Tribological Behaviors of Fluorinated Polyimides at Different Temperatures

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Available online: 03 Mar 2011

To cite this article: Tongsheng Li, Jianshu Tian, Ting Huang, Zhongyuan Huang, Hongyan Wang, Renguo Lu & Peihong Cong (2011): Tribological Behaviors of Fluorinated Polyimides at Different Temperatures, Journal of Macromolecular Science, Part B, 50:5, 860-870

To link to this article: http://dx.doi.org/10.1080/00222348.2010.497023

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Tribological Behaviors of Fluorinated Polyimides at Different Temperatures

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4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)-based copolyimides were synthesized and the tribological properties of the copolyimides with different heat histories were studied at different temperatures. Fluoride-containing polyimide (PI) showed better thermal stability, decreased friction coefficients, and postponed the consequence of friction variation, which depended on temperature, than nonfluorinated PI. Thermal treatments seemed to increase the friction coefficients of copolyimides, and reduced the tensile strengths of the materials. The effects of applied load (P) and sliding speed (V) on tribological behaviors of thermally treated copolyimides were also examined and the variations of friction coefficient depending on PV values were investigated for clear understanding of its relationship between PV value and friction coefficient with different thermal treating time. Distortions of net structures of the chains and molecular motion contributed to variations of tribological properties of thermal treated copolyimides.

Keywords copolyimide, friction, temperature, thermal treated

Introduction

The reduction in mechanical properties with time at elevated temperatures is a key limiting factor in the use of polymers in engineering applications.[1] Low thermal conductivity and low heating resistance of polymers are important limitations for sliding applications, although mechanical,[2] chemical,[3] or thermal[4] interactions favorably control their self-lubricating action. Polyimides (PIs) are a family of high-performance materials with extremely high mechanical strength and thermal stability up to 310°C (long term) or 450°C (short term), having an imide unit either in linear or cyclic form and strong aromatic groups.[5]

Extensive research has been conducted in the area of tailoring the physical properties of the final PI by changing the structure of monomers and thereby preparing PIs suitable for special applications. However, this approach is often restricted because of difficulties in synthesizing new aromatic tetra-carboxylic dianhydrides. Copolymerization is an...
alternative method for modifying the polymer properties to meet a specific requirement. Several copolyimides have been prepared by random copolymerization using either a di-
amine and two different dianhydrides or a dianhydride and different diamines.\textsuperscript{[6–8]}

PIs are finding wide acceptance in tribological applications because of their low friction
against steel counterparts and their self-lubricating ability.\textsuperscript{[9–19]} In much of the earlier work
reported on PI tribology, chemical structures were industrially proprietary. Moreover, most
research done in the field of PI tribology relates to the influence of different fillers due to its
engineering application. Hence, efforts to establish structure and property relations were
hindered.

In this study, thin 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)-based
copolyimide films were synthesized and the effect of temperature on tribological properties
of copolyimide with different fluoride monomer ratios was researched. Furthermore, the
mechanical and tribological properties of copolyimide dependence on thermal treating time
were also studied to understand the mechanism of the copolyimide tribology after thermal
treating and effect of tribological conditions in the rubbing process of different fluoride
copolyimides.

**Experimental Details**

**Materials**

6FDA (from Hoechst) and 4,4′-oxydiphthalic anhydride (ODPA; from Shanghai Research
Institute of Synthetic Resins) were purified by recrystallization from distilled acetic anhy-
dride and dried 24 h at 150°C. 4,4′-diaminodiphenyl ether (ODA; from Shanghai Research
Institute of Synthetic Resins) was also purified, by vacuum desiccation, before use. The
solvent N,N′-dimethylacetamide (DMAc, 99%) was used without further purification.

**PI Preparation**

The PI films were prepared from a traditional two-step method to cope with the infusibility
and insolubility of aromatic PIs. In the first step, poly(amic acid) was produced from a
step-growth polymerization between ODA with different ratios of 6FDA and ODPA, in
order to introduce different amounts of fluoride to the main chain of the PI, shown in Fig. 1.  

![Chemical structure of PI and the synthesis process.](image-url)

**Figure 1.** Chemical structure of PI and the synthesis process.
The conversion of the poly(amic acid) into the PI was done in a second step by intramolecular condensation, and thermal imidization was applied. The typical multistage heating schedule includes 1 h resident time at 100°C, 1 h at 200°C, and 1 h at 300°C, which helps the formation of linear species.\[^{18}\] The final copolymer PI films were obtained by thermal imidization at 350°C for 2 h.

The inherent viscosity (IV) of poly(acrylic acid) (PAA) was measured at a concentration of 0.05 g/L in DMAc at 25°C.

The glass transition temperature, $T_g$, was obtained by dynamic mechanical analysis (DMA 242, Netzsch Co., Germany) in dual cantilever mode, at the heating rate of 3°C/min and frequency of 5 Hz.

**Thermal Treatment of PI Film and Characterization**

The PI films were thermally treated in ovens at 250°C for 200, 400, and 600 h, respectively, for study of the dependence of PI properties on time in the thermal treating process.

The PI films were cut into sizes of 4 × 30 mm to determine the tensile strength. A universal electromechanical testing machine (Model 5567, Instron Co., USA) was used. The gauge length and crosshead speed were set as 20 mm and 0.5 mm/min, respectively.

**Tribological Properties Measurement**

The tribological behavior of the PI under different environmental temperatures was studied on an LKDM-2000 type tribometer (Lanzhou Institute of Chemical Physics, Chinese Academy of Science, China). Figure 2 shows the schematic diagram of the main component

![Figure 2. Schematic diagram of the reciprocating tribometer with a heating oven.](image-url)
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Figure 3. Schematic diagrams of the tribometer: WTM-1E.

of the tester. It has a pin-on-disk contact configuration, the diameter of the disks was 25 mm, the thickness of the PI films was 0.03 mm, and the ball was steel. The disk was fixed in an oven whose temperature was adjustable, and moved with the oven reciprocally. The frictional force transferred to a sensor was recorded in a personal computer during the tests. The environmental temperature was varied from 25 to 350°C.

The dependence of tribological properties of the samples on mechanical conditions was carried out by a ball-on-disk tribometer (WTM-1E, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, China), as shown in Fig. 3. The diameter of the disks was 25 mm and the thickness of the PI films, with different thermal treating time, was 0.03 mm.

In wear tests, the WTM-1E was also employed. The disks were metallographic abrasive papers (800#) with sizes of Ø 25 × 0.6 mm, and the pins were polymers. A piece of PI film pushed out from a mold by a Ø 2.5 mm steel ball was used as the PI pin, as shown in Fig. 4. The wear of the specimen was measured by the weight loss of the pin using an analytical balance (precision: 0.1 mg). The wear rate (K, cm³/N m) in this study was calculated from the following equations.

\[ K = \frac{\Delta m}{LF\rho}, \]

where \( \Delta m \) was the weight loss (mg), \( L \) is the sliding distance (m), \( F \) is the applied load (N), and \( \rho \) is the density of the polymer (g/cm³).

Results and Discussion

Characterization of Fluorinated PI Polymer

The DMA curves of the temperature dependence of tan δ exhibits well-defined dynamic mechanical damping peaks, which are ascribed to the glass transitions of polymer. Figure 5 shows the temperature dependence of tan δ of the PI films with different
fluorinated monomer ratios. The nonfluorinated PI showed the lowest glass transition temperature ($T_g$), at 257°C, and it increased gradually with the increasing of fluorinated monomer ratios, reaching the highest temperature, 287°C, with full fluorinated PI. High electronic polarizability and electronegativity of F atom, together with lack of ether bonds in the monomers, resulted in the higher thermal stability of fluorinated PI.

The thermal treating seemed to cause a decrease in the tensile strength of PI films according to Fig. 6. The PI films thermally treated for different times at 250°C, showed a slightly lower tensile strength than virgin PI films. Furthermore, extending of the thermal treatment time caused decreasing of the PI film tensile strength. Thermal treatment for 600 h decreased the tensile strength of PI films by about 10 MPa. However, the tensile strength increased with increased fluorinated monomer ratio.

Figure 4. PI film pushed out by a steel ball for tribological property measurements.

Figure 5. The DMA curves of the temperature dependence of tan $\delta$ of the PI films.
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Figure 6. Tensile strengths of PI films with various fluorinated monomer ratios under different time of thermal treatment at 250°C.

Friction and Wear Properties

Figure 7 shows the dependence of the friction coefficient of untreated PI films with different ratios of 6FDA monomer, on temperature. The friction coefficients of the PIs at first remained steady at low values, and then increased significantly at special temperatures, and at last, the friction coefficients decreased to very low values as temperature of the environment kept increasing. As the ratios of 6FDA monomer increased, a remarkable alteration of the friction coefficients of PI films occurred at higher temperatures. The friction coefficient of nonfluorinated PI started increasing at about 170°C, to a peak at 210°C, and then rapidly decreased, while the full-fluorinated PI started to increase at 205°C and reached a lower peak at 225°C but then slowly decreased until 260°C after which it rapidly deceased. The friction coefficient of full-fluorinated PI returned to an

Figure 7. Friction coefficient of untreated PI films with various fluorinated monomer ratios with different environmental temperatures.
extremely low value, below 0.05, at 60°C, a higher temperature, compared to nonfluorinated PI.

Figure 8 shows effects of thermal treatment on the PI friction coefficient, velocity 0.06 m/s, applied load 100 N. The thermal treatment increased the friction coefficients of all PIs mentioned in this work, and with prolonged thermal treatment time, the friction coefficients increased slightly. The largest increase of friction coefficient was for 50%-fluorinated PI, from 0.287 with nonthermal treatment to 0.352 with 600 h, by 0.065, while the nonfluorinated PI showed the least variation.

Friction and wear properties are not intrinsic material characteristics, but they strongly depend on the wear mode and experimental test conditions.[5] For the mechanical conditions, applied load (P) and velocity (V) have significant effects.[20] Figure 9 shows the dependence of nonfluorinated PI with different thermal treatment times on the $PV$ value. The friction coefficients first remained stable, then decreased significantly, and then came back to some higher values as the $PV$ value increased. The nonfluorinated PIs with different thermal
treatment times exhibited their lowest friction coefficients at approximately the same $PV$ values. The thermal treatment seemed to raise the lowest coefficient. The friction coefficient of nonthermally treated PI was 0.32 for $PV$ at 0.06, decreased to the lowest value, 0.268, when $PV$ was 0.96, and then increased to 0.321 again when $PV$ was 1.32. The friction coefficient of PI, for thermal treatment of 600 h at 250°C, was 0.332 when $PV$ was 0.06, decreased to its lowest value, 0.321, when $PV$ was 0.84, and then increased to 0.34 when $PV$ was 1.68.

The full-fluorinated PI shown in Fig. 10, displayed similar tribological properties with nonfluorinated PIs. The thermal treatment also helped increase the friction coefficients and the $PV$ value of the lowest friction coefficient. However, all of the friction coefficients were much lower than the nonfluorinated PIs.

Figure 11 shows the effect of different thermal treatment times on abrasive wear rates of the PIs. Thermal treatment decreased the wear rates of the PIs with different fluorinated

Figure 10. Dependence of full-fluorinated PI with different thermal treatment times on $PV$ value.

Figure 11. Wear rate of PI films of various fluorinated monomer ratios with different thermal treatment times (250°C).
monomer ratios slightly. Nonfluorinated PI showed the largest variation of wear rate with the help of thermal treatment, but the time of thermal treating seemed to have little effect.

**Discussion**

The mechanical properties of a polymer depend strongly on temperature, with a transition from the glassy state (with high strength, high stiffness) into the rubbery state (with lower strength and lower stiffness) above the glass transition temperature. Due to the poor heat conductivity of PI, friction heat could accumulate and increase the temperature of friction surfaces, even exceeding the glass transition temperature ($T_g$). Thus, the friction properties of sliding surfaces would be changed, as well as the physical states, because of the mixed effects of the variation of ambient temperature and friction heat accumulation.

The mechanical states of friction surfaces would change as temperature increased. Increasing temperature of the surfaces caused by friction or ambient temperature could make tiny bulges in real contact become partly in the rubbery state. The rubbery state extends over the friction surface as the temperature keeps increasing, and the friction surfaces eventually become totally in the rubbery state, which enlarged the real contact area and the friction coefficient increased dramatically. When the temperature increased sufficiently, a viscous flow state formed in the friction surfaces, extended and increased in thickness, which made friction coefficient decrease to a very low value. The fluorinated PI exhibited more stable thermal properties to withstand the whole thermal process, and the lower surface free energy contributed to the lower friction coefficients.

The friction properties of PI are related to the entanglement structures of the molecular chains. For the reason of the large reduction of the ability of crosslinked polymer segments to penetrate into each other, the friction forces of crosslinked polymers are remarkably less than those of uncrosslinked polymers. The number of crosslinked intra- or intermolecule chains of PI decreased as the time of thermal treatment increased, attributed to motions of molecular chains. Furthermore, the increased motion capacity decreased the degree of crosslinking and the capabilities of motions were strongly affected by time and temperatures of thermal treatment. The moving unit needs enough mobility energy to exhibit physical relaxation; increasing the temperature or time of thermal treatment could improve the mobility energies. Prolonging the time of thermal treatment at high temperatures both decreased the crosslinking degree and increased the motion capacities of molecular chains, increasing the friction coefficients to some extent.

The tribological behaviors-PV value dependence may be due to the various molecular motions at the polymer sliding surface. The effect of applied load $P$ and sliding velocity $V$ leads to the increase of temperature on worn surfaces under sliding conditions. It is known that the sliding between materials always results in heat generation at asperities and hence increases the temperature at two frictional surfaces. Therefore, the PV value exhibited a significant effect on polymer friction properties. Thermal treatment helped reduce the degree of crosslinking of the molecular chains, and thus affected the tribological behaviors—PV value dependence.

**Conclusion**

Fluorinated PIs manifested higher thermal stability behaviors, and exhibited characteristic tribological properties at different temperatures, especially in the high-temperature environment. The main conclusions can be drawn as follows:
(1) Fluorinated PI exhibited higher glass transition temperatures ($T_g$s), and with increased fluorinated monomer ratio, higher $T_g$s occurred. In addition, long-time thermal treatment below $T_g$ decreased the tensile strength of PIs.

(2) A remarkable oscillation of the friction coefficient of PI films was exhibited as temperature increased. The addition of 6FDA monomer increased the temperature at which the friction coefficient was at a minimum.

(3) Thermal treatment on PI affected friction and wear rate. Thermal treatment slightly increased the friction coefficients of PIs, and the friction coefficients also slightly increased as thermal treatment time was prolonged, and increased the friction coefficients of all PIs mentioned in this work. The thermal treatment slightly decreased the wear rates of PIs with different fluorinated monomer ratios.

(4) The thermal treatment helped increase the $PV$ value of the lowest friction coefficient. The friction coefficients of fluorinated PIs were much lower than nonfluorinated PIs for the same conditions.

References