Antiwear and Lubrication Properties of Polyurethane/Polytetrafluoroethylene-Bonded Coating

J. Tian, Y. L. Huang

State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

ABSTRACT: Polytetrafluoroethylene (PTFE) particles were irradiated with ^{60}Co γ-ray to improve their dispersing capacity in polyurethane (PU), which was used as a binder of a PTFE-based bonded solid lubricating coating. The PU/PTFE-bonded solid lubricating coating was prepared on a steel block by spraying and curing at room ambient, and the tribological properties of the PU/PTFE coatings were evaluated on a ring-on-block tester at a speed of 1.25–2.5 m/s and a load of 314–785 N. The wear life of bonded coatings on PTFE volume concentrations, curing humidities and times, coating thickness, and sliding conditions was also investigated. It was found that a 60-μm thickness coating, which has a 40% PTFE volume concentration, cured at 75% relative humidity for 4 days, has a longer wear life of 844 m/μm at 314 N and 1.25 m/s. The PTFE/PU coating was wear-resistant when the load $\times$ speed value was less than 687 Nm/s^{-1}; at same time, the wear life for a thinner coating is sensitive to sliding condition variations. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3454–3459, 2002

Key words: polytetrafluoroethylene (PTFE); polyurethanes; coatings

INTRODUCTION

Bonded solid lubricating coatings are capable of providing solid lubrication.[1] They can provide lubrication in situations where conventional lubricating oils or greases are not applicable. This is why various bonded solid lubricating coatings are finding more and more applications for the lubrication and protection of mechanical parts and devices subjected to working conditions such as vacuums and relatively high or low temperatures.[2–6] In general, polyurethane (PU) coating has excellent wear and corrosion resistance; thus, the friction coefficient of the coating could be reduced by solid lubricants. Polytetrafluoroethylene (PTFE) has been accepted as a good lubricant for its unique structure and characteristics, and much research has been conducted on the application of various organic coatings.[7–16] But the properties of organic coatings are highly dependent on the solid particle volume concentration in the coating.[17] As a matter of fact, most variations in the mechanical, physical, and chemical properties of organic coatings can always be found at a critical volume concentration.[18–21] However, the relationship between the PTFE solid lubricant volume concentration and the tribological properties of PU-bonded solid lubricating coatings is still unknown.

This article deals with the tribological properties, volume concentration of the PTFE solid lubricant in PU coatings related to its curing conditions, coating thickness, and sliding conditions for longer wear life.

EXPERIMENTAL

Materials

Commercial PTFE powder (density 2.2 g/cm^3, provided by Chenguang Research Institute of Chemical Industry of the Ministry of Chemical Industry, Chengdu, China) was irradiated with a 3×10^5-Gy dose of a ^{60}Co γ-ray at a rate of 2.6×10^3 Gy/h to increase its dispersing capacity in the binder.[9,22] Two binders of PU were selected for room-temperature curing. Single-component PU, as one binder, was prepared from poly(methylene)–poly(phenylene isocyanate) (PAPI) with dehydrated castor oil and cured at wet ambient. The ash content and the isocyanate content (NCO) were 50 and 5–8 wt %, respectively. Another binder of PU (PU2k) was from toluene diisocyanates with a prepolyester group and a hydroxyl polyester group and cured at an equal mol ratio between the two groups. The mixed acetone/xylene/cyclohexanone in a volume fraction of 4:2:1 was employed in the present work as a solvent.

Coating preparation

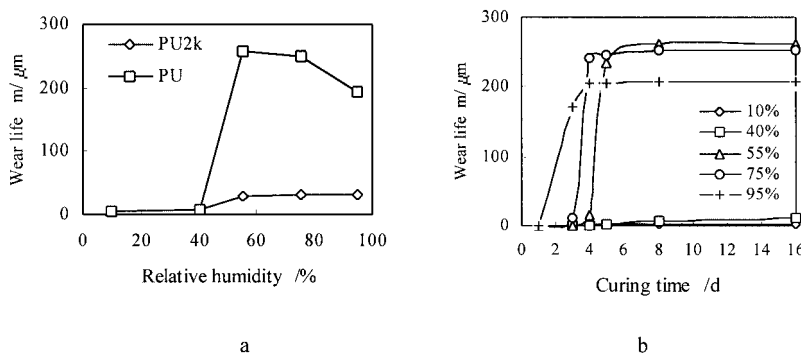The AISI 1045 block was polished with #500, #700, and #900 sandpapers in turn and then cleaned with ace-

Figure 1 (a) Wear life of coatings versus curing humidity and (b) wear life of PTFE/PU coatings versus curing time at different humidities. Load 314 N; speed 1.25 m/s; coating thickness 90 μm; PTFE volume concentration 40%.

tone in an ultrasonic bath for 5 min. The PTFE powder was dispersed in the mixed solvent with ultrasonic stirring for 5 min; then, the binders were mixed into the solvent and each dispersed for 1 min, allowing the formation of coating precursors.

The volume fraction (V_F) of PTFE in the bonded solid lubricant coatings was calculated as follows:

$$V_F = V_{\text{PTFE}}/(V_{\text{PTFE}} + V_{\text{PU}}) = (M_{\text{PTFE}}/\rho_{\text{PTFE}})/(M_{\text{PTFE}}/\rho_{\text{PTFE}} + M_{\text{PU}}/\rho_{\text{PU}}).$$

where V_{PTFE} and V_{PU} refer to volumes of PTFE and PU or PU2k in the coatings, respectively; M_{PTFE} and M_{PU}, to the weights of PTFE and PU or PU2k in the coatings, respectively; and ρ_{PTFE} and ρ_{PU}, to the densities of PTFE and PU or PU2k, respectively.[22] The wet coatings on AISI 1045 steel blocks were prepared by spraying the coating precursors with 0.2 MPa nitrogen gas and curing in a container of relative humidity of 10–95% and temperature of 25°C. The thickness of the wet coatings was controlled by regulating the spraying speed and the composition of nonvolatile constituents in the coating precursors. The thickness of the cured coatings was measured with a MINITEST 1100 microprocessor coating thickness gauge (Elektro–Physik, Koln) which works on the principle that the attractive force between a coating and a magnetic metal is inversely proportional to the distance between them.

Evaluation of the tribological behavior of the coatings

An MHK-500A ring-on-block wear tester (made by the Jinan Testing Machine Factory, China) was used to evaluate the friction and wear behavior of the bonded solid lubricant coatings. An AISI-C-52100 steel ring of 49.2 mm in diameter and 12-mm thick (Hardness Hv 850) was rotated against the PTFE/PU- and PTFE/PU2k-bonded solid lubricant coatings deposited on an AISI 1045 steel block of 12.7 × 12.7 × 19.0 mm, at a

speed of 1.25–2.5 m/s and a load of 314–785 N. The sliding distance was calculated from the product of the sliding speed and the sliding time at the coatings' damage. Then, the wear life of the coatings was calculated after dividing the sliding distance by the corresponding coating thickness in micrometers. Thus, the wear life of the coatings takes a unit of m/μm. All the friction and wear tests were carried out at 20–25°C and a relative humidity of 40–60%, and the data presented in the current work are the averages of three replicate measurements.

Surface analysis

FTIR (10DX Nicolet) measurements were made to identify the functional groups of the coating samples. The surface morphologies of the samples were observed with a JEM-5600LV scanning electron microscope operating at an acceleration potential of 40 kV.

RESULTS AND DISCUSSION

It is well known that the mechanical properties of single-component PU coatings are dependent on the curing conditions. Accordingly, the tribological behaviors of PTFE/PU coatings of 90-μm thickness cured at various humidities and stored for 10 days were evaluated. As shown in Figure 1(a) the wear life of the coatings are short and almost constant below 40% RH. The wear life of PTFE/PU2k slightly increases with increasing humidity, but that of PTFE/PU coatings increases greatly at 55% RH and reaches a maximum value. The variations in the wear life of PTFE/PU coatings with the curing duration at various humidities are shown in Figure 1(b). It is seen that the wear life of coatings cured at humidities of 10 and 40% are below 8.3 m/μm, irrespective of the curing duration. At humidities of 55, 75, and 95%, the wear life of the coatings is closely related to the curing duration, although it comes to a relatively high and stable value at a curing duration of over 4 days. This
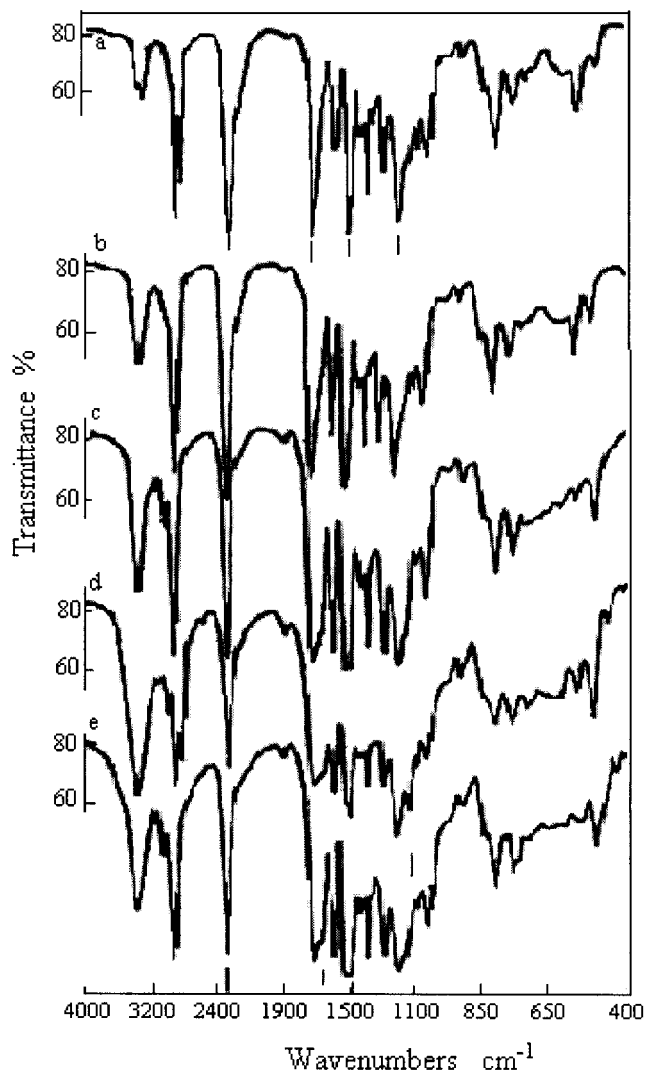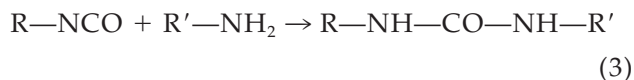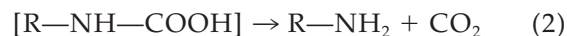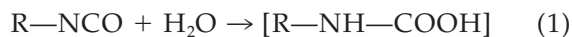
Figure 2 IR spectra of 40-μm PU coatings cured at 25°C: (a) PU binder; (b) 10% humidity after 3 days; (c) 95% humidity after 3 days; (d) 65% humidity after 6 days; (e) 95% humidity after 6 days.

was confirmed by the IR spectra of the coatings cured under various conditions, as shown in Figure 2. The PU coatings of 40-μm thickness were prepared on the clean glass surface by spraying and cured in a designated environment. A small piece of coating was peeled off and pressed with KBr. The peaks at 1525 and 1223 cm^{-1} originate from the different vibrations of the phenyl group, and a peak at the adsorption of 1730 cm^{-1} is the carbonyl (—CO—) group. These peaks of PU binders are single peaks. With increasing curing time, NCO is consumed by the hydroxyl group in humid air. This would be confirmed by the decrease of —NCO— peaks at 2272 cm^{-1} and the appearance of new adsorption peaks at 1730, 1525, and 1223 cm^{-1} (Table I). NCO is consumed greatly when the relative humidity was around 65%, but slightly at 10%. The chemical reactions during the curing process of the coatings can be described as follows:

TABLE I
IR Shifts (σ) of PU-cured Coatings

Function group	Wavenumbers (cm^{-1})	New wavenumbers (cm^{-1})	σ (cm^{-1})
Phenyl	1223	1159	58
Phenyl	1525	1510	22
Carbonyl	1730	1670	60

$$R—NCO + H_2O \rightarrow [R—NH—COOH] \quad (1)$$

$$[R—NH—COOH] \rightarrow R—NH_2 + CO_2 \quad (2)$$

$$R—NCO + R'—NH_2 \rightarrow R—NH—CO—NH—R' \quad (3)$$

Because the curing of PU is strongly dependent on the reaction between the —NCO radical in the binder and the —OH radical originated from H$_2$O in humid air, a certain relative humidity in air is essential for the curing chemical reactions. If the humidity is too high, the reaction on the coating surface would be too quick and an instantly generated cured film would retard the penetration of the —OH radical into the coating and the evaporation of the solvent or CO$_2$ from the coating, and, consequently, the curing reactions of the inner coating would be prohibited. This is the reason why a relative humidity of 95% is not helpful to promote wear life. It is suggested that PTFE/PU coatings should be cured at a humidity of 55–75% and more than 4 days under room temperature. The curing process of PU2k can be illustrated as follows:

$$R—NCO + R'OH \rightarrow R—NH—COOR' \quad (4)$$

Since the equivalent —OH group and —NCO group directly react in the coating, reaction (4) is the dominant reaction therein. Thus, it is likely that the curing process of PU2k could be independent of the —OH from humid air. The relationship between the wear life of the PTFE/PU coatings and the volume concentration is shown in Figure 3. The wear life of the
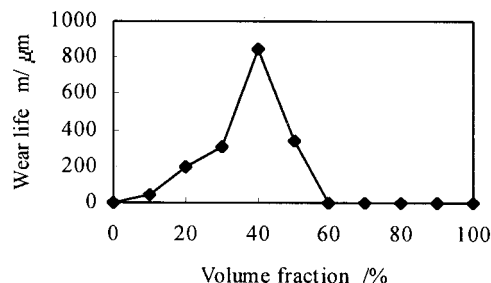

Figure 3 Wear life of PTFE/PU coatings versus PTFE volume concentration. Coating thickness 60 μm; load 314 N; speed 1.25 m/s.
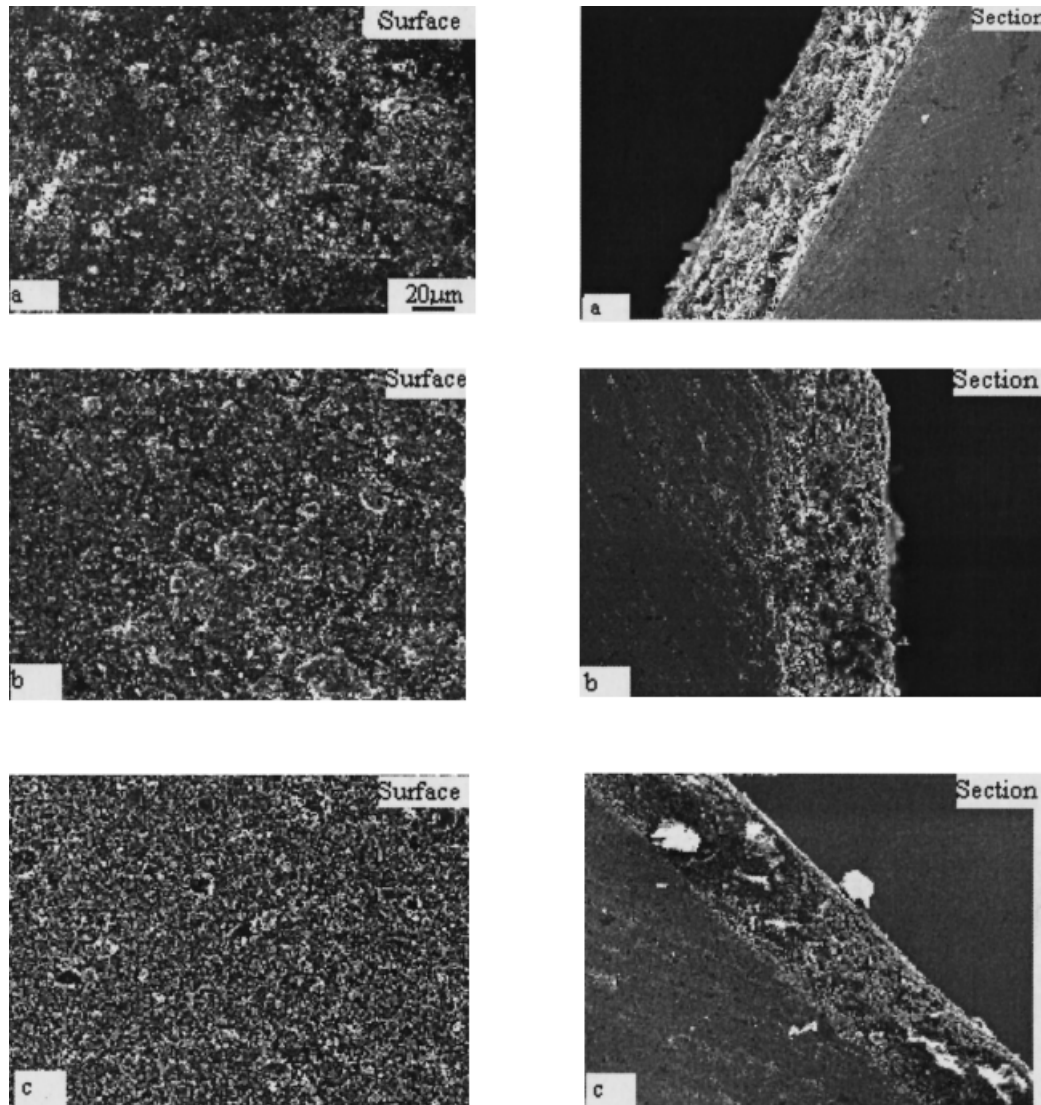
Figure 4 Surface and section morphology of PTFE/PU coatings with different PTFE volume concentrations: (a) 20%; (b) 40%; (c) 60%.

coating determined with the ring-on-block tester reaches the highest value at 40% volume concentration; it is about 844 m/μm at 314 N and 1.25 m/s. The dispersion quality is a very important factor in the performance of a PTFE dispersion and of a bonded lubricating coating. The oil absorption (OA) paste consists of dispersed single-irradiated PTFE particles, each having a layer of oil on its surface together with sufficient oil to fill the space between the particles which are assumed to be packed as densely as possible. Using a description of the OA paste, a procedure is based on it to calculate the critical volume concentration of an irradiated PTFE in a precursor system.[23] The critical volume concentration corresponds to the irradiated PTFE volume concentration at which the binder just fills the voids between the packed irradiated PTFE particles. According to the OA (40%) of irradiated PTFE particles in linseed oil, the critical

volume concentration value is 50%.[10] It is obvious that the volume concentration for the longest wear life of a coating is less than the critical volume concentration value. In addition, as shown in Figure 3, at too low a volume concentration (below 10%) or too high a volume concentration (above 60%) value, the coatings fail abruptly. Figure 4 shows SEM pictures of the coating surfaces and sections. PTFE particles agglomerate and laminate in coatings when the volume concentration is below 20% [Fig. 4(a)]. But the binder is not enough to bind each PTFE particle when the volume concentration reaches 60% [Fig. 4(c)], and, therefore, the coating is easy to deform and smear and then easily worn off.[22] Only when the volume concentration of the coating is 40% does it gives a suitable lubricant and binder for a longer-wear-resistant coating [Fig. 4(b)].

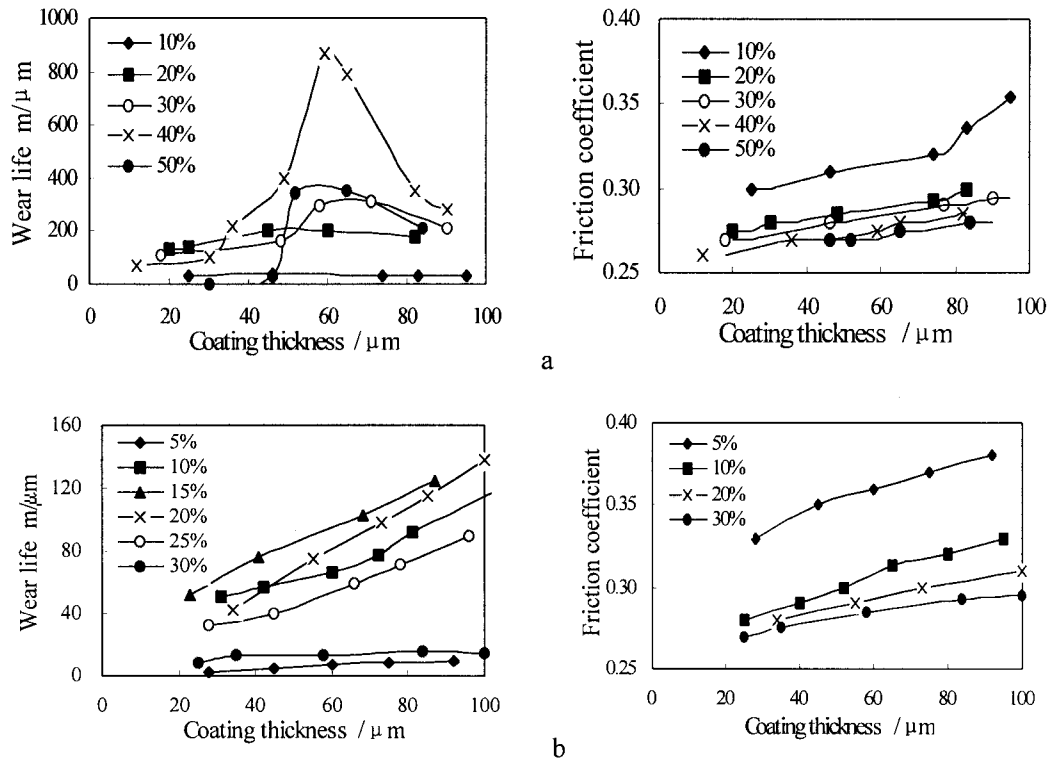From the standpoint of a protective function, the thickness of the coating is an important factor for

Figure 5 (Left) Wear life and (right) friction coefficients of (a) PTFE/PU and (b) PTFE/PU2k coatings at different volume concentrations versus coating thickness. Load 314 N; speed 1.25 m/s.

abrasion resistance.[10] Figure 5 shows the relationship between the wear life and the thickness of various PTFE/PU coatings. PTFE/PU coatings show the highest wear life at 60-μm thickness [Fig. 5(a)]. It is different for the wear life of the PTFE/PU2k coating, which increases with increasing thickness. Moreover, a 15% volume concentration is suitable for the PTFE/PU2k coating for a longer wear life. This is smaller than is the optimum volume concentration of PTFE/PU coatings [Fig. 5(b)]. Such a difference seems to depend on the different curing mechanisms. The curing of PTFE/PU coatings is strongly dependent on the reaction between the —NCO radical in the binder and the —OH radical originated from H_2O in humid air. If the wet coating is too thick, —OH cannot penetrate into the inner coating of the cured surface film, and, consequently, the curing reactions of the inner coating would be retarded. Thus, the thicker coating does not have a longer wear life because the curing process might be incomplete in the coating. But the curing reaction of the PTFE/PU2k coating is dependent only on the mol ratio between the —NCO group and the —OH of the polyester group, the equivalent —OH group and —NCO group directly react in the coating, and the curing process results in a thicker coating. On other hand, the wear life increases with increasing soft coating thickness in the PTFE/PU2k coating because of the contact pressure reduction, and, thus, the wear life increases with increasing thickness. The wear life

of PTFE/PU coatings is much longer than that of the PTFE/PU2k coating at the same thickness. It is assumed that the process of the curing reaction is slow between —NCO and —OH in the PTFE/PU coatings, and active —OH and —NH on the surface of the irradiated PTFE particles could react with —NCO to form a strong bond between the binder and the PTFE particle.[22] The friction coefficient of coatings decreases with an increasing volume concentration value because of the increasing PTFE lubricant, and it slightly changes above a 40% volume concentration in the PTFE/PU coatings. It almost linearly increases with an increasing thickness for PTFE/PU coatings and PTFE/PU2k coatings (Fig. 5) because the thicker coating enhances the contact area to increase the friction force.

The wear behaviors of PTFE/PU coatings under various sliding conditions on a ring-to-block test are shown in Figure 6. The wear life is shown in the speed range of 1.25–2.50 m/s at a constant load of 314 N and the load range of 314–785 N at a constant speed of 1.25 m/s (Fig. 6). The wear life of the 60-μm-thick coating linearly decreases with an increasing load $\times$ speed value, and it reaches a shorter wear life above 687 Nms^{-1}. But the wear life of the 90-μm-thick coating remains at a stable value at the 687 Nms^{-1} of load $\times$ speed region because the thicker coating enhances the contact area to reduce the load for the unit area and it abruptly decreases above 687 Nms^{-1}. The wear life of the 60-μm-thick coating is much longer than
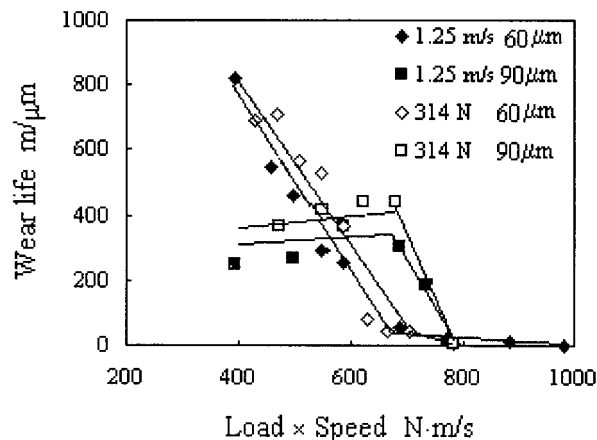
Figure 6 Wear life of PTFE/PU coatings plotted against speed × load value.

that of the 90-μm-thick coating below 550 Nms^{-1}. Thus, the PTFE/PU coating had wear resistance when the load × speed value was less than 687 Nms^{-1}; at same time, the wear life for the thinner coating was sensitivite to sliding condition variations.

CONCLUSIONS

1. PTFE/PU coating of 60-μm thickness cured at room temperature, at 75% RH, and for 4 days has a longer wear life: 844 m/μm at 314 N and 1.25 m/s.
2. The longer wear life of PTFE/PU and PTFE/ PU2k coatings were obtained at a volume concentration of PTFE of 40 and 15%, respectively, and both are less than the critical volume concentration of 50%.
3. The wear life of PU coatings containing irradiated PTFE particles is strongly dependent on the curing process. The maximum load × speed value of PTFE/PU coatings for protection application is about 687 Nm s^{-1}, and the wear life for

a thinner coating is sensitive to sliding condition variations.

References

1. Bartz, W. J.; Xu, J. Wear 1987, 115, 167–184.
2. Flautt, M. C.; Wong, R.; Walsh, J. F.; Kinkelaar, E. W. U.S. Patent 4 347 278, 1982.
3. Uchiyama, Y. Wear 1981/1982, 74, 247–262.
4. Tanaka, K.; Uchiyama, Y.; Toyooka, S. Wear 1973, 23, 153–172.
5. Gambhir, N. S. Chem Age India, 1988, 39, 243–254.
6. Nosaka, M.; Oike, M.; Kikuchi, M.; Nagao, R. Y.; and Mayumi, T. Lub Eng 1996, 52, 221–233.
7. Barrett, L. D.; Flamme, B.; Hahn, D. R.; Pelloski, P. E. U. S. Patent 5 415 895, 1995; Barrett, L. D.; Flamme, B.; Hahn, D. R.; Pelloski, P. E. U. S. Patent 5 166 251, 1992. Tanaka, T.; Tamura, H.; Uenaka, K.; Hakakoshi, S. U. S. Patent 5 091 098, 1992.
8. Tian, J.; Xu, J. F.; Xue, Q. Polym Mater Sci Eng (in Chinese) 1997, 13(5), 109–113.
9. Tian, J.; Xue, Q. J Appl Polym Sci 1998, 69, 435–441.
10. Tian, J.; Xue, Q. Paint Ind (in Chinese) 1997, 4, 16–18.
11. Tian, J.; Zhou, Zh. F.; Xue, Q. Corros Sci Protect Technol (in Chinese) 1997, 9, 182–184.
12. Zhou, Zh. F.; Tian, J.; Xu, J. Chin. Patent ZL92 112 149.0, 1998.
13. Handa, T.; Saito, H.; Takazawa, H. Zairyo-to-Kankyo 1996, 45, 160–166.
14. Corros Prevent Control 1986, June, 70–71.
15. Braza, J. F.; Farst, R. E. Wear 1993, 162–164, 748–756.
16. Carton, J. F.; Vannes, A. B.; Zambeclli, G.; Vincent, L. Tribol Int 1996, 29, 445–455.
17. Huisman, H. F. J Coat Technol 1984, 56, 65–79.
18. Patton, T. C. Paint Flow and Pigment Dispersion: A Theological Approach to Coating and Ink Technology, 2nd ed.; Wiley: New York, 1979.
19. Weiss, K. D. Prog Polym Sci 1997, 22, 203–245.
20. Rao, R. V. J Color Soc 1982, Oct./Dec., 20–23.
21. Bierwagen, G. P.; Rich, D. C. Prog Org Coat 1983, 11, 339–352.
22. Tian, J.; Huang, Y. L. J Adhes Sci Technol 2002, 16, 47–57.
23. Huisman, H. F. J Coat Technol 1984, 56(712), 65–79.