

Influence of the Dispersion of Nano Titanium Dioxide on the Tribological Performance of Fabric Self-Lubricating Liner

Xiaowen Qi,¹ Zhining Jia,² Yulin Yang¹

¹College of Mechanical Engineering, Yanshan University, Qinhuangdao 066004, People's Republic of China

²Chengde Petroleum College, Chengde 067000, People's Republic of China

Correspondence to: Z. Jia (E-mail: ysuja@163.com)

ABSTRACT: Nanoparticles with unique properties have been widely used in various fields. The tribological performance of the fabric self-lubricating liner, which is used as the main component of spherical plain bearings, directly affects the bearing service life. The purpose of this study was to prepare a self-lubricating liner enhanced with nano titanium dioxide (nano-TiO₂) by dispersion technology. The effects of several factors on the dispersion of nano-TiO₂ were studied in detail. The effects of the dispersion of nano-TiO₂ on the tribological properties of a self-lubricating liner were analyzed comparatively. The best dispersing conditions were determined through experiments and statistical characterization. From the results of the tribological tests, the fabric self-lubricating liner reinforced with nano-TiO₂ showed better antifriction and wear-resistant properties than that without nanoparticles. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2100–2105, 2013

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INTRODUCTION

The fabric self-lubricating liner, which is finding ever-increasing use in numerous industrial applications, such as spherical plain-bearing materials, especially in aerospace engineering, is a kind of fabric-enhanced polymer-based composite.^{1–3} This is due to their advantages of good strength, low density, and high performance/cost ratio. The tribological properties of the fabric self-lubricating liner have an important effect on the performance of spherical plain bearings. With the development of aviation, the performance requirements of self-lubricating spherical plain bearings are increasingly demanding, so researchers have been asked to improve the performance of the self-lubricating liner.⁴

With the development of nanotechnology, polymer-based composites filled with nanoparticles are being used more and more widely. Some nanoparticles added to the composites can improve their wear properties, reduce their friction coefficients, and improve their mechanical properties. Nanoparticles added to the matrix resin of self-lubricating fabrics have an important influence on the tribological properties of fabric self-lubricating liners.^{5–8} Because nanoparticles have larger specific surface areas and higher surface energies, they are easily aggregated in the process of preparation and application. So, the advantages of the nanoparticles are affected, and the function of the

nanoparticles is lost. Thus, it is necessary to improve the dispersion of nanoparticles in self-lubricating liners.^{9–12}

In this study, the dispersion performance of nano titanium dioxide (nano-TiO₂) in self-lubricating liners was examined by physical and chemical dispersion methods. Meanwhile, the effects of the dispersion on the tribological properties of the self-lubricating liners were evaluated.

EXPERIMENTAL

Dispersion Tests

Nano-TiO₂ particles (with an average particle size ranging from 30 to 50 nm, weight = 0.1 g) were put into a beaker, and then, 30 mL of diluent (ethyl acetate/alcohol = 1 : 1) and dispersant were added. After ultrasonic oscillation and mechanical stirring, the nano-TiO₂ solution was put into a test tube and put in a quiet place to observe sedimentation. Three replicate sedimentation tests were performed to enhance the accuracy of data. Figure 1 shows the schematic diagram of the sedimentation test (test tube diameters = 18 × 180 mm). As shown in the figure, the higher the height of sedimentation was, the worse the dispersion of nanoparticles was.¹³

Preparation of the Self-Lubricating Liner

The well-dispersed nano-TiO₂ solution was put into phenol resin with a volume of 30 mL. Meanwhile, the pretreated polytetrafluoroethylene (PTFE)–aramid fabric (which was dipped in

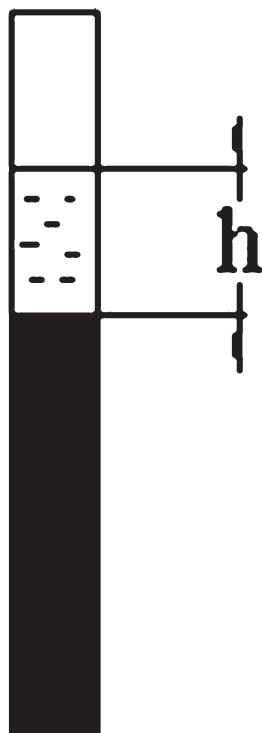


Figure 1. Image of the sedimentation test (h means the height of sedimentation).

acetone for 12 h, boiled in distilled water for 15 min, and then cleaned with alcohol in an ultrasonic generator type DS-1510, frequency = 40 kHz, power = 60 W, Shanghai Shengxi Ultrasonic Instrument Co., Ltd.) was immersed into the mixed phenolic resin. During the mechanical stirring and ultrasonic oscillations, the diluent gradually volatilized. After a certain period of time, the PTFE–aramid fabric was removed from phenolic resin, rolled, and parched at 110°C. Finally, the self-lubricating liner was prepared. In comparison, the average gain with impregnating resin of the fabric reached 30%.

Tribological Tests

Before the tribological tests, the surface of the AISI-1045 steel substrate was polished with 320- and 600-grade waterproof sandpaper to a surface roughness of 0.30–0.45 μm. It was then washed in alcohol for 20 min by an ultrasonic generator and dried in the air. The PTFE–aramid fabric with self-lubricating properties was stuck on the steel surface with a phenolic adhesive resin and cured at 180°C for 2 h under 0.15 MPa of pressure. The friction and wear tests were performed on a block-on-ring wear tester. Figure 2 shows the contact schematic diagram of the friction pair. The widths of the liner and rotating ring were 7 and 10 mm, respectively. The tests were carried out at a linear velocity of 0.942 m/s at room temperature. The load was 1000 N, and the time of the friction and wear test was 180 min. Each experiment was repeated three times to ensure the reliability and accuracy of the data.

RESULTS AND DISCUSSION

Influence of the Ultrasonication Time on the Dispersion

The ultrasonication time is an important factor in the dispersion of nano-TiO₂. Figure 3 illustrates the influence of the

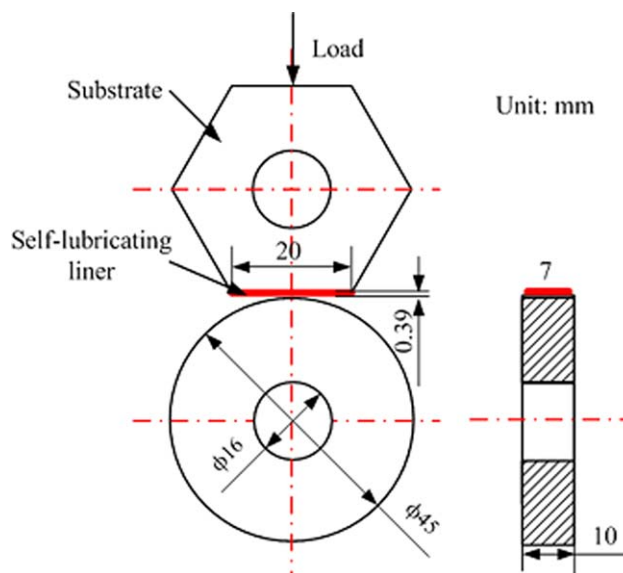


Figure 2. Contact schematic diagram for the friction pair (ϕ means the diameter of specimen). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ultrasonication time on the dispersion of nano-TiO₂. As shown in figure, the dispersion height of nano-TiO₂ in the diluent was different with different ultrasonication times. When the mixture was sonicated for 20 min at high-temperature and high-pressure, a strong shockwave and jet current decreased the probability of the aggregation of nano-TiO₂ because of the effect of ultrasonic cavitation. Therefore, the nanoparticles were well dispersed, and the nanoparticles dispersed evenly in the diluent. Correspondingly, the height of sedimentation was the lowest. When the mixture was sonicated for 10 min, the energy of the ultrasonic oscillations was insufficient to break up the aggregation of the nanoparticles. This caused the nanoparticles to aggregate again, and sedimentation took place soon after the nano-TiO₂ solution was put into the test tube and left in a quiet place. When the mixture was sonicated for 30 min, the temperature of water in the

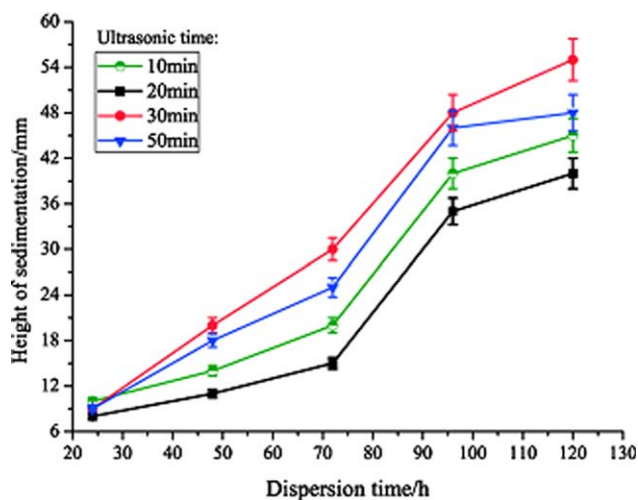


Figure 3. Height of sedimentation with the time of ultrasonic oscillations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

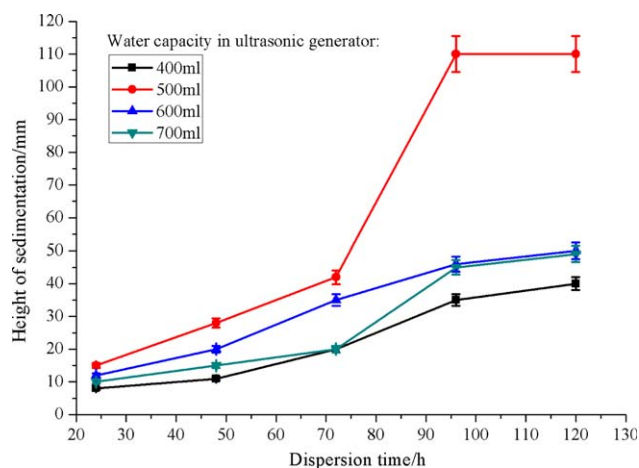


Figure 4. Height of sedimentation with the capacity of water in the ultrasonic cleaners. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ultrasonic generator increased gradually along with an increase in the heat energy; this increased the probability of the aggregation of nanoparticles. Serious aggregation was observed as a result. When the ultrasonication time was extended to 50 min, the effect of aggregation reduced a little because of the effect of cavitation.

Influence of Water Capacity in an Ultrasonic Generator on the Dispersion

The effect of ultrasonic cavitation had an important impact on the dispersion of nano-TiO₂. However, the effects of the ultrasonic wave on the dispersion and aggregation were controlled by the *cavitation threshold*, which is the lowest sound intensity or resonant amplitude for the liquid cavitation. When the ultrasonic cavitation existed in the ultrasonic wave field, the nanoparticles were dispersed by means of drastic mechanical vibration; otherwise, the nanoparticles were aggregated.¹⁴

As shown in Figure 4, when the water capacity was 400 mL (the minimum allowable water capacity of the ultrasonic instrument), the height of sedimentation was the lowest. Therefore, the best effect of dispersion was achieved. A possible reason was that the intensity of the ultrasonic wave reached an optimum value when the capacity of the water was 400 mL.

Influence of the Dispersing Agent Content on the Dispersion

The nanoparticles were dispersed temporarily by methods of physical dispersion, such as ultrasonic oscillations and mechanical stirring. Nevertheless, the nanoparticles aggregated again after the operation stopped. So, the sodium hexametaphosphate was used as a dispersing agent added to solution to obtain an effect of persistent dispersion.

Figure 5 illustrates that the nano-TiO₂ dispersed well when the mass of sodium hexametaphosphate was 1% that of nano-TiO₂. The nano-TiO₂ absorbed opposite ions and formed a double electrode layer. The repulsion potentials between the nanoparticles were enhanced as a result. That is, a good dispersion of nanoparticles was achieved through the Coulomb's forces between the double electrode layers.

Equation (1) shows that $1/k$ was reciprocal with \sqrt{C} , so the double electrode layer became thinner when the density of the

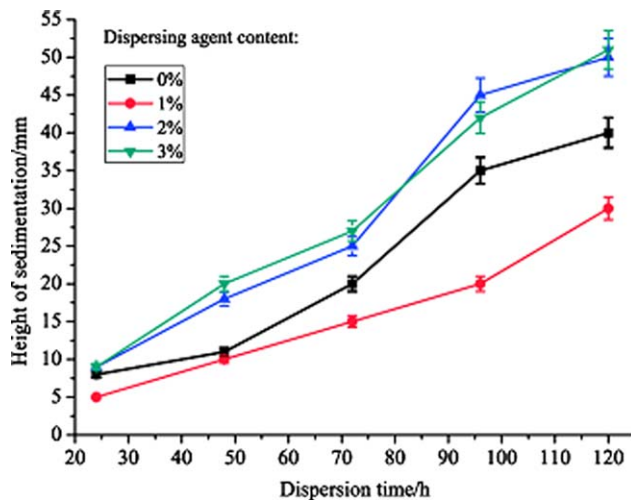


Figure 5. Height of sedimentation with the density of sodium hexametaphosphate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dispersing agent was increased. Then, the nanoparticles seriously aggregated.¹⁵

$$k = [2e^2 N_A C Z^2 / (k_B T \xi)]^{\frac{1}{2}} \quad (1)$$

where ξ is the dielectric constant, e is the electron charge, Z is the atomicity, N_A is Avogadro's constant, C is the molarity of electrolyte, T is the temperature (K), k is the spread extent of double electrode layer, $1/k$ is the thickness of the double electrode layer, and k_B is Boltzmann's constant.

Dispersion of the Nano-TiO₂ in the Fabric

Qualitative Analysis. Figure 6 shows the dispersion status of nano-TiO₂ on the surface and cross section of self-lubricating fabric liner. Figure 6(a) indicates that the nano-TiO₂ dispersed evenly on the surface of phenolic resin at low magnification. Figure 6(b) shows that the grain size of dispersed nano-TiO₂ was about 50 nm. Figure 6(c) presents the cross-sectional topography of the self-lubricating liner. Figure 6(d) indicates the energy dispersive X-ray analysis (EDXA) image of the Ti element on the cross section, where the bright spots represent the Ti element. The shape of the bright spots in Figure 6(d) is anastomotic with the shape of phenolic resin in Figure 6(c); this demonstrates that the nano-TiO₂ was dispersed evenly in the phenolic resin.

Quantitative Analysis. The images in Figure 7 are divided into four parts, and the nanoparticles were counted in each gridding. Obviously, the bigger the standard deviation (a_i) was, the worse the dispersion of the nanoparticles was. This could be calculated from the following equation:¹⁶

$$a_i = \sqrt{\frac{\sum a^2 - N\bar{a}^2}{N}} \quad (2)$$

where a is the number of nanoparticles in each gridding, \bar{a} is the average value of nanoparticles in each gridding, and N is the amount of gridding.

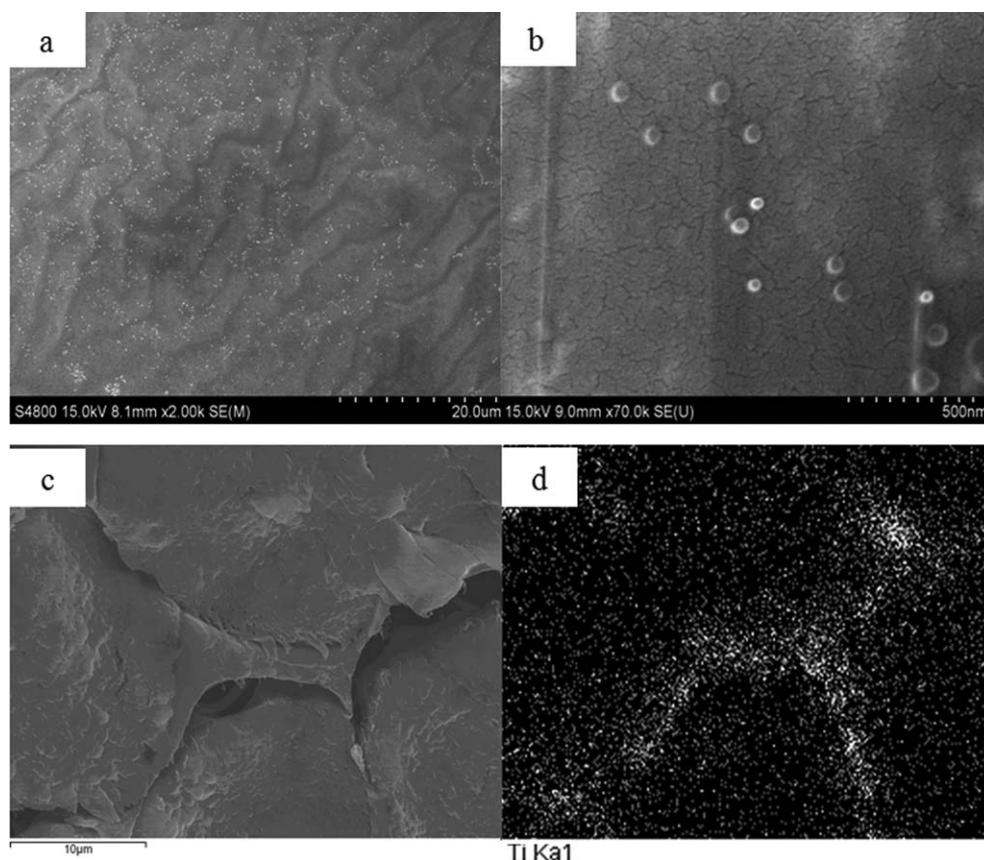


Figure 6. SEM images of the surfaces and cross section of the self-lubricating liner with 1 wt % TiO_2 .

According to eq. (2), the calculated standard deviations of the number of particles were 1.12 [Figure 7(a)], 1.80 [Figure 7(b)], 2.29 [Figure 7(c)], 1.79 [Figure 7(d)], 1.66 [Figure 7(e)], and 2.17 [Figure 7(f)]. From the results, the standard deviations of the six samples were between 1.1 and 2.3 and were maintained in a smaller range; this indicated that the dispersion of TiO_2 was basically uniform.

Contrast Tests of Tribology

Figure 8 shows the friction coefficient curves of the self-lubricating liners without nano- TiO_2 and with undispersed and dispersed nano- TiO_2 . As shown in the figure, the self-lubricating liner with dispersed TiO_2 displayed the best antifriction effect compared with other self-lubricating liners. When the undispersed nano- TiO_2 was added in the self-lubricating liner, the diameter of nano- TiO_2 was bigger. When the aggregation of nanoparticles was severe, this deteriorated the properties of the pure self-lubricating liner. However, when the dispersed nano- TiO_2 were added to the self-lubricating liner, the diameter of nano- TiO_2 was small, and the dispersion of nano- TiO_2 was even, so the nanoparticles could combine with the resin matrix well, and the nanoeffects (reinforcement) of the nanoparticles could play well. Because the load was lower under conditions of high speed and light load, the spherical nano- TiO_2 showed a rolling movement during the process of frictional contact. Slide contact was changed into rolling contact, and the best antifriction effect was obtained.

Figure 9 shows the wear rate curves of the self-lubricating liners without nano- TiO_2 , with undispersed nano- TiO_2 , and dispersed nano- TiO_2 . Among all of the self-lubricating liners, that shown in bar C showed the best wear resistance because the nano- TiO_2 combined well with the resin matrix and the fabrics. However, when the undispersed nano- TiO_2 (directly mixed TiO_2 particles and resin matrix) were added to the self-lubricating liner, the aggregation of nanoparticles was severe; this reduced the bond strength between the resin matrix and fabric, and partial stress concentration was produced. Therefore, the wear rate of B was similar to that of A.

Wear Surface of the Self-Lubricating Liner

Figure 10 illustrates the microstructure surface wear of the self-lubricating liner under the conditions of high speed and light load. Figure 10(a) presents the wear features of the pure fabric. During the process of friction, PTFE, the resin, and abrasive dust were mixed together under the influence of pressure and friction. A great number of microscratches was observed on the wear surface. Figure 10(b) shows the wear features of the fabric contained undispersed nano- TiO_2 . The scratches were also obvious, and the wear-resistant effect was not good. Figure 10(c) shows the wear features of the fabric-contained dispersed nano- TiO_2 . Because of the antifriction and wear-resistant effects of nano- TiO_2 , the PTFE fabric was barely worn and was clear; this showed the self-lubrication action well. To illustrate the tribological properties, the original features of liner are also presented in Figure 10(d).

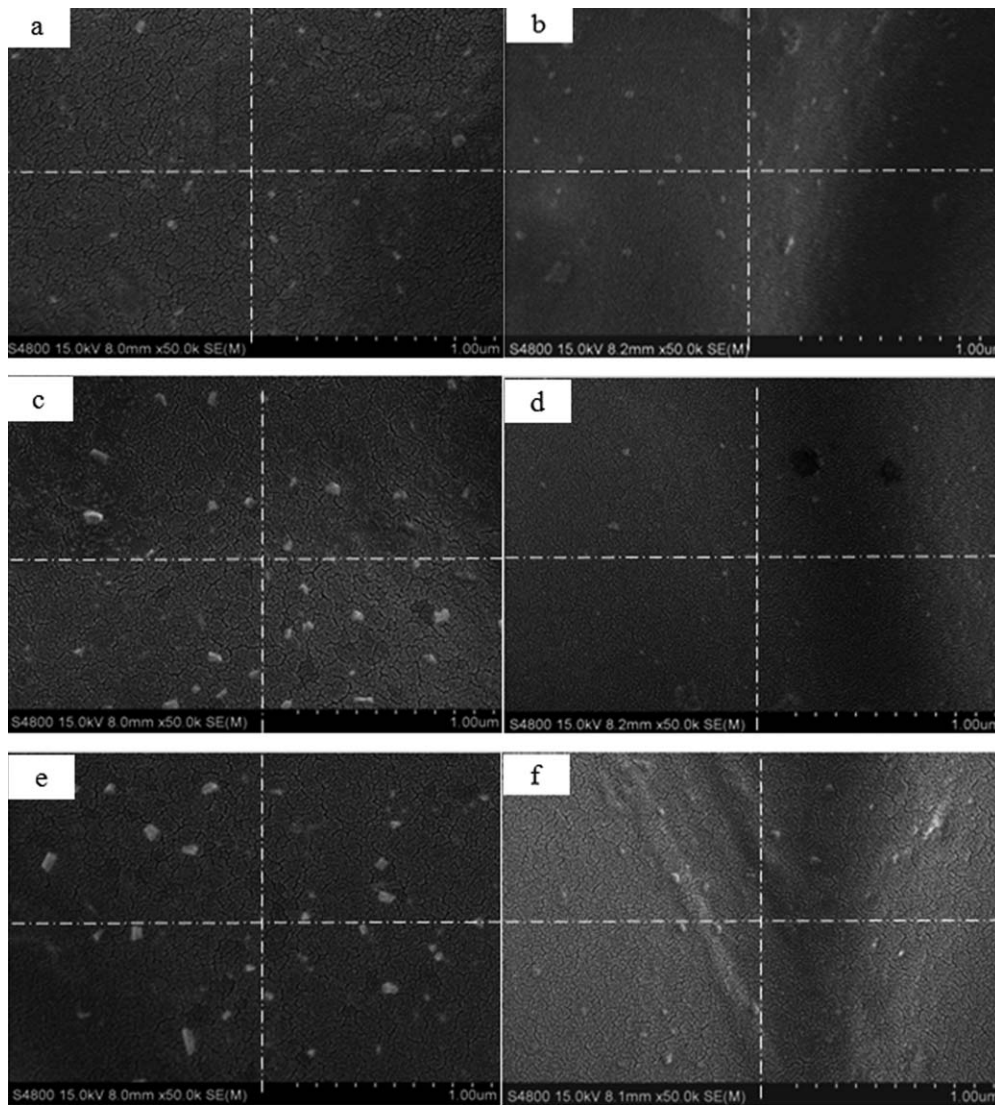


Figure 7. Images of nano-TiO₂ for different positions in the resin.

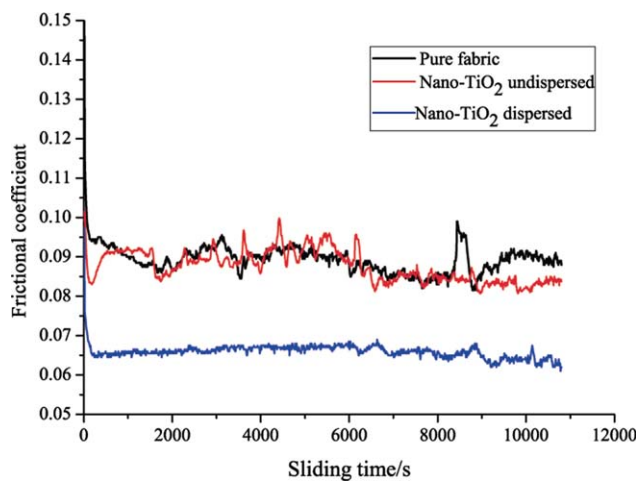


Figure 8. Friction coefficient curve of the self-lubricating liner. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

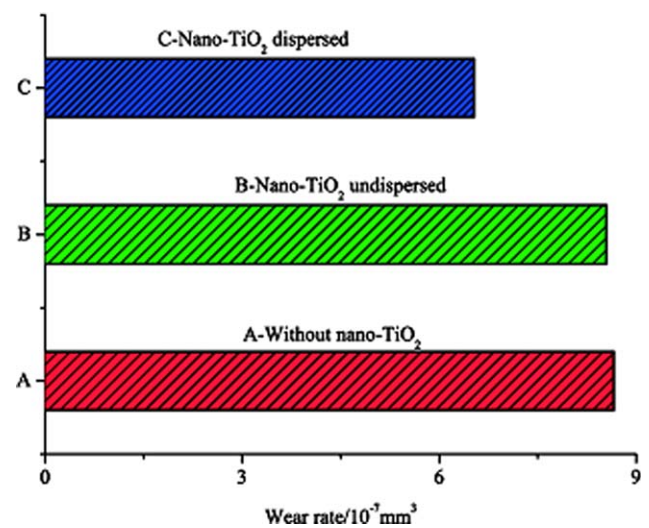


Figure 9. Wear rate curve of the self-lubricating liner. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

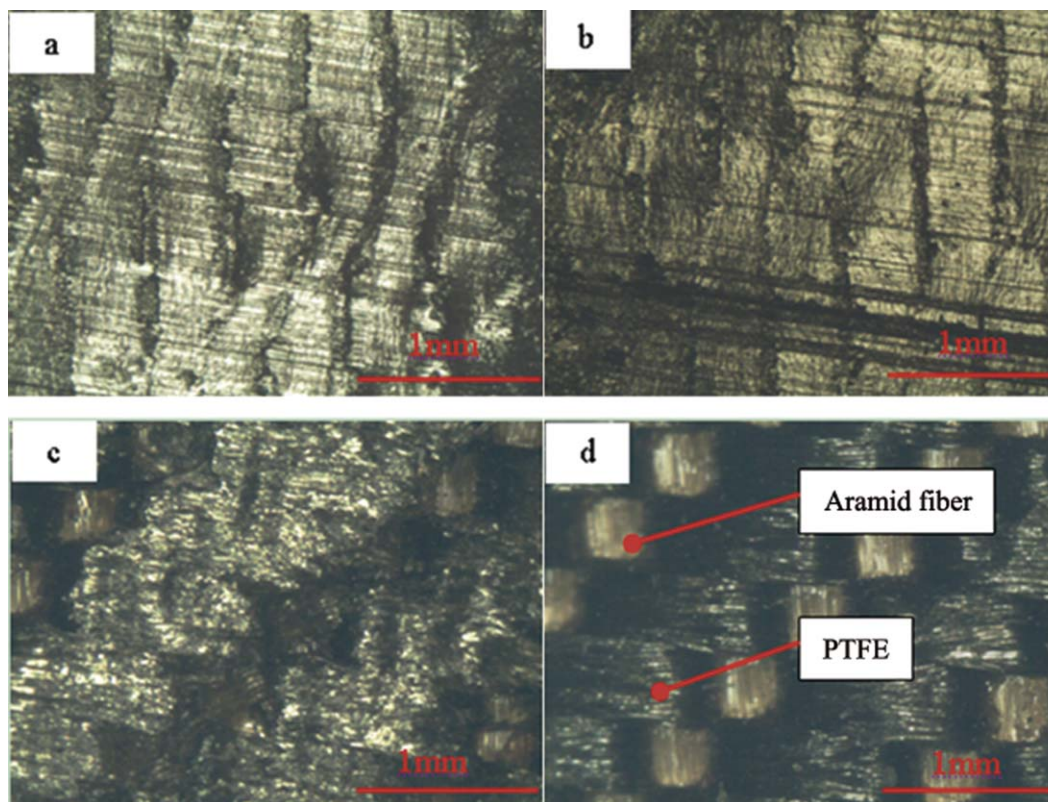


Figure 10. Surface image of the self-lubricating liner under the conditions of high speed and light load. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The dispersion properties of nano-TiO₂ in a diluent of phenolic resin were researched; this prepared for the dispersion of nano-particles in the phenolic resin. The time of ultrasonic oscillation, water capacity in an ultrasonic generator, and quality of the dispersing agent had a great influence on the dispersion of nano-TiO₂. The best dispersion technology was determined under the following conditions: time of ultrasonic oscillation = 20 min, water capacity in the ultrasonic generator = 400 mL, and quality of dispersing agent = 1% nano-TiO₂.

Qualitative and quantitative analysis was used to characterize the dispersion of nano-TiO₂ particles in the self-lubricating liner. The point method was used to analyze the uniformity of the distribution of nanoparticles, and this made the characterization more perfect.

Tribological tests were carried out to evaluate the effect of the dispersion of nano-TiO₂ in the self-lubricating liner on the friction and wear properties. The results show that the self-lubricating liner containing dispersed nano-TiO₂ showed a better tribological performance.

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