate of the PI hybrids first decreases and then increases with increasing content of AT. The wear rate of the hybrid containing 3 wt.-% AT is more than 6 times lower than that of pure PI.

(3) Tensile tests on the PI hybrids show that the strength and the toughness of PI/AT hybrid materials are improved simultaneously when the content of AT is below 5 wt.-%.

(4) SEM examination of worn surfaces shows that the type of wear changed from adhesive wear of pure PI into abrasive wear of the PI hybrids with adding AT to PI matrix.

(5) Debris analysis suggests that AT as a filler inside the PI matrix could restrain the formation of bigger debris; during the friction process a chemical reaction of pure PI occurs but not of the hybrids.

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