

Polymer-Based Self-Lubricating Material

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Received 16 November 1999; accepted 25 July 2000

ABSTRACT: A low-friction coefficient material with color based on proper selection of polar conditions of pigment and liquid lubricant was developed. Bush-type bearings were made from poly oxymethylene reinforced with inorganic fillers, including polar compounds of white carbon and glass powder, and nonpolar compounds of carbon black and graphite. The fillers were coated with different levels of titanate, and with polar lubricants such as cetyl alcohol and palmitic acid, and nonpolar lubricants of motor oil, and paraffin. The frictional properties at constant velocity and at constant loading, and the relationships between materials polarity are discussed. An excellent self-lubricating material of frictional coefficient less than 0.02 was obtained. That is superior to the most current commercial products claiming $\mu = 0.05 \sim 0.06$. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1514–1519, 2001

Key words: polyethylene; oilless bearing; friction coefficient; inorganic powder reinforcement; titanate coating; bush type

INTRODUCTION

Bearing members made from self-lubricating composite materials prepared from polymers have become popular in the friction and lubrication fields, for the advantages of self-lubrication, rust-resistance, light weight, ease of production, low cost, and high compatibility. A significant percentage of conventional metal bearing members have been gradually replaced by self-lubricating material.

There are three categories in the current self-lubricating materials prepared from poly oxymethylene (POM). The first type is POM reinforced with inorganic fillers, such as carbon fibers or glass fibers,^{1–5} providing partial solid contact friction. Although the mechanical strength is increased by the addition of solid lubricants, the

frictional coefficient of the material is also increased. The second type is made by adding solid lubricants, such as metal sulfides, graphite, and polytetrafluoroethylene (PTFE) to the matrix. These solid lubricants reduce the frictional coefficient, although the mechanical strength of the matrix is impaired.^{6–9} The third kind incorporates inorganic fillers and oils.^{10–14} Self-lubricating materials containing either liquid lubricants, such as grease and fillers, or solid lubricants, have also been developed for the manufacture of bearing members. Because of the effect of liquid oils, there is a boundary lubrication on the contact surface, providing a lower value of frictional coefficient. Those products, however, are not completely satisfactory in frictional coefficient and in the capacity of liquid oils, especially at high loading. A black self-lubricating bearing member of POM containing 4 wt % of grease has been claimed to provide a frictional coefficient greater than 0.6.¹⁵ We want to lower that value.

According to tribology, the friction will be reduced if there is enough oil existing between bear-

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Contract grant sponsor: National Science Council.

Journal of Applied Polymer Science, Vol. 80, 1514–1519 (2001)
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ing and counter shaft. We applied the proper selection of polar properties to obtain a high-liquid lubricant content and to avoid the contact of bearing and counter shaft.

Conventional fillers or solid lubricants without any surface treatment, such as graphite or carbon black, are used directly with nonpolar liquid lubricants. They are black in color, and so are the products. Carrying more polar liquid lubricants with nonpolar graphite or carbon black, and even carrying more nonpolar liquid lubricant with hydrophilic white carbon, were not studied in this field before. This experiment is the first achievement to our knowledge.

EXPERIMENTAL

The materials used in this experiment were POM from Asahi Kasei (Osaka) Tenac 5050, glass powder from Potters Industries Inc. (England), white carbon (Cabosil M-5) and motor oil from China Petroleum Co. (Taiwan), graphite, paraffin, palmitic acid, copper palmitic acid, and cetyl alcohol from Hayashi Pure Chemical (Osaka), and titanate (Tyzor TE) from DuPont (Taiwan). Most fillers were pretreated with titanate at levels of 1, 2, and 3 wt %, respectively. The ratios of matrix, filler and liquid lubricant were POM 100:glass powder (10, 20, and 30 wt %), or white carbon (2, 4, and 6 wt %), or carbon black (2, 4, and 6 wt %), or graphite (5, 10, and 15 wt %): liquid lubricant 4 ~ 10 wt %.

Each system was mixed with a Brabender (Duisburg Type 81440, W. Germany) at conditions of 60 rpm and 185°C first to produce a pellet form, and to make an injection molding into a bush bearing of $\phi 50 \times \phi 40 \times 30$ mm at 185 ~ 200°C. All specimens were tested for frictional coefficient and temperature of contacting surface with a radial thrust machine at either: 1. constant velocity and at various levels of loading, or 2. at constant loading and various levels of velocities. The specimens were tested against a H45 steel counter shaft for 20 min at each step, then increasing the velocity or loading step by step until the specimen was destroyed.

RESULTS AND DISCUSSION

The frictional coefficient varies greatly with the conditions of both sliding velocity and loading (Fig. 1). When tested at a constant sliding veloc-

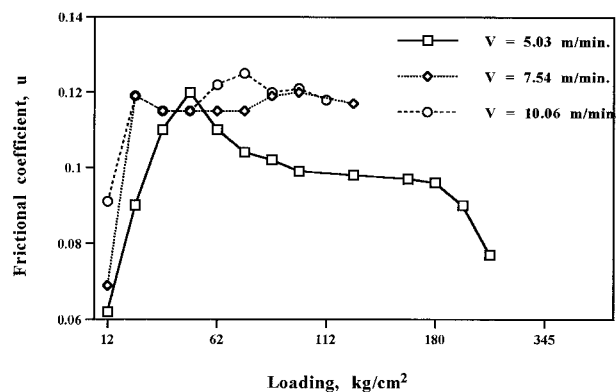


Figure 1 Relationship between frictional coefficient and loading using pure POM under different sliding velocities.

ity, the frictional coefficient was increased with sliding velocity.

All the curves are terminated at the condition when the contact temperature and frictional coefficient are increased abnormally.

The time-temperature and time-load relationships are the main characteristics of the polymer-based material in the friction process. These relationships indicate that metal-polymer contact is sensitive to the shear rate, to the temperature of the surround medium, and to the loading period. The frictional coefficient is a total presentation of the friction feature between two contact bodies.

In addition, the molecular structure of POM is a long linear chain of methylene and oxygen atom. The electronegativity of the oxygen atoms is shielded by hydrogen atoms on the outside. Therefore, the total (apparently) electronegativity of POM is reduced to a value lower than that of normal H atoms next to methylene groups, and then lowering the adhesion strength with the metal surface of the count body (oxide compounds).

Another advantage of POM as a base friction pair compound is the rheological properties of thermal plastics, which deform with friction according to the physico-mechanical properties of polymers depending on the type of stress-strain state. Viscose polymers show experimentally that when the shear rates are not high, elastic and forced elastic strain takes place in the surface layers and aspirates of polymers at certain pressures, leading to brittle fracture on the surface layer of the POM (polymer mechanics). At low loading, these phenomena are accelerated and the frictional coefficient increased with the sliding

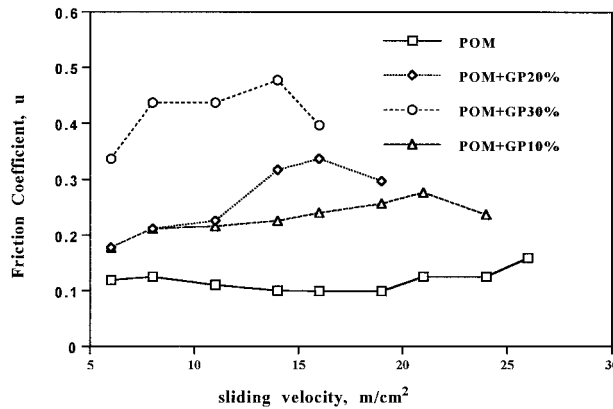


Figure 2 Relationship between frictional coefficient and sliding velocity using composites containing different levels of glass powder; loading of 36.9 kg/cm².

velocity. As the loading increases, the frictional coefficients of all velocities are increased, reaching a maximum value when the effects of sliding velocity become a minor factor because of thermal evolution from the friction surface, breaking of the polymer molecules, etc. At this point, the movement becomes much more viscose, leading to an increase in the frictional coefficient. Most investigators have studied the friction property of materials using steel indentors to test the relationship of loading and frictional coefficients in the range of 10 ~ hundreds of kg/cm² for polymers. Shooter and Taber¹⁶ found that the frictional coefficient depends, to a slight extent, on the load value and is somewhat increased as the load increases.

As the velocity increases, the position of maximum peak of the curve shifts toward lower loads side. The peak height also reduced more quickly at the lower velocity. It is observed that the product of contact pressure and sliding velocity, usually referred to as the PV value, for which a maximum is observed, is almost constant. At the range of maximum frictional coefficient, the corresponding load will be taken for the experimental condition of testing the relationship between frictional coefficient and sliding velocity at constant loading. The reason for this is that the frictional coefficient is calculated from graphic curve recorded by a thrust machine, where the transmission signal of the load cell is too weak to be measured on the recording paper properly, especially for the materials of very low frictional coefficient. To obtain a correct value of frictional coefficient, we selected the loading of first peak at which shows the highest frictional coefficient.

This allows us to assume that the reason for this behavior is an increase in temperature in the friction zone as a result of frictional heating. The poor thermal conductivity of the polymer material makes it easier to accumulate heat and change to a vicious-liquid state at a fine local surface layer after the peak.

The relationships between frictional coefficient and sliding velocity for POM pigmented with different levels of glass powder was found (Fig. 2). Clearly, the pure POM bearing showed the longest working life and the lowest value of frictional coefficient, which was relatively constant for the full range of velocity up to about 27 m/min. After pigmenting with glass powder compounds, the frictional coefficient was increased according to the amount of pigment, thus decreasing the working life of the bearing. It can also be noted that the amount of pigment has an effect on frictional coefficient. The glass powder is a compound of silica and sodium oxide, possessing a high modulus and hardness in comparison with the polymer matrix and counter body. This scratches the body pair's surfaces and causes the increased friction. Another disadvantage of glass powder pigments is that the matrix surface can be damaged by the reinforcement because there is no chemical bonding between them.

The results of the relationship between loading and frictional coefficients at a constant sliding velocity for glass powders treated with titanate compound was obtained (Fig. 3). As expected, the frictional coefficient of each specimen decreased with increasing amounts of titanate up to 2%, above which it then decreased. The best treat-

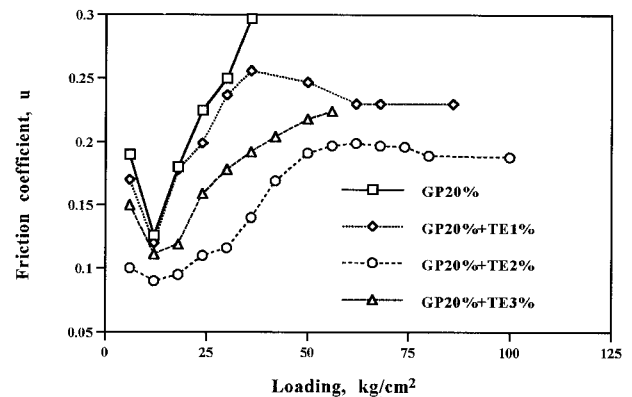


Figure 3 Relationship between friction coefficient and loading using composites containing 20% glass powder treated with/without different amounts of titanate; sliding at velocity of 5.03 m/min.

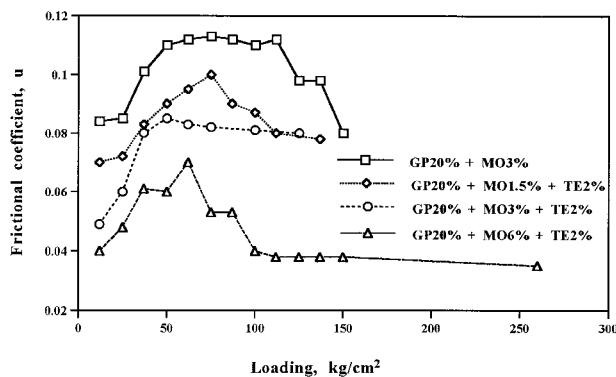


Figure 4 Relationship between friction coefficient and loading using composites containing 20% glass powder treated with/without different amounts of motor oil; sliding at velocity of 10.06 m/min.

ment condition with the lowest value of frictional coefficient is 2% titanate. Because the titanate forms a protection film of organic compound on the surface of glass powder particles, this prohibits the contact of these particles with the surface of the count body. Although the results are poorer than those of pure POM, the frictional coefficient is substantially reduced. Based on these results, we selected a treatment of 2% titanate as an optimum condition for all the processing of pigments.

All of the phenomena of frictional properties discussed previously (Figs. 1–3) belong to solid friction without any liquid lubricant. The POM pigmented with glass powder only can reinforce the mechanical strength of matrix, with no benefit for the frictional properties at all. That is the reason that white carbon or glass powder is never used in self-lubricating bearings. Naturally, the voids of white carbons or glass powders adsorb much water on their surfaces by the hydrophilic properties. Those hydrophilic surfaces could be changed into hydrophobic ones by treatment of titanate molecules. A hydrophobic surface, therefore, could carry much more nonpolar liquids. Motor oil at levels of 1.5, 3, and 6% was introduced into the matrix, together with 20% glass powder, which was pretreated with 2% titanate. The relationship between loading and frictional coefficient at a constant sliding velocity of 10.06 m/min was found (Fig. 4). In addition to the pigment process, treating the inorganic pigments with titanate first and then adding motor oil liquid lubricant before pigmenting, could improve the frictional coefficient of moving bodies substantially. In the contact situation with sliding, motor oil molecules

would be adsorbed much better on the surface of glass powder treated with titanate by van der Waal's force than the case without titanate treatment. Motor oil was held in the matrix by titanate compounds during injection molding, and more liquid lubricants could enhance the smoothness of sliding and reduce the contact of counter bodies, thus reducing the frictional coefficient. In the process of injection molding, most of the oil would be squeezed out in the case of nontitanate coating. Six percent motor oil provided the best friction properties and the longest working life (Fig. 4).

In place of 20% glass powder with motor oil for the bearing composition, 10% graphite with three levels of palmitic acid also were tested, with the graphite treated with and without 2% titanate. Testing at a sliding velocity of 5.03 m/min, the relationships between frictional coefficient and loading were obtained (Fig. 5), indicating results different from the latest one. Their frictional coefficients are very low compared with the former figures, although the amount of lubricant and the role of titanate does not seem to contribute significantly to the frictional property. The frictional coefficient generally decreases greatly in comparison with glass powder pigmented and lubricated with motor oil, although there are two differences in the amount of palmitic acid and in the contribution of titanate. First, the glass powder and palmitic acid are polar compounds, whereas graphite and motor oil are nonpolar ones. Thus, the combined strength of glass powder and titanate is greater than that of graphite and titanate. Therefore, during sliding, the breakdown of film attraction may occur between graphite and titanate because of the weak bonding. Also, the polar

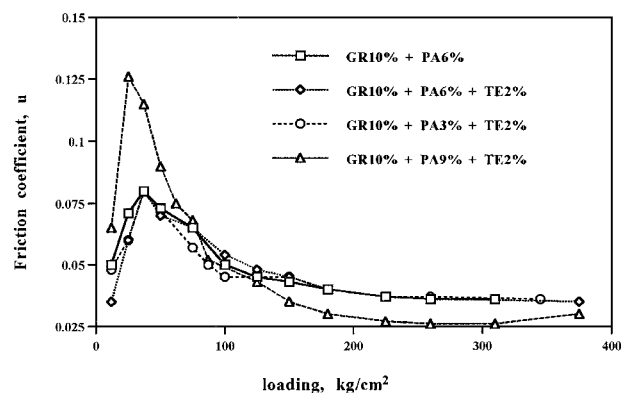


Figure 5 Relationship between friction coefficient and loading using composites containing 10% graphite treated with/without titanate and different amounts of palmitic acid; sliding velocity of 5.03 m/min.

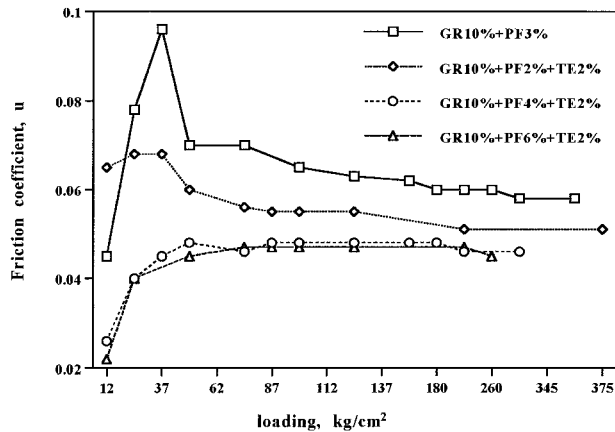


Figure 6 Relationship between friction coefficient and loading using composites containing 10% graphite treated with/without titanate and different amounts of paraffin; sliding at velocity of 5.03 m/min.

ends of titanate adsorb the carboxyl group of palmitic acid to form three components of lubricant, including POM matrix, graphite, and titanate of palmitic acid, that enhance the capability of moving. Second, the palmitic acid is in a solid state below 63°C and forms a liquid at the higher temperatures produced by the loading and frictional heat. Those factors led to the higher content of palmitic acid having higher frictional coefficients at low loading side, even worse than the lower content and without titanate treatment. The larger amount of palmitic acid would cause a lowest friction value at high loading condition, referring to the curves of GR10% + PA6% and GR10% + TE2% + PA9%. The frictional coefficients of this system are as low as 0.025 and the components have a long working life.

The polar property of palmitic acid shows a very different mode in friction condition for the system of graphite and titanate. Replacing the palmitic acid with a nonpolar paraffin in this system, an interesting feature of the relationship between frictional coefficient and loading is obtained (Fig. 6). Even with only 6% paraffin, the frictional coefficient became as low as 0.02 at low loading. The contribution of titanate also increases, as well as the increase of paraffin.

The hydrophilic ends of titanate turn to the outside of graphite, so that the nonpolar paraffin exits between the oxide's surface of steel shaft and matrix and pigments. In that condition, the role of paraffin for lubrication will be effective at high loading.

Another system of white carbon treated with 2% titanate and cetyl alcohol up to 10% was stud-

ied. The resulting relationship between frictional coefficient and loading at constant sliding velocity of 5.03 m/min is similar to the system with graphite, titanate, and palmitic acid (Fig. 7). However, the titanate and liquid lubricant of cetyl alcohol seems to have no advantage from the viewpoint of the order of content amount. Comparing Figure 7 with Figure 3, however, it can be seen that both titanate and cetyl alcohol mixtures have lower friction. Titanate molecules connect solidly to the surface of white carbon at one end and the other ends adsorb the nonpolar end of cetyl alcohol, putting the polar end outside. Some molecules of cetyl alcohol adsorb to the oxide surface of the steel shaft with their polar ends. In that situation, the bearing members moved and were lubricated smoothly showing low coefficient of friction at low loading. With increased loading, the van der Waal's force of hydrogen bonds between steel shaft and bearing clearly appears to increase with loading up to about 130 kg/cm².

An overall comparison of test results was made with bearings, including a commercial product (referred to as standard), WC 4% + TE 2% + PF 9% system, GP 20% + TE 2% + MO 6% system, and GR 10% + TE 2% + PA 6% system (Fig. 8). Their testing conditions maintained at constant loading value of 36.88 kg/cm². This loading value, being the condition shown the highest frictional coefficient of a material, was selected for the convenience of calculation as described previously. The present bearings show excellent operation properties over a long range of sliding velocities. The frictional coefficient of "standard" specimen,

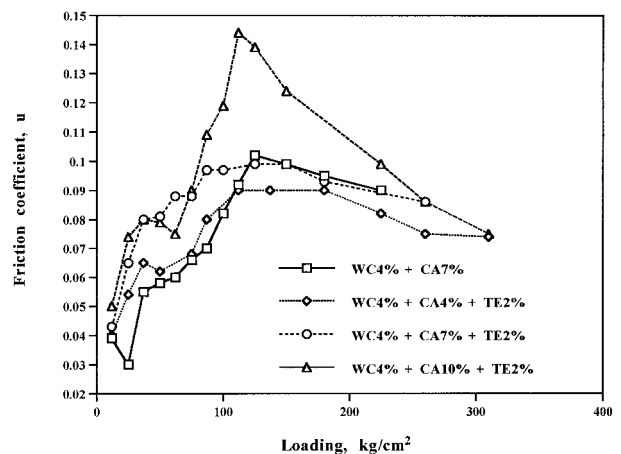


Figure 7 Relationship between friction coefficient and loading using composites of 4% white carbon treated with/without titanate and different amounts of cetyl alcohol; sliding at velocity of 5.03 m/min.

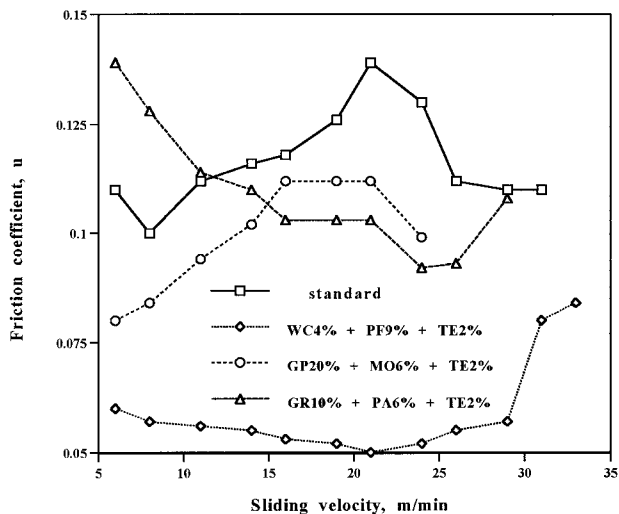


Figure 8 Relationship between friction coefficient and sliding velocity using various kinds of composites; loading of 36.88 kg/cm².

a commercial product, would fall into its claimed range of 0.05 ~ 0.06 at a normal use condition loading other than 36.88 kg/cm². By the results (Fig. 8), the present product (specimen of WC 4% + PE 2% + TE 2%) is about at length half the value of the commercial one.

CONCLUSIONS

A friction coefficient of 0.02 can be obtained, using proper combinations of the polarities of pigment, titanate, and lubricant, even including white carbon, previously considered unsuitable for the re-

inforcement of bearing members. A level of 2% by weight of titanate was the optimum condition. Any color of bearing could be made with the materials proposed by this study.

The authors would like to thank the National Science Council for the financial support of this study.

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