

In Situ Synthesis and Properties of PMR PI/SiO₂ Nanocomposites

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ABSTRACT: Phenylethynyl-terminated polymerization of monomer reactant thermosetting polyimide (PI) was synthesized, and the PI/SiO₂ nanocomposite films were prepared via *in situ* polymerization of monomer with the nano-SiO₂ particles. Analysis indicated that the surfaces of the nano-SiO₂ slightly react to the PI, and nano-SiO₂ was homogeneously dispersed in the PI at low filling content while agglomerate was a presence of high filling content. Thermogravimetric analysis showed that the decomposition temperatures of the PI/SiO₂ nanocomposites were increasing as the increasing of filler contents when the

nano-SiO₂ content was below 9 wt %, but it showed a decreased tendency when it was above 9 wt %. Tribological studies showed that the nano-SiO₂ contributed to the significant decreasing of the friction coefficient and wear rates of the PI at dry sliding condition of low filler content, and the PI/SiO₂ nanocomposites could be promising material used as tribomaterial in dry sliding condition against GCr15 steel. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 488–493, 2012

Key words: thermoset polyimide; silicas; nanocomposites

INTRODUCTION

Polyimides (PIs) play important roles in the development of advanced technologies because of their excellent thermal and thermooxidative stabilities and outstanding mechanical and electrical properties.^{1,2} Polymerization of monomer reactants (PMRs) thermosetting PIs are a variety of thermosetting polymers used in high-mechanical and high temperature environment. They are reasonably easy to process and have been applied to high performance applications, particularly those for the aerospace industry, such as composite matrix and adhesive for aircraft structures and turbofan engine components. The phenylethynyl-terminated PI designated PETI-5, which was considered to be the most excellent thermosetting PIs for use as a composite matrix and adhesive, was developed in NASA Langley Research Center and exhibited excellent mechanical properties, solvent resistance, acceptable processability, and high glass transition temperature of 270°C.^{3,4}

The addition of nanoparticles in polymers for the enhancement of thermal and tribological performances is of significant importance, and this area has become quite promising as newer nanomaterials for

the future are being economically and routinely fabricated. These nanocomposites exhibit enhanced thermal and dimensional stability, stiffness, strength, low thermal expansion and fire retardancy and also unusual magnetic, optical, electronic properties than their counterpart.^{5–7} Furthermore, many studies have been carried out on tribological properties of PI-based nanocomposites, but almost all of them are focused on the thermoplastic PIs.^{8–11} Therefore, it is of significant interest to investigate the effect of addition of nanoparticles into PMR thermosetting PI. In this article, the phenylethynyl-terminated PMR thermosetting PI and its nanocomposites reinforced with nano-SiO₂ were prepared via *in situ* PMR processes. The reinforcing effect of nano-SiO₂ on the thermal and tribological properties of the PI/SiO₂ nanocomposites was investigated. It is expected that this work will broaden the application of nanoparticles filled PMR thermosetting PI composites.

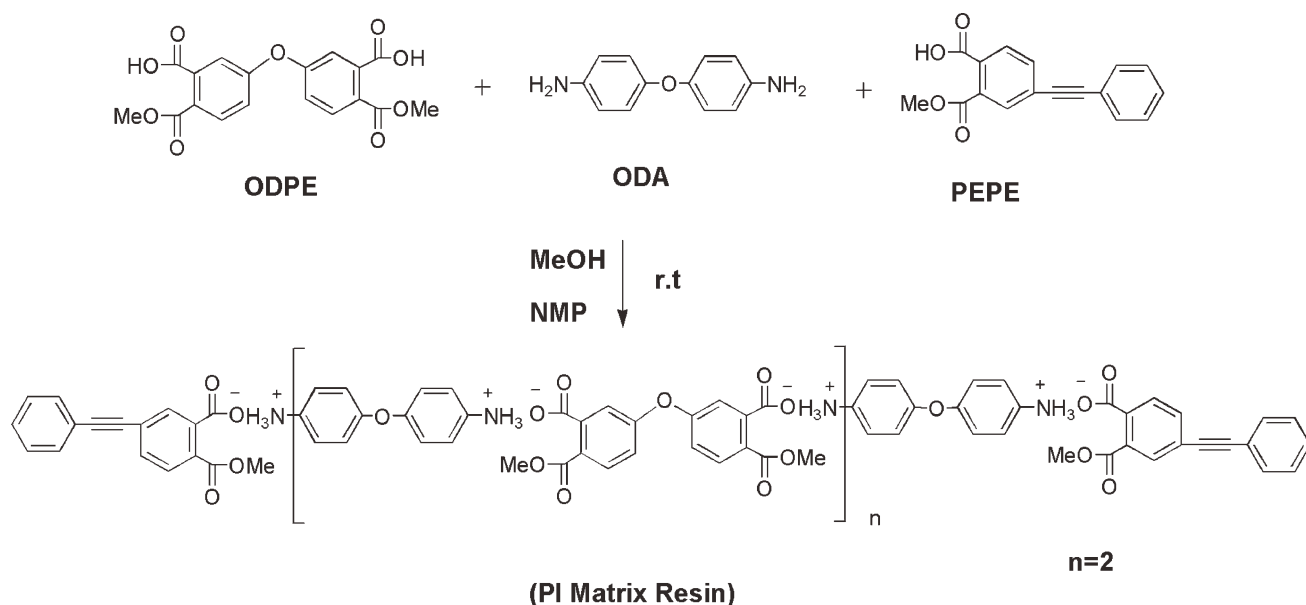
EXPERIMENTAL

Materials

4,4'-Oxydianiline (ODA; Sinopharm Chemical Reagent, China) and 4-phenylethynylphthalic anhydride (PEPA; Changzhou Sunlight Pharmaceutical, China) were used as-received. 4,4'-Oxydiphthalic anhydride (ODPA; Shanghai Synthetic Resin Institute) was dried at 140°C for 6 h in vacuum prior to use. 1-Methyl-2-pyrrolidinone (NMP) were distilled in vacuum and stored in sealed flask. Pure nano-SiO₂

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Scheme 1 The chemistry of PMR type PI matrix resin.

particles (size: 20~50 nm) were supplied by Zhoushan Mingri Nanomaterial, China.

Preparation of film specimens

Dimethyl ester of 4,4'-oxydiphthalic acid (ODPE) and monomethyl ester of 4-phenylethynylphthalic acid (PEPE) were prepared according to the method of Serafini et al.¹² ODA (1.86 g) and methyl alcohol (MeOH, 20 mL) were placed in a 100-mL flask fitted with magnetic stirrer and reflux condenser. The mixture was refluxed for 2 h, with stirring, to yield the ODPE solution. The PEPE solution was prepared by refluxing a mixture of PEPA (1.49 g) and MeOH (15 mL) for 3 h. To a solution of ODA (1.8 g) in NMP (7.5 mL) in a 100-mL three-necked flask fitted with stirrer, N₂ inlet, and gas outlet, ODPE and the PEPE solutions in MeOH were added successively. The mixture was stirred for 3–5 h at room temperature to yield a homogeneous matrix resin solution with a solid content of 30–40 wt % (Scheme 1). For the preparation of PI/SiO₂ nanocomposites, nano-SiO₂ particles were added to the resin solution in different concentration by weight and subjected to ultrasonication for 60 min to ensure the uniform dispersion. The homogeneous matrix resin and composite solution were painted on steel blocks and put in an air-circulation oven at 100, 200, 300, and 375°C for 1 h, respectively, to yield the film specimens.

Characterization

The friction and wear behavior of the samples were evaluated using an MRH-03 (Jinan Yihua Tribology Testing Technology, China) type ring-on-block test

rig. The schematic contact diagram of the frictional couple is shown in Figure 1. The upper block, with a size of 19.05 mm × 12.32 mm × 12.32 mm, was the prepared film on block specimen. The lower ring, with a size of Φ49.22 mm × 13.06 mm was made of GCr15 steel, a standard bearing steel. In this study, sliding speeds of 0.515 m/s, and applied load 200 N were selected, and a sliding period of 1 h was maintained. Before each test, the steel ring was abraded to reach a surface roughness of about 0.10 μm. Then, the ring and the film on the block were cleaned with acetone. The length of the wear track on the films was measured using an optical microscope to an accuracy of 0.01 mm. Then, the wear volume loss, *V*, of the blocks was calculated by the following equation^{8,13}:

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

where *V* is the wear volume loss (mm³), *B* is the width of block sample (mm), *R* is the radius of the steel ring (mm), and *b* is the length of the worn track on the block specimen (mm). The specific wear rate *K* (mm³/Nm) was calculated as below^{8,13}:

$$K = V/(d \times L),$$

where *d* is the sliding distance (m) and *L* is the load (N).

Fourier-transform infrared spectroscopy (FTIR) measurements were performed with a Bruker IFS66v/S spectrophotometer. The test samples were prepared by molding of the resin powder, collected

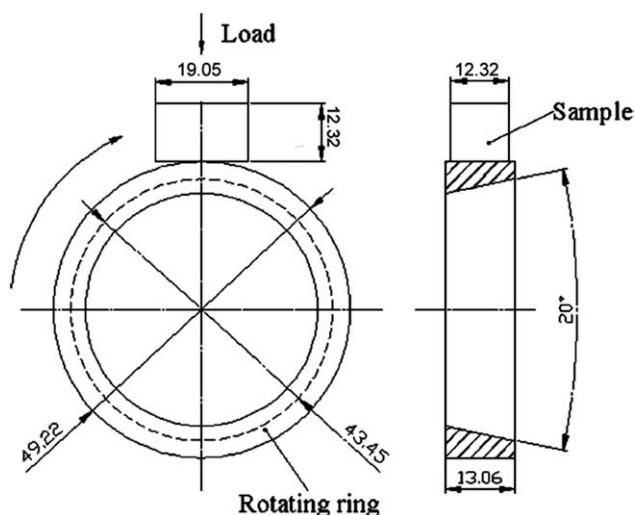


Figure 1 Schematic contact diagram of the frictional couple (unit: mm).

by scraping the film sample with a knife, with pure KBr in disc as usual. For field emission scanning electron microscopy (FESEM) examination, nanocomposites were fractured, and then coated with gold film. The center of the fractured surface for each sample was examined using a field emission scanning electron microscope JEM-6701F (JEOL, Japan). Thermogravimetric analysis (TGA) measurements were carried out using a Perkin-Elmer 7 series thermal analysis system in air at a heating rate of 10°C/min. The X-rays photoelectron spectroscopy (XPS) analysis was carried out using unmono-chromated Mg Ka X-radiation using Al/Mg dual anode at 20 KV under 300 W and the base pressure in the sample chamber was about 10^{-7} Pa.

RESULTS AND DISCUSSION

Characterization of PI and PI/SiO₂ nanocomposites

The phenylethynyl-terminated PMR thermosetting PI matrix resin solution was prepared using monomers of PEPA, ODPE, and ODA at a molar ratio of 2: n : ($n + 1$) in a mixture of MeOH and NMP at room temperature, with $n = 2$, giving a calculated molecular weight of about 1600. This solution was stable at room temperature for a storage period of 2 weeks during which no precipitation, gelation, or phase separation was observed.¹² The PI matrix resin solution was thermally cured to yield a cross-linked material after passing through a series of thermal chemical reactions. The crosslinked matrix resin showed good adhesion to steel, which ensured the film specimens being retained in the dry sliding test process.

The FTIR spectra of the PI and its composites reinforced with SiO₂ are listed in Figure 2. All samples exhibited obvious absorption peaks arising from the asymmetric and symmetric stretchings of C=O groups in imide rings at about 1779 and 1720 cm⁻¹. Another characteristic absorption of the imide group arising from C—N stretching appeared at around 1380 cm⁻¹ for all samples. The results showed that the PIs matrix had formed through the thermal imidization procedure.^{1,8} The peaks at 1079 and 1052 cm⁻¹ were for C—O—C stretching vibration in PI. When the nano-SiO₂ was added into polymer matrix, these peaks increased in intensity and combined into one large peak with the increasing of nano-SiO₂ content. The peak of Si—O—Si stretching vibration was at 1080 cm⁻¹.¹⁴ It can be deduced that the increasing of nano-SiO₂ will cause the increasing in intensity and combination of this absorption peak.

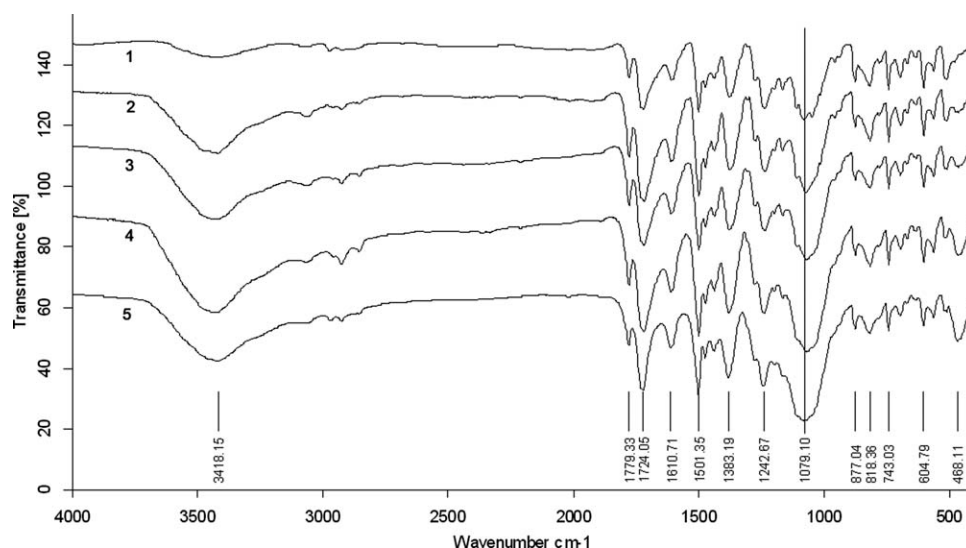


Figure 2 FTIR spectra of PMR thermosetting PI (1) and its nanocomposites with nano-SiO₂ content of 5 wt % (2), 9 wt % (3), 16 wt % (4), and 25 wt % (5).

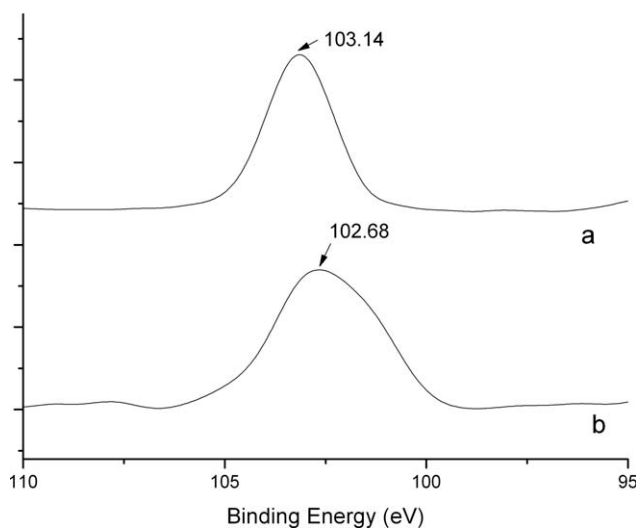


Figure 3 The XPS spectra of pure nano-SiO₂ (a) and PMR PI/SiO₂ nanocomposites of 9 wt % nano-SiO₂ content (b).

XPS has been carried out to examine the surface properties of PI/SiO₂ nanocomposites. The XPS spectra of Si 2p of pure nano-SiO₂ (a) and PMR PI/

SiO₂ nanocomposites of 9 wt % nano-SiO₂ content are shown in Figure 3. It can be seen that the Si 2p peak of pure nano-SiO₂ is 103.14 eV, which is the typical Si 2p peak of SiO₂. The peak of Si 2p in PI/SiO₂ nanocomposite is 102.68 eV at the 9 wt % nano-SiO₂ content. This confirmed that the silica are present at (or near) the surface of the nanocomposite particles.¹⁵ In fact, the binding energy between 103.1 and 102.7 eV was assigned to the Si—O bond under a different environment. It can be rational to infer that the *in situ* PMR process would endow the good interfacial interaction between the nano-SiO₂ and thermosetting PI resin.

Figure 4 is a representative high magnification FESEM micrograph of pure PI and PI/nano-SiO₂ of filler content of 9 and 25 wt %. The micrograph revealed that at low nano-SiO₂ content of 9 wt %, the nano-SiO₂ particles was difficult to be observed, and the fracture surface was smooth. At high nano-SiO₂ content of 25 wt %, the agglomerates of nano-SiO₂ are observed to be distributed on the surface. It can be deduced that the nano-SiO₂ was homogeneously dispersed in the PI at low content while agglomerate is a presence of high filler content.

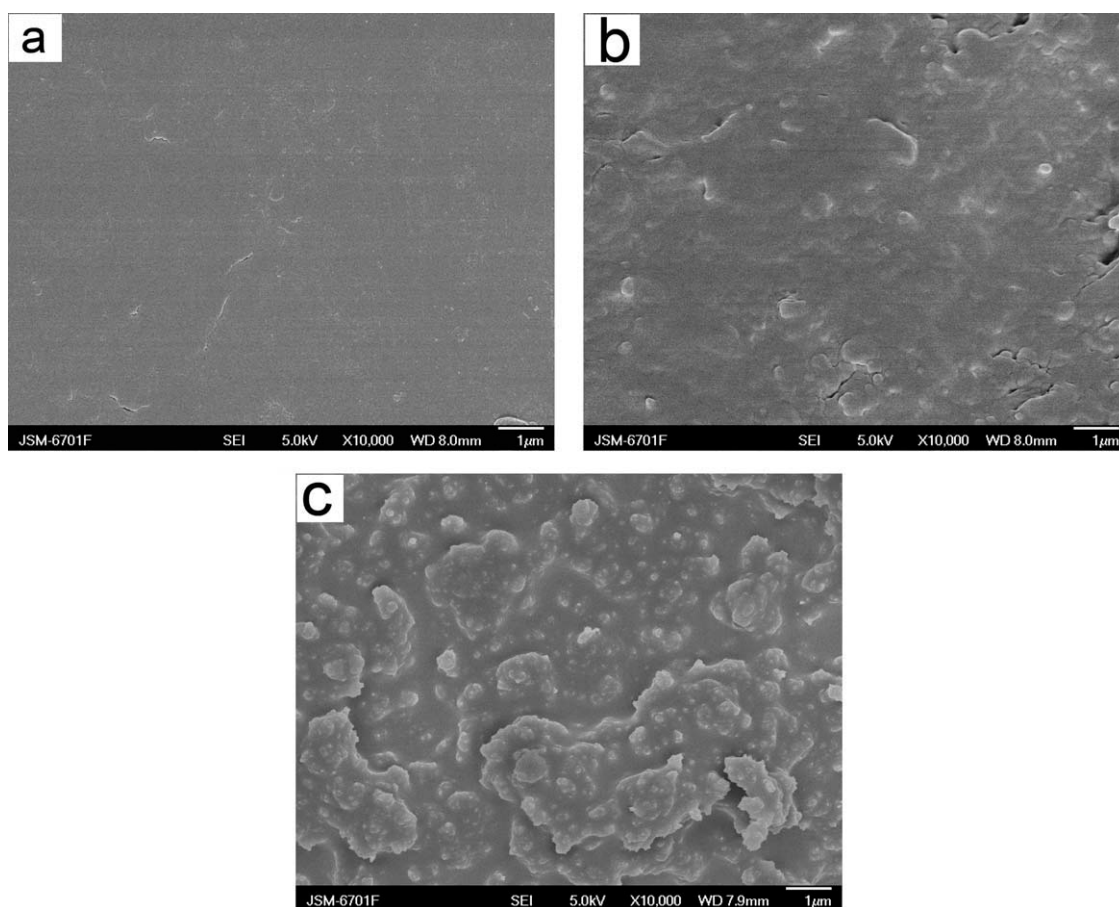


Figure 4 FESEM micrographs of fracture surfaces of pure PI (a) and PI/SiO₂ nanocomposites at various nano-SiO₂ content of 9 wt % (b) and 25 wt % (c).

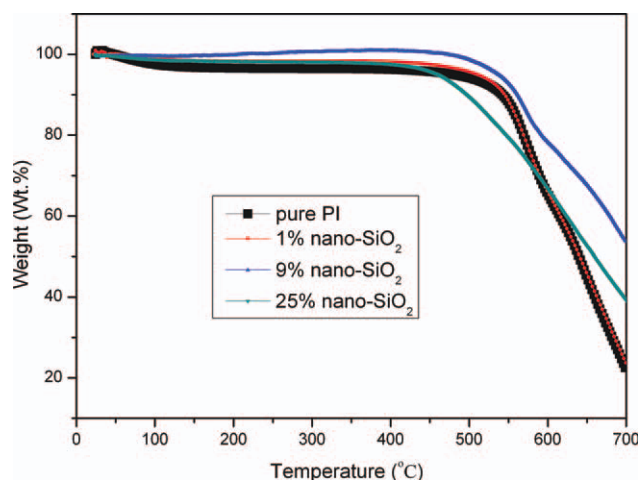


Figure 5 TGA curves of PI and PI/SiO₂ nanocomposites at a heating rate of 10°C/min in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal and tribological performance of PI and PI/SiO₂ nanocomposites

TGA is a technique used to accurately track the *in situ* weight changes of a sample during a heating process, thereby providing information on thermal degradation. The TGA curves of the PI and PI/SiO₂ nanocomposites are shown in Figure 5, and thermal analysis data from the TGA curves of the PIs are summarized in Table I. From Figure 5, the TGA curve of 1 wt % SiO₂ nanocomposite were similar to that of pure PI, and the TGA curve of them are almost superposed at the rear end. However, the TGA curves of 9 and 25 wt % SiO₂ nanocomposites are different from that of the pure PI. For the thermal stability of the PI and PI/SiO₂ nanocomposites, Table I gave the temperature of 5 and 10% weight loss in air. It was shown that the thermal stability of the nanocomposite was higher than pure PI when the nano-SiO₂ contents were below 17 wt % as the data of T_{d5} and T_{d10} . The temperature values of T_{d5} and T_{d10} for nanocomposite increased with the increasing of nano-SiO₂ contents when it was below 9 wt %. However, the temperature values of T_{d5} and T_{d10} of the PI/SiO₂ nanocomposites had a decreased trend as the increasing of nano-SiO₂ contents when the nano-SiO₂ content was above 9 wt %. At nano-SiO₂ content of 25 wt %, temperature values of T_{d5} and T_{d10} are 460 and 496°C, which are both lower than the values 480 and 542°C of pure PI, respectively. These mean that the nano-SiO₂ contents can prevent the thermal degradation of polymer matrix at low filler content and contribute to thermal degradation at high filling content. Generally, the decomposition temperature of the nanocomposites was higher than the pure resin due to the trapping of the polymer moieties in nanofiller networks.^{16–18} In

these PI/SiO₂ nanocomposites, the trapping of the PI moieties in silicon networks and reaction between them could contribute to the increasing of thermal stability at low nano-SiO₂ contents, but they would cause the PI resin to yield a worse crosslinked network at high nano-SiO₂ contents, which cause the decreasing of PI matrix thermal stability.

The friction coefficients and wear rate of PI/SiO₂ nanocomposites are studied with respect to the content of nano-SiO₂, and the results are displayed in Figure 4. When compared with the pure PI resin, the addition of nano-SiO₂ particles significantly reduced the friction coefficient as shown in Figure 6(a). The friction coefficient of nanocomposites decreased as nano-SiO₂ content increasing, then it reached a relatively stable value. The lowest friction coefficient of nanocomposite with 13 wt % nano-SiO₂ was 0.2. When compared with the value of 0.38 for pure PI, the change of friction coefficient was 47%. The variation of wear rate for the PI/SiO₂ nanocomposites as a function of nano-SiO₂ content is shown in Figure 5(b). The nanocomposites with nano-SiO₂ content below 5 wt % presented the decreasing of wear rate, while they registered rapidly increasing wear rate tendency at a high mass fraction. The wear rate of the pure PI resin was 3.48×10^{-6} mm³/Nm. In the case of nanocomposites, it decreased to 2.89×10^{-6} mm³/Nm at a low mass fraction of 5 wt % and the change ratio was 17%. With 25 wt % of nano-SiO₂, it increased to 13.01×10^{-6} mm³/Nm, which was 3.7 times higher than that of pure PI resin. It is concluded that the nano-SiO₂ contributed to the decreasing of the friction coefficient and wear rates of the PI at low content. First, this result can be attributed to the interfacial interaction of the nanolevel reinforcements.^{8–11,19,20} Namely, as the nanoparticles are well dispersed in PI matrix at nanolevel at low filler content, the interfacial interaction and reaction between matrix and nanoparticles was high due to the strong specific surface area of the nanoparticles as shown by the results of FTIR and XPS analyses. This would increase the nanocomposite material load-carrying capacity and heat distortion temperature (Fig. 5), which would be favorable for triboengineering parameters. Second, the nanoparticles will contributed to form more coherent and

TABLE I
Data of Thermal Analysis of the PI and PI/SiO₂ Nanocomposites

Nano-SiO ₂ contents (wt %)	0	1	5	9	13	17	25
T_{d5} (°C) ^a	480	509	524	537	496	510	460
T_{d10} (°C) ^b	542	544	555	561	542	550	496

^a Temperature at 5% weight loss.

^b Temperature at 10% weight loss.

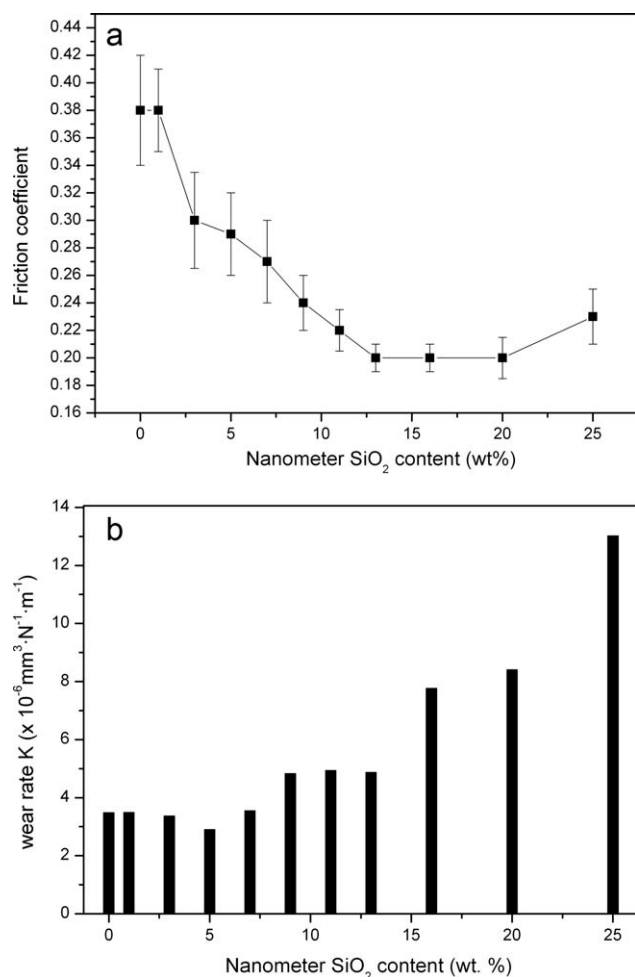


Figure 6 Variation of friction coefficient (a) and wear rate (b) of PI/SiO₂ nanocomposites versus SiO₂ content.

uniform transferfilms, which will protect the specimens and the steel counterpart and provide friction reducing ability.^{19,20} Third, this PMR PI endows the nanocomposites good homogeneous structure at low filler content because of the *in situ* polymerization of monomer with the nano-SiO₂ particles [Fig. 4(a)]. This *in situ* process will make the nano-SiO₂ linking more strongly than conventional filling methods of mechanical stirring or melt mixing. However, at high mass fraction, the interfacial interaction between the PI matrix and the nano-SiO₂ would be worsened due to the aggregation of the nanoparticles as shown in Figure 4(b), which would lead to the poorer wear-resistance and friction-reduction of nanocomposites. In a word, the addition of nano-PI/SiO₂ to PI endowed the nanocomposites better tribological properties than pure PI under dry sliding condition at low content. Thus, we think that these PI/SiO₂ nanocomposites would be promising materials in dry sliding condition against GCr15 steel. Based on a synthetic consideration of the friction

coefficient and wear rate, the nanocomposite of 9 wt % nano-TiO₂ will be best for practical use.

CONCLUSIONS

Phenylethynyl-terminated PMRs thermosetting PI and its nano-SiO₂ nanocomposites were synthesized and analyzed. FTIR and XPS analyses indicated that the surfaces of the nano-SiO₂ slightly react to the PI. FESEM micrographs showed that nano-SiO₂ was homogeneously dispersed in the PI at low content, whereas agglomerate is dispersed in the presence of high filling content. TGA of the nanocomposites indicated that the decomposition temperature of the PI/SiO₂ nanocomposites was increasing as the increasing of filling contents when the nano-SiO₂ contents were below 9 wt %, but it showed a decreased trend as the increasing of nano-SiO₂ contents when the nano-SiO₂ content was above 9 wt %. The friction and wear properties studies showed that the nano-SiO₂ contributed to the decreasing of the friction coefficient and wear rates of the PI. In synthesis consider of the low friction coefficient and wear rates, the PI/SiO₂ nanocomposite of 9 wt % content could be promising material used as tribo-material in dry sliding condition against GCr15 steel.

References

- Mittal, K. L. *Polyimides: Synthesis, Characterization and Application*; Plenum: New York, 1998.
- Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Practical Guide to Polyimides*; iSmithers Rapra Publishing: Shrewsbury, 2007.
- Hergenrother, P. M.; Smith, J. G., Jr. *Polymer* 1994, 35, 4857.
- Hergenrother, P. M. *SAMPE J* 2000, 36, 30.
- Ho, C. Y.; Lee, J. Y. *J Appl Polym Sci* 2006, 100, 1688.
- Mark, J. E. *Acc Chem Res* 2006, 39, 881.
- Chen, B. K.; Chiu, T. M.; Tsay, S. Y. *J Appl Polym Sci* 2004, 94, 382.
- Cai, H.; Yan, F. Y.; Xue, Q. J. *Mater Sci Eng A* 2004, 364, 94.
- Shi, Y. Y.; Mu, L. W.; Feng, X. *J Appl Polym Sci* 2011, 121, 1574.
- Tanaka, A.; Umeda, K.; Yudasaka, M.; Suzuki, M.; Ohana, T.; Yumura, M.; Iijima, S. *Tribol Lett* 2005, 19, 135.
- Satyanarayana, N.; Skandesh Rajan, K. S.; Sinha, S. K.; Shen, L. *Tribol Lett* 2007, 27, 181.
- Serafini, T. T.; Delvigs, P. G.; Lightsey, R. *J Appl Polym Sci* 1972, 16, 905.
- Wang, J. Z.; Yan, F. Y.; Xue Q. J. *Tribol Lett* 2009, 35, 181.
- Haldorai, Y.; Lyoo, W. S.; Noh, S. K.; Shim, J. J. *React Funct Polym* 2010, 70, 393.
- Garcia, M.; Rooij, M.; Winnubst, L.; Zyl, W. E.; Verweij, H. *J Appl Polym Sci* 2004, 92, 1855.
- Xiong, M.; You, B.; Zhou, S.; Wu, L. *Polymer* 2004, 45, 2967.
- Tai, H.; Sargienko, A.; Silverstein, M. S. *Polymer* 2001, 42, 4473.
- Yu, Y. Y.; Chen, C. Y.; Chen, W. C. *Polymer* 2003, 44, 593.
- Wang, Q. H.; Xu, J.; Shen, W. *Tribol Intl* 1997, 30, 193.
- Schwartz, C. J.; Bahadur, S. *Wear* 2003, 237, 261.