Effect of grafted polytetrafluoroethylene nanoparticles on the mechanical and tribological performances of phenol resin

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1. Introduction

Phenol resins (PF), notwithstanding the century-long history, are still attracting a great deal of research interests. They are important technical materials and irreplaceable in many fields, especially in thermal insulation, coating, aeronautic utilities, electro-optical devices and composite materials due to their thermal stability, high char yield, structural integrity, and solvent resistance. Phenol resin-based friction materials usually contain a large number of reinforcing and filling constituents such as reinforcing fibers, abrasives, binders, fillers, and friction modifiers (solid lubricants) [1–6]. This accounts for the great dependence of their properties on the interactions and synergetic effects among the multiphase ingredients. In this sense, it is very important to correctly select and properly combine the different components so as to satisfy a number of requirements for the properties of the friction materials, such as good wear resistance, stable friction coefficient, and reliable strength at a wide range of rigorous conditions.

In recent years, there have been considerable interests in nanoparticles on account of their distinct advantages over microcomposites because that the performance improvement is often acquired at relatively low concentration of the nano-fillers [7]. Many researchers have found that a great variety of nano-inorganic reinforcements, such as metal oxidation nanoparticles, silicon compounds, carbon nanotubes (CNTs) and some other nanoparticles [8–19] could largely improve the tribological properties of polymers as well as the mechanical properties. Li et al. [8] investigated the tribological characteristics of polytetrafluoroethylene (PTFE) composites filled with zinc oxide (ZnO) nanoparticles and found that the anti-wear property of the polymer could be improved without deterioration of the friction coefficient. Goyal et al. [9] reported that the microhardness and dynamic mechanical properties of nano-alumina (Al2O3)/polyetheretherketone (PEEK) composites increased with the increasing content of Al2O3. An increase in the friction coefficient and the lowest wear rate were observed under specific conditions. Wang et al. [10,11] incorporated silicon nitride (Si3N4) and silica (SiO2) nanoparticles into PEEK and indicated that the composites exhibited much lower wear rates and friction coefficients than the neat PEEK. Moreover, a thin, uniform and tenacious transfer film was formed on the surface of the counterpart. Lai et al. [12] studied the effect of SiO2 size on the friction and wear behaviors of polyimide (PI)/SiO2 hybrids by sol–gel processing and found that the friction coefficient and wear rate of the PI hybrids firstly decreased and then increased with the increasing size of SiO2. By introducing small amounts of CNTs, the mechanical properties, electrical properties and the tribological properties of composite materials can be improved tremendously [13–19]. However, few reports have been available on the tribological behaviors of organic nanoparticles modified polymers.

It is well known that nanoparticles tend to agglomerate due to their large surface area and high surface energy. It has been extensively reported that nanometer particles were very difficult to disperse into polymer matrix by mechanic dispersive mixing due to the agglomeration of nanoparticles and high viscosity of polymer.
Thereby, it is very important to select a proper preparation method by which nanoparticles can be well dispersed into polymer matrix in order to study their small size effect in tribomaterials.

The objective of this paper was to study the effect of organic nanoparticles (nano-PTFE) on the tribological properties of reinforced PF composites. Nano-PTFE was modified by irradiation grafting acrylic acid for better dispersion in the composites. The nano-PTFE reinforced PF composites were synthesized by means of in situ polymerization. According to this method, monomers can penetrate into the agglomerated nanoparticles easily due to the small molecular chain and react with the activated sites inside and outside the agglomerates [20,21]. The molecular chains could grow larger and the nano-PTFE particles would be better dispersed in polymer matrix.

2. Experimental details

2.1. Materials

Phenol (analytical reagent grade) was purchased from Shanghai LingFeng chemical reagent Co., Ltd. Formaldehyde (analytical reagent grade) was supplied by Sinopharm Group Chemical Reagent Co., Ltd. Ammonia water (analytical reagent grade) was provided by Shanghai Jufeng Chemical Technology Co., Ltd. Ethanol (analytical reagent grade) was purchased from Shanghai First Chemical Factory. Actone (analytical reagent grade) was obtained from Shanghai Dahe Chemical Co., Ltd. Nano-PTFE was supplied by Shanghai Institute of Applied Physics, Chinese Academy of Science. All the reagents were used without further purification.

2.2. Synthesis of PF and PTFE/PF nanocomposites

Appropriate amount of phenol and ammonia water were put into a three neck flask heated in oil bath and stirred under reflux, and then the formaldehyde was added in batches to the mixed solution. The temperature was maintained around 70 °C until the solution became obviously stratified and hard to stir, the water was removed as well as phenol under 0.6 MPa vacuum. The products were kept in vacuum oven for 24 h at the temperature of 50 °C before ground into powder. The nanoparticles were added after the reaction carrying out for about 90 min.

2.3. Preparation of the friction specimen

The dried PF or PF nanocomposite powder, for hot compressing process, was put into a metal mould and pressed under the pressure of 10 MPa, then degassed. Typical multi-stage schedule was employed including 15 min resident time at 120 °C, followed by a relatively rapid temperature rise to 170 °C, being maintained for 0.5 h under 20 MPa, and an unloading as soon as the temperature dropped to 110 °C. For friction measurement, the specimens were cut and ground to the size of 6 mm × 7 mm × 30 mm.

2.4. Friction and wear test

The tribological tests were conducted on an M-2000 friction and wear tester. The contact schematic diagram of the frictional couple is shown in Fig. 1.

During the tests, the friction coefficient was calculated from the friction force torque according to the following equation:

\[ \mu = \frac{M}{W \times r} \]  

(2.1)

where \( \mu \) is the friction coefficient, \( M \) the friction force torque (N mm), \( W \) the load (N), \( r \) the radius of the steel ring (mm). Sliding was performed under ambient conditions over a period of 120 min at a sliding speed of 0.42 m/s. The ambient temperature was 20 ± 3 °C and the relative humidity was 35 ± 5%. Before each test, the surface was polished with abrasive paper to Ra 0.17–0.23 μm for the specimen and Ra 0.09–0.11 μm for the counterpart. Then the counterpart ring and the PF or its composite blocks were cleaned with acetone followed by drying. At the end of each test, the width of the wear scar was measured with a measuring microscope, and the wear volume \( V \) of the specimen was calculated from the following equation:

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

(2.2)

where \( V \) is the wear volume (mm³), \( B \) the width of the specimen (mm), \( r \) the radius of the counterpart ring (mm), and \( b \) the width of the wear scar (mm). The wear rate \( K \) of the specimen was calculated from the following equation:

\[ K = \frac{V}{F} \]  

(2.3)

where \( K \) is the wear rate (10⁻⁶ mm³/N × m), \( V \) the wear volume (mm³), \( P \) the applied load (N) and \( L \) the sliding distance (m). In this study, three replicates of friction and wear tests were carried out to minimize data scattering, and the average was reported in this work (GB/T 3960-1983).

2.5. Analysis methods

The PTFE nanoparticles were characterized by an Atomic Force Microscope (AFM, Nanoscope IV, Veeco, USA). The specimen was prepared as follows: a small amount of nano-PTFE was mixed with 200 ml ethanol before treated in an ultrasonic bath for 3 h. A droplet of such solution was spotted onto the mica for the analysis.

The differences between nano-PTFE and grafted PTFE nanoparticles were analyzed by a Fourier Transform Infrared Spectroscopy (FTIR, NEXUS-470, Thermo Nicolet, USA).

The flexural strength and Rockwell hardness of the specimens were tested by an universal electronic testing machine (CMT-4104, Shenzhen Sans Material Testing Co. Ltd. China) and Rockwell hardness tester (XHK-150, Shanghai Material Testing Machine Co.), respectively. The average value of five replicated measurements was adopted as the final result.

To investigate the wear mechanism, the worn surfaces and debris of the specimen were sprayed with a thin layer of gold and then examined by a scanning electron microscopy (SEM, 5136MM, TESCAN s.r.o., Czech). The transfer films formed on the surface of
the counterpart ring were characterized by an optical microscopy (OM).

The dispersion of grafted PTFE nanoparticles in PF matrix was analyzed by an S-4800 field emission scanning electron microscopy (FESEM, HITACHI). The specimens were sprayed with a thin layer of gold before the test.

3. Results and discussion

3.1. Characterization of the nanoparticles

Fig. 2 shows a three dimensional atomic force microscopy image of nano-PTFE. It can be seen that the size of PTFE particles is about 20–80 nm.

Fig. 3 shows FTIR spectra of untreated-PTFE nanoparticles and acrylic acid grafted nano-PTFE. It can be found that several special peaks on the spectrum of acrylic acid grafted PTFE nanoparticles appear, compared with that of untreated PTFE nanoparticles. The band at about 1450 cm\(^{-1}\) belongs to the stretching mode of methyl group. The band at 1650 cm\(^{-1}\) is clearly assigned to the stretching mode of carboxyl groups, indicating the presence of COOH on the surfaces of PTFE. The band in 2800–2900 cm\(^{-1}\) region is attributed to C–H stretching. In addition, the broad shoulder in the 3200–3600 cm\(^{-1}\) region suggests the presence of hydroxyl groups and this region also appears on the spectrum of pure PTFE nanoparticles, which is attribute to the traces of water in the KBr pellet used for the analysis which is inaccessible to be fully removed.

3.2. The mechanical properties of PF composites

Fig. 4 shows the dependence of flexural strength and Rockwell hardness of modified nano-PTFE reinforced PF composites on PTFE content. It can be seen that the incorporation of modified nano-PTFE significantly enhances the flexural strength of PF composites.
and the highest flexural strength is obtained at the PTFE content of 1.8 wt%. It is also found that the composite with higher content (above 1.8 wt%) of nano-PTFE exhibits poor flexural strength. The results indicate that the modified nano-PTFE particles have good interfacial adhesion with PF matrix, which may due to the concentration and functional group of PTFE nanoparticles what we will discuss below.

In general, surface hardness is one of the most important factors that govern the wear resistance of materials. Harder surface would have higher wear resistance. Fig. 4 shows Rockwell hardness of the specimens. The addition of modified nano-PTFE increases the hardness of PF composites and the composite with 3 wt% nano-PTFE shows the highest value.

3.3. Friction and wear properties

The friction coefficient and wear rate of grafted nano-PTFE reinforced PF composites were investigated under a load of 200 N, a sliding velocity of 0.42 m/s and dry conditions. Fig. 5 shows the dependence of friction coefficient of nano-PTFE reinforced PF composites on PTFE content.

Compared with the pure PF, the friction coefficients of the grafted nano-PTFE reinforced PF composites decreases with the increasing of nanoparticles content and the friction coefficient reaches the minimum value at the nano-PTFE content of 5 wt%.

Fig. 6 shows the dependence of wear rate of grafted nano-PTFE reinforced PF composites on PTFE content. It can be seen that the incorporation of nano-PTFE can reduce the wear rate of PF. It is also found that PF composite reinforced by 1.8 wt% grafted nano-PTFE exhibits the best anti-wear property. When the content of grafted

![Fig. 5. Dependence of the friction coefficient on the content of grafted PTFE nanoparticles of PF composites.](image)

![Fig. 7. FTIR spectra of pristine-PF (a), grafted PTFE modified PF (b).](image)

![Fig. 6. Dependence of the wear rate on the content of grafted PTFE nanoparticles of PF composites.](image)

![Fig. 8. The FESEM morphologies of the PF nanocomposites (magnification: 50,000).](image)
Fig. 9. The SEM morphologies of the worn surfaces of PF and PF nanocomposites (magnification: 400; load: 200 N; sliding velocity: 0.42 m/s; test duration: 120 min).
Fig. 10. Optical micrographs of the transfer films formed on the surface of counterpart ring (magnification: 200; load: 200 N; sliding velocity: 0.42 m/s; test duration: 120 min).
Fig. 11. The SEM morphologies of the wear debris of PF and PF nanocomposites (magnification: 1000; load: 200 N; sliding velocity: 0.42 m/s; test duration: 120 min).
nano-PTFE exceeds 1.8 wt%, the wear rate of PF nanocomposites increases with the increasing content of nano-PTFE.

3.4. Discussion

It is known that the tribological property of a composite is dependent on the property of matrix and reinforcement as well as the interfacial adhesion between the matrix and reinforcement [22, 23]. PTFE has good self-lubrication properties and shows an unusual ability in reducing the friction and wear of the polymers. For the nanocomposites made up of grafted nano-PTFE particles and PF, the PTFE in the matrix near the surface is exposed and acts as the lubricating thin film on the worn surface. This will produce a smoother worn surface and reduce the friction and wear rate of the PF composites. In the case of the composites present in this paper, the interfacial adhesion of the composites has close relationship with the concentration and functional group of PTFE nanoparticles. The molecular structure of the grafted nano-PTFE is rich in carboxyl group, while PF rich in hydroxyl group, both of which can form ester or hydroxyl bond (Fig. 7), that results in better interfacial adhesion and makes nano-PTFE disperse in the PF more evenly, which gives full play to PTFE in improving the tribological performance of the PF composites. However, the agglomerations are inevitable when the content of PTFE exceeds to a certain value (Fig. 8).

Fig. 7 shows FTIR spectra of pristine PF and acrylic acid grafted PTFE nanoparticles modified PF. Compared with the pure PF (Fig. 7a), it is hard to distinguish the absorption of –CO–O– and –O–CH– stretching from benzyl hydroxy –C–O– and pheno-lic –C–O– stretching at the band of 1000 cm⁻¹ and 1240 cm⁻¹. But the band at 1700 cm⁻¹ is clearly assigned to the stretching mode of carboxyl groups, which indicates the presence of ester.

Fig. 8 shows the FESEM images of PF nanocomposites. As seen in Fig. 8a, the image of PF modified with 1.8 wt% grafted PTFE nanoparticles identifies the presence of some individual nano-PTFE embedded within the PF matrix. In contrast, poor dispersion of 5 wt% grafted nano-PTFE in the PF composites can be observed in Fig. 8b, especially the aggregation shown in the red circle labeled. This implies that proper amount of grafted nano-PTFE can be well separated in PF matrix.

To make clear the tribological mechanisms of grafted nano-PTFE reinforced PF, the morphologies of the worn surfaces and debris of the nanocomposites blocks were observed by a scanning electron microscope and transfer films formed on the surface of the counterpart ring were investigated by an optical microscopy. The SEM images of the worn surfaces of PF and PF nanocomposites are shown in Fig. 9. The worn surface of pure PF (Fig. 9a) is rough, displaying holes and ploughed marks, indicating fatigue and abrasive wear. Since PF is somewhat brittle, it should crack and break away easily from the surface of the specimen and form brittle cleavage fracture surfaces. The fragments can generate the third body friction, which leads to higher friction and wear rate. By contrast, the scuffing on the worn surfaces of the PF nanocomposites decreases with the increasing content of nanoparticles, and relatively smooth surfaces can be observed (Fig. 9b–d). However, the worn surfaces of composites with higher content of nanoparticles show holes and ploughed marks, indicating the fatigue and adhesive wear (Fig. 9e–i). It may be attributed to the agglomeration of particles at higher fractions.

Fig. 10 presents the optical micrographs of the transfer films formed on the surface of the counterpart ring. It can be seen that the transfer film on the worn surface of the counterpart ring sliding against the unfilled PF composite is rough and sparse (Fig. 10a), which corresponds to the poor wear-resistance of the pure PF composite. Similarly, the transfer films formed from 0.1 wt% to 1 wt% nano-PTFE filled PF composite are rough and many plucked scars appear on the counterpart ring surface (Fig. 10b and c). Contrary to the above, the transfer film formed from 1.8 wt% nano-PTFE filled PF composite is comparatively thin, uniform and continuous while slightly plucked scars appear on the counterpart surface (Fig. 10d), which conforms to the best wear-resistance of the 1.8 wt% nano-PTFE filled PF composite. The transfer films formed from 3 wt% to 5 wt% nano-PTFE filled PF composite are thicker but uniform with few signs of scuffing (Fig. 10e and f), which agree to the increasing of wear rate of the nano-PTFE-filled PF composite.

Debris is a product of friction experiments, and it is helpful to comprehend the friction and wear mechanisms. Fig. 11 shows the morphologies of debris of the nanocomposites. Debris of the PF nanocomposites is considerably smaller than that of pure PF. When the content of nanoparticles is less than 1.8 wt%, the size of debris of PF composites decreases with the increasing content of nanoparticles, however, the debris size of the hybrid materials increase when the content of nanoparticulate exceeds 1.8 wt%. Considering the wear rate, the size of the debris agrees well with the wear resistance of nano-PTFE reinforced PF.

In this work, FTIR, FESEM, SEM and OM were applied to analyze the tribological mechanism. As stated above, the grafted nano-PTFE in the matrix near the surface acts as the lubricating thin film on the worn surface, then the good dispersion of nano-PTFE in the PF matrix (Fig. 8a) means that the component of the lubricating thin film is uniform (Figs. 9d and 10d), obviously, a uniform film is good for improving the wear resistance of the composite. That can interpret the reason why there exists a threshold (1.8 wt%) of the concentration of nano-PTFE in the matrix (Fig. 6) for the wear loss rate of composites, when the concentration of nano-PTFE in the matrix is bigger than the threshold, the wear loss rate of composites does not continuously decrease with the increase of the concentration of nano-PTFE in the matrix because bigger concentration of nano-PTFE in the matrix tends to lead a poorer dispersion of nano-PTFE in the PF matrix, as shown in Fig. 8b.

4. Conclusion

Nano-PTFE reinforced phenol resin (PF) composites were prepared by in situ polymerization method and mixed with different fractions of nano-PTFE. The tribological properties of PF composites were investigated by a block-on-ring friction and wear tester. The friction and wear mechanism was discussed by analyzing the worn surface, wear debris and transfer films. Main conclusions can be drawn as follows:

(1) The addition of modified nano-PTFE increases the mechanical properties of PF nanocomposites. The highest flexural strength is obtained at the nano-PTFE content of 1.8 wt%, while the highest Rockwell hardness at 3 wt%.

(2) The incorporation of nanometer PTFE into PF leads to a significant improvement on the tribological properties. The friction coefficient of nanocomposites reduces to 0.175 when the content of grafted PTFE nanoparticles reached 5 wt%. In other words, the friction coefficient decreases about 34%. The wear rate of nanocomposites considerably decreases with the increasing of nano-PTFE content until it reaches 1.8 wt%. When the content of nano-PTFE exceeds 1.8 wt%, the wear rate exhibits a gentle increase with the increasing content of the nano-PTFE.

(3) The interfacial interaction between the grafted PTFE nanoparticles and PF matrix increases through chemical bonding, representing an attractive route to give full play to PTFE in improving the tribological performance of the PF composites. The transfer films affect tribological properties of the nano-PTFE reinforced PF composites and a continuously thinner transfer film leads to a lower wear rate.
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References