

Synthesis and Properties of Organosoluble Polyimide/Clay Hybrids

SHENG-HUEI HSIAO,^{1*} GUEY-SHENG LIOU,² LI-MING CHANG¹

¹ Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, Third Section, Taipei 10451, Taiwan, Republic of China

² Department of Chemical Engineering, I-Shou University, 1 Hsuen-Cheng Road, First Section, Ta-Hsu Hsiang, Kaohsiung 84008, Taiwan, Republic of China

Received 14 March 2000; accepted 20 August 2000

ABSTRACT: A soluble polyimide prepared from 7,7'-bis(4-aminophenoxy)-4,4',4'-tetramethyl-2,2'-spirobichroman and 4,4'-hexafluoroisopropylidenediphthalic anhydride was mixed with organo-modified montmorillonite or synthetic mica in *N,N*-dimethylacetamide. The content of the clay minerals was 1, 2, and 4 wt %, respectively. Transparent, flexible, and tough films could be cast from the hybrid solutions. The hybrid films were characterized with wide-angle X-ray scattering (WAXS), transmission electron microscopy, thermomechanical analysis, thermogravimetric analysis, and differential scanning calorimetry. The WAXS results revealed that the montmorillonite was dispersed more homogeneously than the synthetic mica in the polyimide matrix. In both polyimide/clay hybrids the addition of clay caused thermal expansion coefficients to decrease, and the thermal stability was slightly enhanced. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2067–2072, 2001

Key words: organosoluble polyimide/clay hybrid; nanocomposite

INTRODUCTION

Polyimides have excellent thermal stability and mechanical properties, and attempts are being made to use them for different applications in a variety of advanced technologies.^{1,2} Interest in these materials is particularly high in areas related to microelectronics, where miniaturization, large-scale integration, and high-speed signal processing in semiconductor-based components are important technical issues. With the ever-increasing sophistication in electronics devices (smaller and faster), new demands are being placed on the materials comprising these devices.

It would be desirable to reduce the thermal expansion coefficient (TEC), moisture pickup, and dielectric constant, because these properties of polyimides are not sufficient for advanced electronics uses.

Clay is an inexpensive material. It has high mechanical strength and chemical resistance toward acid and alkali treatment. Montmorillonite is a clay mineral consisting of layered silicates (1 nm thick). Typically the layers of such silicates are composed of octahedral alumina or magnesia sandwiched in between two tetrahedral silica sheets. When three-valent aluminum ions are partially substituted by divalent magnesium ions, or divalent magnesium ions are partially replaced by lithium ions, the individual layers are anionically charged. Counterions such as sodium, potassium, or calcium are located in the interlayer

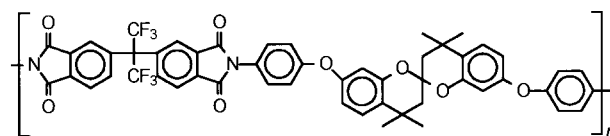
Correspondence to: S.-H. Hsiao (shhsiao@ttu.edu.tw).

Journal of Applied Polymer Science, Vol. 80, 2067–2072 (2001)
© 2001 John Wiley & Sons, Inc.

galleries.³ The presence of gallery ions is responsible for the water swelling of clay minerals. In addition to natured bentonite sources, layered silicates are readily available by synthetic routes, for example, by heating talcum with Na_2SiF_6 or by combining magnesium sulfate and lithium chloride with water-soluble sodium silicate. Ion-exchange reactions of Na^+ or K^+ with various organic cations such as alkylammonium cations render the normally hydrophilic silicate surface organophilic⁴ and achieve separation and dispersion of the silicate layers with the polymer matrix to form polymer-clay nanocomposites. Polymer matrix nanocomposites are a relatively new class of materials with dimensions typically in the range of 1–100 nm. In general, because of the ultrafine phase dimensions involved, nanocomposites exhibit new and improved properties when compared to their micro- or macrocomposite counterparts.⁵ The recent development of nanocomposites was stimulated by the development of thermoplastic organoclay/nylon 6 nanocomposites by Toyota.^{6–8}

Polyimide/clay nanocomposites were described by Toyota's researchers^{9,10} and Lan et al.¹¹ as derived from poly(amic acid) and montmorillonite. These polyimide/clay hybrids contained only a few percent of dispersed montmorillonite and showed excellent gas barrier properties and low TCE. However, problems may arise in these polyimide/clay systems because the poly(amic acid)s are thermally and hydrolytically unstable. The water released from imidization can create microvoids in bulk materials. Even in the production of thin films, the thermal imidization must be carefully controlled in order to minimize depolymerization and maximize the degree of imidization. Moreover, these polyimides and the corresponding hybrids are neither soluble nor fusible after the imidization process. This causes difficulties in fabrication and may limit their applications. We therefore used a soluble polyimide as the matrix to prepare organosoluble polyimide/clay nanocomposites and now report a preliminary analysis of their properties. The polyimide employed, SBA-6FDA, was derived from 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA) and a spiro-linked diamine 7,7'-bis(4-aminophenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman (SBA). It was soluble and thermoplastic as described in our previous publication.¹² The hybrid materials may find good applications in the microelectronics industry.

The structure of the SBA-6FDA is shown below.



SBA-6FDA

EXPERIMENTAL

Materials

The diamine SBA (mp 173–175°C) was prepared using a two-step reaction from 7,7'-dihydroxy-4,4',4',4'-tetramethyl-2,2'-spirobichroman and *p*-chloronitrobenzene.¹² The dianhydride 6FDA (Hoechst–Celanese) was used as received. Kunipia F (KF) was supplied by Kunimine Ind. Co. and is a Na^+ type montmorillonite with a cation exchange capacity of 119 meq/100 g. Somasif ME 100 (ME) is a synthetic fluoromica that was supplied by CO-OP Chemicals Co.; it is a Na^+ type synthetic mica with a cation exchange capacity of 70–80 meq/100 g.

Preparation of Organophilic Clays

In a 500-mL beaker were placed about 9 g of dodecylamine, 4.8 mL of concentrated hydrochloric acid, and 100 mL of water. This solution was heated at 80°C to dissolve the ammonium salt of dodecylamine. In another beaker, 20 g of KF or ME were dispersed in 400 mL of deionized water at 80°C. The dispersion of clay was added to the solution of the ammonium salt of dodecylamine, and this mixture was stirred vigorously for 1 h. A light brown precipitate was isolated by filtration, dispersed in 400 mL of hot water, and stirred for 1 h. This process was repeated twice to remove the residual ammonium salt of dodecylamine. The product was then filtered and dried.

Synthesis of SBA-6FDA Polyimide

An amount of 6FDA (3.55 g, 8 mmol) was added to a stirred solution of 4.18 g (8 mmol) of SBA in 50 mL of *m*-cresol containing 1 mL of isoquinoline at ambient temperature. After being stirred for 6 h, the solution was heated to reflux and held there for 3 h. After cooling, the resultant polymer solution was poured slowly with stirring into 500 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried to give a quantitative yield of the SBA-6FDA polyimide. The inherent viscosity of this polyimide was 0.73 dL/g, which was mea-

sured at a concentration of 0.5 g/dL in DMAc at 30°, indicating that its molecular weights were high enough to be useful. IR (film): 1784, 1728 (imide ring, C=O stretch), 1378 (C—N stretch), 723 cm⁻¹ (imide ring deformation).

Preparation of Hybrid Films

A polymer solution was made by dissolving 0.6 g of SBA-6FDA samples in 4 mL of *N,N*-dimethylacetamide (DMAc). A polymer solution was made by dissolving 0.6 g of SBA-6FDA sample in 4 mL of DMAc. An amount of dodecylammonium ion-intercalated clay (6, 12, and 24 mg) was stirred in 4 mL of DMAc at 90°C for 1 h. The clay dispersion was then added to the polyimide solution, and the mixture was stirred vigorously at ambient temperature for 5 h. Then the hybrid solution was spread onto a clear glass substrate, which was placed in a vented oven at 100°C for 5 h and 200°C for 12 h to yield a polyimide/clay hybrid film of approximately 20 μm.

Measurements

The FTIR spectra of the polyimide film samples were recorded on a Horiba FT-720 FTIR spectrometer. The degree of swelling of the layered silicates and interlayer distance of the nanocomposites was studied by wide-angle X-ray scattering (WAXS) using a Siemens Kristalloflex D5000 apparatus with Ni-filtered Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) and a scanning rate of 3°/min over a range of $2\theta = 5\text{--}40^\circ$. The TEC (α) was measured with thermomechanical analysis (TMA) on a DuPont TMA 2940 (room temperature to 300°C temperature range, 10°C/min heating rate). All the polyimide/clay hybrid films were determined in duplicate. The α values were determined from the dimension change in the 30–150°C range on their second TMA heating traces. Thermogravimetry (TG) was performed on a DuPont 951 TG analyzer. Experiments were carried out on 5–11 mg samples heated in flowing nitrogen or air (10 mL/min) at a heating rate of 20°C/min. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC 7 in flowing nitrogen at a heating rate of 20°C/min. The glass-transition temperatures (T_g s) were read as the midpoint of the heat capacity jump and were taken from the second heating scan after quick cooling from 400°C. The TMA was conducted with a Perkin–Elmer TMA 7 instrument using a loaded penetration probe, and an applied constant load of 30 mN

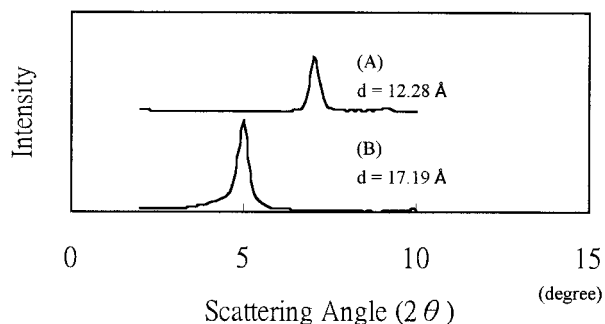


Figure 1 The X-ray diffraction curves of the synthetic mica ME (curve A) and the dodecylammonium ion-exchanged ME (curve B).

also determined the T_g values. These TMA experiments were conducted in duplicate from 30 to 300°C at a scan rate of 10°C/min. The apparent T_g values were taken as the onset temperatures of probe displacement on the second TMA traces. The morphology was examined by means of transmission electron microscopy (TEM) measurements on thin sections from the hybrid film using a Jeol 2000FX TEM with an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

Synthesis and Morphology

Two different types of layered silicates (montmorillonite KF and synthetic mica ME) were employed in the synthesis of polyimide/clay nanocomposites. Similar to procedures reported previously by Yano et al.,⁹ the layered silicates were swollen in hot water and ion exchanged with dodecylammonium ions. When the layered silicates were intercalated with the ammonium ions, they became organophilic and could be homogeneously dispersed in organic solvents such as DMAc. The X-ray diffraction curves of nonmodified and ion-exchanged synthetic mica ME and montmorillonite KF are presented in Figure 1 and Figure 2, respectively. After the exchange by dodecylammonium ions, the d spacing increased from 12.28 to 17.19 Å for ME and increased from 12.11 to 17.19 Å for KF. The interlayer distance of these two organophilic silicates was similar to that reported in the literature.³

Polyimide/clay nanocomposites based on polyimide SBA-6FDA containing 0, 1, 2, and 4 wt % organophilic layered silicates were prepared. The WAXS and TEM evidenced the formation of nano-

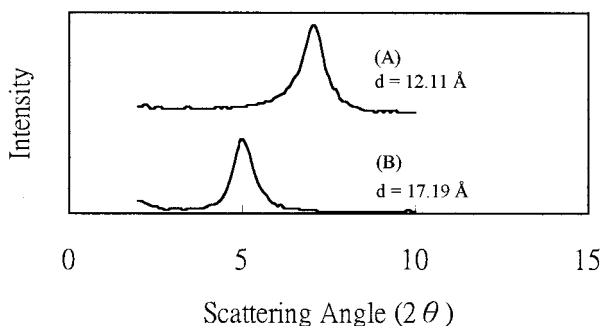


Figure 2 The X-ray diffraction curves of the monmorillonite KF (curve A) and the dodecylammonium ion-exchanged KF (curve B).

composites. The X-ray diffraction curves of the polyimide/clay hybrids are shown in Figure 3. In the polyimide/montmorillonite KFs with 1–4 wt % KF, there were no obvious clay peaks appearing in their X-ray diffraction curves. This indicated that these silicate layers of dodecylammonium-exchanged montmorillonite were exfoliated and dispersed homogeneously in the polyimide matrix. This was direct evidence that the polyimide/clay formed nanocomposites. A TEM micrograph of a section of the polyimide/clay hybrid film of 4KF/SBA-6FDA (polyimide SBA-6FDA containing 4 wt % organophilic montmorillonite) is shown in Figure 4. The dark lines are the intersections of the silicate layer of 1-nm thickness. This TEM photograph proves that most silicate layers of montmorillonite were dispersed homo-

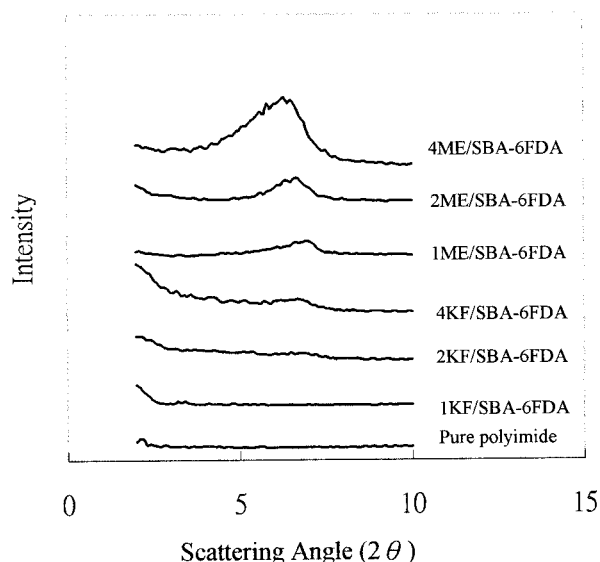


Figure 3 The X-ray diffraction curves of the soluble polyimide/clay hybrids.

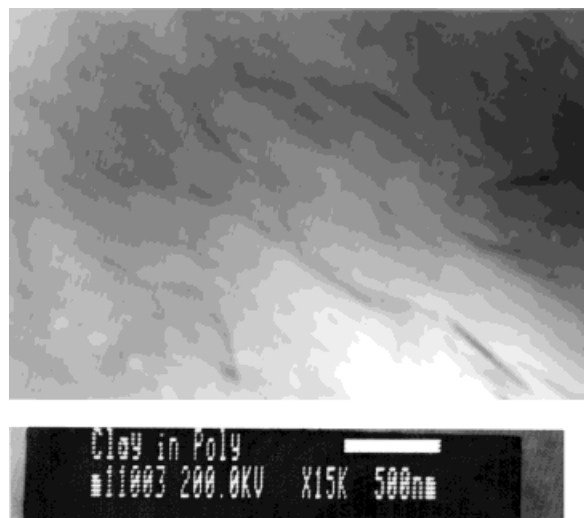


Figure 4 A TEM micrograph of a cross section of the polyimide/clay nanocomposite 4KF/SBA-6FDA.

neously into the polyimide matrix, although some, but very limited, clusters or agglomerated particles were also detected. However, as also shown in Figure 3, a part of layered silicates was not dispersed homogeneously into the polyimide matrix when ME was used. This may have been due to incomplete ion exchange or to the lower ion-exchange capacity (70–80 meq/100 g) of the synthetic mica as compared to KF (119 meq/100 g). It was demonstrated that the ability to delaminate and disperse the layered silicate in a medium was related to a number of factors, including the exchange capacity of the silicate, the polarity of the medium, and the chemical nature of the interlayer cations.^{13,14} These results indicated that the dispersibility of the organophilic clay in DMAc was important for synthesizing the polyimide/clay hybrids when the clay was dispersed at the molecular level. Nevertheless, all the hybrids films were as transparent as neat polyimide, even though the hybrid included 4 wt % montmorillonite or synthetic mica. This fact was attributable to the molecular level dispersion of clay with a size (approximately 200 nm) that was smaller than the wavelength of visible light.

Thermal Properties of Polyimide/Clay Hybrids

The thermal properties of the polyimide/clay hybrids were evaluated by TMA, DSC, and dynamic TG. Some thermal behavior data are summarized in Table I. Clay consists of stacked silicate sheets which have a much smaller TEC than that of polyimide. Therefore, it was expected that the

Table I Thermal Behavior Data of Soluble Polyimide/Clay Hybrids

Polymer Code	α^a (ppm/°C)	T_g (°C)		T_d^d (°C)		Char Yield ^e (%)
		DSC ^b	TMA ^c	In N ₂	In Air	
SBA-6FDA	66	254	247	485	477	31.5
1ME/SBA-6FDA	61	252	243	496	491	32.6
2ME/SBA-6FDA	57	243	240	475	507	33.4
4ME/SBA-6FDA	52	246	244	478	516	36.6
1KF/SBA-6FDA	63	250	240	489	496	32.5
2KF/SBA-6FDA	56	239	238	500	527	43.5
4KF/SBA-6FDA	55	223	238	489	500	43.8

^a The thermal expansion coefficient between 30 and 150°C by TMA at a heating rate of 10°C/min.

^b The midpoint temperature of the baseline shift on the second DSC heating trace of the sample after quenching from 400°C.

^c The onset temperature of probe displacement on the second TMA trace in which the TMA experiments were conducted with a penetration probe of 1.0-mm diameter and using an applied constant load of 30 mN (0.038-MPa stress) with a heating rate of 10°C/min.

^d The decomposition temperature at which 10% weight loss was recorded by TG at a heating rate of 20°C/min.

^e Residual weight percent at 800°C in nitrogen.

TEC of the polyimide/clay hybrid should be smaller than that of the neat polyimide. As shown in Table I, in both cases of polyimide/clay hybrids, the TEC was lowered when the addition of clay was higher than 2 wt %. The decreasing trend was similar to that reported in the literature.⁹ If polyimide is used for electronics applications, it is important to match the TEC to that of the silicon substrate. These hybrids would be suited for such a use. The T_g values of the polyimide/clay hybrids determined by DSC generally decreased with increasing addition of clay, especially for the montmorillonite KF hybrids. This may be attributed to the fact that the dodecyl groups in the organophilic clays provided a significant plasticizing effect, thus resulting in a reduction in the T_g . The decrease in T_g was more significant in the montmorillonite KF hybrid because of its better dispersion in the hybrids, as evidenced by the WAXS patterns. The T_g s (or called apparent $T_{g,s}$) of the polyimide/clay hybrids were also determined by TMA. The trend of T_g variation with the hybridized amount of clay was the same as that seen in the DSC experiments. However, the T_g s measured by TMA were slightly different from those determined by DSC experiments because of the distinctive nature of the testing methods. The results of the dynamic TG showed that in most cases the decomposition temperatures (at 10% weight loss) and the char residue of the polyimide/clay hybrids were higher than that of the neat polyimide. Therefore, the inclusion of organophilic clays in polyimide SBA-6FDA slightly increased the thermal stability of the hybrids.

Moreover, all the polyimide/clay hybrids could be cast into transparent, flexible, and creasable thin films. Although their tensile properties were characterized, it was rather difficult to correlate the strength and modulus with the type and the addition amount of the clay. Further research is needed to understand the effect of clay on the fracture of these nanocomposites.

CONCLUSIONS

We presented some examples of organosoluble polyimide/clay nanocomposites with layered silicates as the inorganic phase, in which the organosoluble polyimide SBA-6FDA was developed in this laboratory and the clays were intercalated with dodecylammonium ions. Transparent, flexible, and tough polyimide/clay hybrid films could be readily obtained by dispersing the organophilic clays in the polyimide solution, followed by solution casting. X-ray diffraction analysis and TEM showed that individual silicate layers were dispersed in the polymer matrix. The TEC of the composite films containing modest amounts of silicate was reduced because of the dispersion of silicate layers within the polymer matrix. The polyimide/clay hybrids generally exhibited a slightly increased thermal stability but a slightly decreased glass-transition temperature as compared to the neat polyimide.

REFERENCES

1. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*; Blackie: London, 1990.

2. Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
3. Zilg, C.; Mülhaupt, R.; Finter, J. *Macromol Chem Phys* 1999, 200, 661.
4. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1174.
5. Giannelis, E. P. *Adv Mater* 1996, 8, 29.
6. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
7. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1185.
8. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A Polym Chem* 1993, 31, 983.
9. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A Polym Chem* 1993, 31, 2493.
10. Yano, K.; Usuki, A.; Okada, A. *J Polym Sci Part A Polym Chem* 1997, 35, 2289.
11. Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 573.
12. Hsiao, S.-H.; Yang, C.-Y. *Macromol Chem Phys* 1997, 198, 2181.
13. Hofmann, H. *Angew Chem* 1956, 68, 53.
14. Hofmann, H. *Angew Chem* 1968, 80, 736.