

# Polyimide Nanocomposite with a Hexadecylamine Clay: Synthesis and Characterization\*

JIN-HAE CHANG,<sup>1</sup> DAE-KEUN PARK,<sup>1</sup> KYO JIN IHN<sup>2</sup>

<sup>1</sup> Department of Polymer Science and Engineering, Kumoh National University of Technology, Kumi 730-701, South Korea

<sup>2</sup> Department of Chemical Engineering, College of Engineering, Kangwon National University, Chunchon 200-701, South Korea

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**ABSTRACT:** A poly(amic acid) was prepared by the reaction of 3,3'-dihydroxybenzidine and pyromellitic dianhydride in *N,N*-dimethylacetamide. Hexadecylamine was used as an organophilic alkylamine in organoclay. Cast films were obtained from blend solutions of the precursor polymer and the organoclay. The cast film was heat treated at different temperatures to create polyimide (PI) hybrid films. We set out to clarify the intercalation of PI chains to hexadecylamine-montmorillonite (C<sub>16</sub>-MMT) and to improve thermal and tensile properties and the gas barrier. It was found that the addition of only a small amount of organoclay was enough to improve both the thermal and the mechanical properties of PIs. Maximum enhancement in the ultimate tensile strength for PI hybrids was observed for the blends containing 4% C<sub>16</sub>-MMT. The initial modulus monotonically increased with further increases in C<sub>16</sub>-MMT content. Water vapor permeability was decreased with increasing clay loading from 1 to 8 wt %. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2294–2301, 2002

**Key words:** polyimides; organoclay; nanocomposites

## INTRODUCTION

The heterocyclic polymer polyimide (PI) has been synthesized from cyclization of the precursor polymer. PIs are commonly synthesized from diamine and dianhydride in a two-stage process.<sup>1–3</sup> However, analogous to aromatic heterocyclic polymers, PIs are generally difficult to process because of their nonmelting behavior and poor solubility in conventional organic solvents. Consequently, potential applications are limited.<sup>4,5</sup>

Many attempts have been tried to modify and improve their processability but, in general, these rigid, rodlike polymers are insoluble and intractable or processable only under extreme conditions. This is attributable to the strong enthalpic interactions and the minimal increase in conformational entropy associated with their dissolution and/or melting.<sup>6</sup> A great deal of research effort on the PIs has been concentrated on increasing processability with minimal effect on the thermal stability and the mechanical properties of these polymers.<sup>7–9</sup>

Nanoscale composites of polymers with organoclay have been studied extensively.<sup>10–14</sup> In comparison with conventional polymer matrix composites, nanostructured materials often possess a combination of physical and mechanical proper-

Correspondence to: J.-H. Chang (changjinhae@hanmail.net).

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ties not present in conventional composites. Even at low concentrations of clay content (<10 wt %), the strength and modulus can be substantially increased, whereas the gas permeability rate is reduced because of the planar orientation of the clay sheets.

In our previous work,<sup>15</sup> dodecylamine ( $C_{12}$ -) and hexadecylamine ( $C_{16}$ -) were used as aliphatic alkylamines in organo-montmorillonite (MMT) in a PI matrix, and characterized not only by their thermal and mechanical properties but also by their gas permeability and morphology. Based on that work, we concluded that the hybrid effect of  $C_{16}$ -MMT was better than that of  $C_{12}$ -MMT in a PI matrix.

Mathias et al.<sup>16,17</sup> reported that a series of hydroxy-containing PIs, containing pendant hydroxyl groups ortho to the heterocyclic imide nitrogen, were prepared by solution condensation of aromatic dianhydrides with bisaminophenols. Polybenzoxazoles (PBOs) were synthesized from the PIs using a carboxy-benzoxazole intermediate. This approach is advantageous because two heterocyclic polymers, PI and PBO, can be obtained from the same starting materials with the proper heat treatment. They also observed that the OH-imide rearranged to a carboxy-benzoxazole, intermediately followed by decarboxylation, above 400°C, to result in a final fully aromatic benzoxazole product. The precursor was then converted to a high-temperature heterocyclic polymer that has high thermal and mechanical properties. In this study, we examine the synthesis of an aromatic precursor polymer bearing biphenyllic hydroxyl groups and the thermal cyclization from precursor to PI. Our approach is based on the reaction of 3,3'-dihydroxybenzidine (DHB) and pyromellitic dianhydride (PMDA), which is a precursor of PI. We synthesized PI/organoclay hybrids using  $C_{16}$ -MMT by a solution intercalation method. This study examines the thermal and mechanical properties and the morphologies of PI hybrids.

## EXPERIMENTAL

### Materials

Source clay, Kunipia-F ( $Na^+$ -MMT), was obtained from Kunimine Co., Japan. By screening  $Na^+$ -MMT with a 325-mesh sieve to remove impurities, we obtained a clay having a cationic exchange capacity of 119 mequiv/100 g. Hexade-

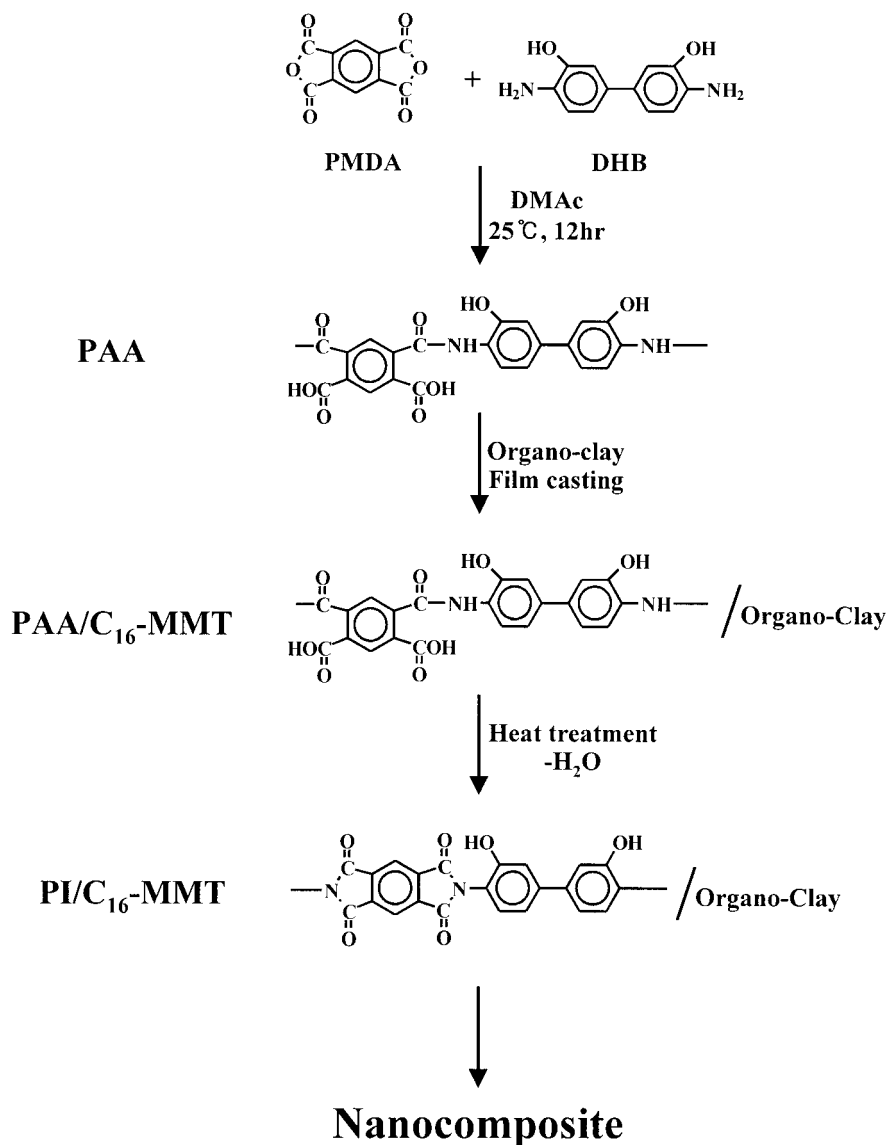
cylamine was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. All reagents were purchased from either TCI (Tokyo, Japan) or Aldrich. Commercially available solvents were purified by distillation. DHB and PMDA were also commercially available, and were used as received. *N,N*-Dimethylacetamide (DMAc) was purified and dried over molecular sieves before use. Common reagents were used without further purification.

### Preparation of Organophilic-MMT and PI/Organophilic-MMT Hybrid Films

A dispersion of  $Na^+$ -MMT was added to the solution of ammonium salt of hexadecylamine ( $C_{16}$ -). This organophilic-MMT, termed  $C_{16}$ -MMT, was obtained through a multistep route.<sup>12,18</sup>

Poly(amic acid) (PAA) was synthesized from DHB and PMDA in DMAc by the low-temperature method.<sup>19</sup> DBH [5.0 g (23 mmol)] and DMAc (50 mL) were placed in a 250-mL, three-neck flask. This mixture was stirred at 0°C for 30 min under a nitrogen atmosphere. PMDA [5.04 g (23 mmol)] in DMAc was added to the solution. The solution was stirred vigorously at 0°C for 1 h, and then at room temperature for 12 h, yielding a 10 wt % DMAc solution of PAA. The inherent viscosity of the resulting PAA solution in DMAc was 1.50 dL/g, measured at a concentration of 0.4 g/dL at 30°C.

Because the synthetic procedures for polymer/organoclay nanocomposites with different weight percentages of  $C_{16}$ -MMT were very similar, only a representative example for the preparation of PI/ $C_{16}$ -MMT (2 wt %) is given. A mixture of 50.0 g of the DMAc dispersion of 0.8 g  $C_{16}$ -MMT, 40.0 g of PAA solution, and excess DMAc was stirred vigorously at room temperature for 1 h. The solution was cast onto glass plates, and the solvent was evaporated in a vacuum oven at 50°C for 1 day. The films were then cleaned in an ultrasonic cleaner three times for 5 min each. These films with solvent removed were dried again in a vacuum oven at 50°C for 1 day. The film thickness was 10–15  $\mu$ m. The films were then thermally treated at different heat-treatment temperatures to heterocyclize.<sup>7–9</sup> No fixed tools were used for orientation on the glass plate during heat treatment, given that orientation exerts an influence on some characteristics of film specimens, such as tensile properties and morphology. The chemical structures of each polymer are shown in Figure 1.



**Figure 1** Preparation of PI/organoclay hybrid.

### Characterization

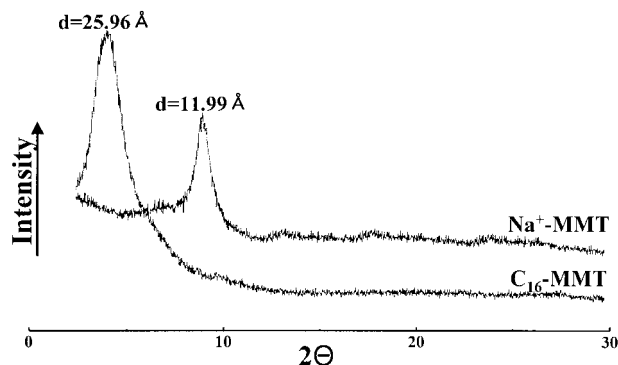
Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used on a DuPont 910 instrument (DuPont, Wilmington, DE) at a heating rate of 20°C/min. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Rigaku X-ray diffractometer (D/Max-IIIB; Rigaku, Tokyo, Japan), using Ni-filtered Co-K $\alpha$  radiation. The scanning rate was 2°/min over a range of  $2\theta = 2\text{--}30^\circ$ .

The tensile properties of the solution-cast films were determined using an Instron mechanical tester (Model 5564) at a crosshead speed of 2 mm/min. The specimens were prepared by cutting

strips 5 × 70 mm long. An average of at least eight individual determinations was used. The experimental uncertainties in tensile strength and modulus were  $\pm 1$  MPa and  $\pm 0.05$  GPa, respectively.

The water vapor permeability rates were measured following ASTM E-96 and using a MOCON (Model DL 100). The values of water vapor transmission rate were obtained at 38°C.

The morphology of the fractured surfaces of the extrusion samples was investigated using a Hitachi S-2400 (Hitachi, Japan) scanning electron microscope (SEM). The fractured surfaces were sputter-coated with gold using an SPI sputter



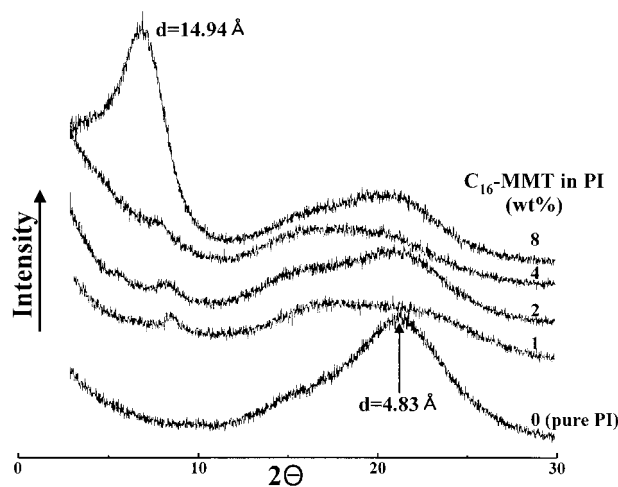
**Figure 2** XRD patterns of  $\text{Na}^+$ -MMT and  $\text{C}_{16}$ -MMT.

coater for enhanced conductivity. TEM micrographs of ultrathin sections of PI/ $\text{C}_{16}$ -MMT hybrid samples were taken on an EM 912 Omega transmission electron microscope (Omega Optical, Brattleboro, VT) using an acceleration voltage of 120 kV.

## RESULTS AND DISCUSSION

### Dispersibility of Organoclay

Figure 2 shows the XRD patterns of the  $\text{Na}^+$ -MMT and  $\text{C}_{16}$ -MMT. The apparent peak of the organo-MMT was observed to have longer inter-layer spacing than that of  $\text{Na}^+$ -MMT. The inter-layer spacings were  $2\theta = 8.60^\circ$  ( $d = 11.99 \text{ \AA}$ ) for  $\text{Na}^+$ -MMT and  $2\theta = 3.95^\circ$  ( $d = 25.96 \text{ \AA}$ ) for  $\text{C}_{16}$ -MMT, respectively.



**Figure 3** XRD patterns of PI/ $\text{C}_{16}$ -MMT hybrids as a function of organoclay loading.

**Table I** Effect of  $\text{C}_{16}$ -MMT Content on Thermal Stabilities of PI/Clay Hybrid Films

Clay (wt %)	$T_D^i$ <sup>a</sup> (°C)	$T_D^{\text{max}}$ <sup>b</sup> (°C)	$\text{wt}_R^{900}$ <sup>c</sup> (%)
0	386	495	59
1	403	513	59
2	411	514	60
4	414	518	62
8	416	518	64

<sup>a</sup> Initial weight reduction onset temperature.

<sup>b</sup> Maximum weight reduction onset temperature.

<sup>c</sup> Weight percent of residue at 900°C.

The X-ray diffraction curves of pure PI and 1–8 wt % PI/ $\text{C}_{16}$ -MMT hybrid films are represented in Figure 3. With increasing organoclay content from 1 to 4 wt %, PI/ $\text{C}_{16}$ -MMT films showed a small diffraction peak at  $2\theta = 7.56^\circ$  ( $d = 13.57 \text{ \AA}$ ), as opposed to the diffraction peak at  $2\theta = 3.95^\circ$  ( $d = 25.96 \text{ \AA}$ ) for  $\text{C}_{16}$ -MMT. This peak value indicates the possible presence of partial intercalated clay layers of organoclay dispersed in PI. When the amount of organoclay increased to 8 wt %, a strong peak appeared at  $2\theta = 6.87^\circ$ , corresponding to a  $d$ -spacing of  $14.94 \text{ \AA}$ . This shift from 25.96 to  $14.94 \text{ \AA}$  in the  $d$ -spacing of the  $\text{C}_{16}$ -MMT layers after imidization can be explained by the fact that PAA molecules outside the MMT layers squeezed the clay layers during the solvent removal process in imidization, causing a reduction in the spacing between the clay layers.<sup>20</sup> This also implies that a large amount of organoclay cannot be exfoliated in the PI, and exists in the form of an intercalated layer structure as a result of dehydration to PI.

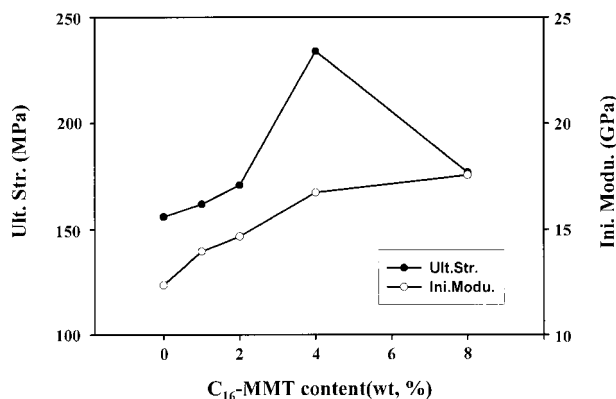
### Thermal Stability

The thermal stabilities of PI and their nanocomposites in  $\text{N}_2$  were studied by TGA. Table I sum-

**Table II** Tensile Properties of PI/ $\text{C}_{16}$ -MMT Hybrid Films

Clay (wt %)	Ultimate Strength (MPa)	Initial Modulus (GPa)	E.B. <sup>a</sup> (%)
0	156	12.36	2
1	162	13.96	2
2	171	14.67	2
4	234	16.75	2
8	177	17.67	2

<sup>a</sup> Elongation percent at break.



**Figure 4** Effects of C<sub>16</sub>-MMT loading on tensile properties of PI/C<sub>16</sub>-MMT hybrids.

marizes the experimental results. Initial weight loss ( $T_D^i$ ) was observed at 386–416°C, depending on the composition of the clay in the PI hybrids. The  $T_D^i$  of the PI/C<sub>16</sub>-MMT hybrids is increased with increases of the organoclay content in the range studied. At 2 wt % loss of the PI/C<sub>16</sub>-MMT, the  $T_D^i$  is increased by 17 and 30°C for PI with the organoclay content of 1 and 8 wt %, respectively. This increase in the thermal stability of the hybrids may result from the barrier effect of the MMT layer structure, as well as the strong interaction between the organoclay and PI molecules.<sup>21,22</sup> The temperatures at which maximum rates of weight loss were observed ranged from 495 to 518°C. The weight of the residue at 900°C increased with clay loading from 1 to 8 wt %, ranging from 59 to 64%. A comparison of the thermal stability values leads to the conclusion that the hybrids with higher organoclay contents are more thermally stable, although all the nanocomposites show fairly good thermal stabilities.

### Mechanical Properties

As shown in Table II, addition of C<sub>16</sub>-MMT to the matrix polymer significantly increased tensile

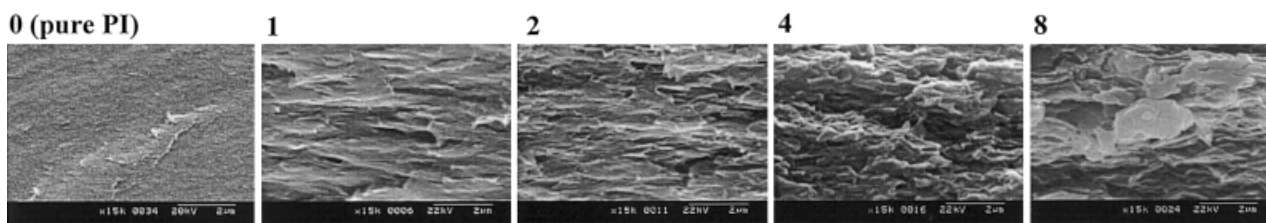
properties of the hybrids. The strength of the hybrids containing even 1% of C<sub>16</sub>-MMT content was higher than that of pure PI. At 4% C<sub>16</sub>-MMT, the strength value of PI hybrid was 1.5 times higher than that of pure PI. For PI/C<sub>16</sub>-MMT hybrid, the strength values increased linearly with increasing organoclay content up to 4 wt % and then decreased above 4% C<sub>16</sub>-MMT content. As shown in Table II, the values of the ultimate strength increased from 156 to 234 MPa and then decreased to 177 MPa with increasing organoclay content from 0 to 8 wt % (see Fig. 4). This suggests that the C<sub>16</sub>-MMT domains can agglomerate above 8% organoclay content in the PI matrix. This was cross-checked by SEM and TEM.

The initial modulus increased with increasing amounts of organoclay in the polymer matrix. The effects of C<sub>16</sub>-MMT content on the modulus are listed in Table II: the values of the initial moduli increased from 12.36 to 17.67 GPa with increasing organoclay content (Fig. 4). This enhancement of the modulus is ascribed to the high resistance exerted by the MMT itself. Additionally, the stretching resistance of the oriented backbone of the polymer chain in the gallery also contributes to the enhancement of the modulus. The percentage values of elongations at break of all the samples were 2%, and remained constant regardless of organoclay loading.

### Morphology

SEM micrographs of fracture surfaces of PI with different C<sub>16</sub>-MMT contents from 0 to 8 wt % are shown in Figure 5. The micrographs of the PI hybrids from 1 to 4 wt % clay contents showed dispersed platelet orientation morphology and the wave patterns appeared to be uniformly distributed over the fracture surface. When the clay content was increased to 8 wt %, however, agglomerated clay particles resulting from increasing clay content were observed in the PI hybrids.

### PI / C<sub>16</sub>-MMT (wt%)

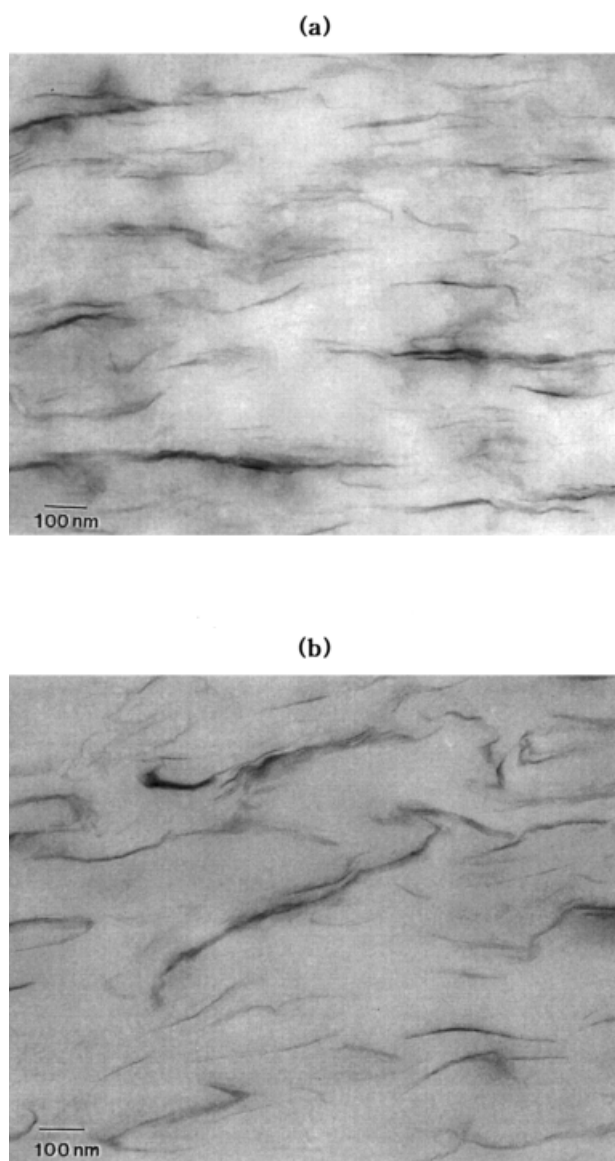


**Figure 5** SEM micrographs of PI hybrids as a function of C<sub>16</sub>-MMT loading ( $\times 15,000$ ).



This is in agreement with the mechanical property trends, which illustrate that tensile strength decreased drastically when the clay content was 8 wt % for PI/C<sub>16</sub>-MMT (see Table II).

Considering the preceding results, the existing state of clay particles could be determined to affect the tensile properties and morphologies of each polymer/clay hybrid. In the case of low clay contents (below 4 wt %), the clay particles may be dispersed in the polymer matrix without a large agglomeration of particles. On the other hand, the agglomerated structure formed and became denser in the polymer matrix at 8 wt % clay content.



**Figure 6** TEM micrographs of PI/C<sub>16</sub>-MMT hybrid films containing (a) 4 wt % and (b) 8 wt % C<sub>16</sub>-MMT.

**Table III** Permeability of PI/C<sub>16</sub>-MMT Hybrid Film

Clay (wt %)	Water Vapor (cm <sup>3</sup> /m <sup>-2</sup> day <sup>-1</sup> )	
	PI	$P_c/P_p^a$
0	86.97	1.00
1	79.21	0.91
2	76.58	0.88
4	16.20	0.18
8	10.76	0.12

<sup>a</sup> Relative permeability rate.

More direct evidence for the formation of a true nanoscaled composite was provided by using TEM analysis of an ultramicrotomed section. The micrograph in Figure 6(a) displays well-dispersed individual MMT layers, apparent as dark lines, for the 4 wt % C<sub>16</sub>-MMT hybrid film. Compared to this result, the 8 wt % C<sub>16</sub>-MMT hybrid film shows more banded or aggregated lines in Figure 6(b).

#### Water Vapor Permeability

Because we are interested in developing polymeric materials with improved barrier properties, we studied the permeability of water vapor in PI hybrid films. The results of the effect of clay loading on the barrier characteristics of the nanocomposite films are summarized in Table III. Water vapor permeabilities calculated from the data are shown as relative permeabilities [composite permeability/polymer permeability ( $P_c/P_p$ )]. As shown, there was an 82% reduction in the permeability coefficient for the 4 wt % PI/organoclay film, as compared to that of the PI film without clay loading. Interestingly, the permeability of the hybrid was reduced by nearly an order of magnitude at only 8 wt % organoclay in spite of aggregation of clay particles in the polymer matrix. This dramatic lowering of permeability in the hybrid is ascribed to the presence of dispersed large aspect ratio clay layers in the polymer matrix, as shown in other nanocomposite cases.<sup>23-25</sup>

#### Optical Translucency

The synthesis of polymeric nanocomposites, although more difficult than the fabrication of traditional composites, does not represent a serious problem when the material is not destined for optical applications. Optical nanocomposites

PI/C<sub>16</sub>-MMT (wt%)0  
(pure PI)

1

2

4

8

(amic acid) was synthesized by me low-temperature solution polymerizat 3,3'-dihydroxybenzidine (DHB) ; melleitic dianhydride (PMDA) ; -dimethylacetamide (DMAc). The c s were thermally treated at varie peratures. The polyimide containing roxyl group rearranges to result in aromatic polybenzoxazole rboxylation at temperatures higher th C. These stepwise cyclizations we itered by elemental analysis, FT-IR ; R. Microanalysis results confirmed ical compositions of poly(amic ac imide, and polybenzoxazole, respectio lo-dehydration from poly(amic acid) imide exhibit between 150 and 250°C . And cyclo-decarboxylation benzoxazole were shown 400-500°C. samples were stable up to 625°C ogen and were shown excellent therm alities. Polybenzoxazole showed bet mal stability than polyimide. But hanical property of polybenzoxazole v er than that of polyimide. Howev imide showed crystalline pattern in w le X-ray. Otherwise, polybenzoxaz benzoxazole are not soluble at e natic polyimides (PIs) belong to a cla heterocyclic polymers known for the mechanical properties, high resistan solvents, excellent thermo-oxidati lity, and low density<sup>1-5</sup>. The anding properties have been the drivin behind investigation of these polyme use in fibers, films, coatings a osites<sup>6-8</sup>. Also, polybenzoxazol ) are rodlike polymers w ided chain conformations. The ners, as like PI, have excellent therm oxidative stability and good hydrolyt solvent resistance<sup>1-5</sup>. rditionally, PIs and PBOs are general echanical properties. PIs are comr nthesized from diamine and dianhydi two-stage process. And PBOs nthesized by the reaction of die hydroxy benzene with terephthalic ac ophthalic acid. The direct th arrangement of pyromellitic dianhy (MDA) and 3,3'-dihydroxybenzidine (I s monomers in polyimide has not ported, although such derivatives en utilized in the synthesis has PIs BOs, respectively. Less well known rmal rearrangements of iydroxyl-containing PIs to PBOs. PBOs en synthesized from PIs via a carb nnoxazole intermediate. This app we examine the synthesis of the a precursor polymer bearing bipi hydroxyl groups and the s cyclization from precursor to PBO with different thermal conditions. thermal rearrangement may als monitored by means of i spectroscopy (FT-IR), nuclear m resonance (NMR), and thermogra analyzer (TGA), as we will be dis subsequently. And then, we investiga thermal stabilities, tensile propertie solubilities with cyclization from pr to PBO via PL

**EXPERIMENTAL**  
*Synthesis of the polymer*

**Figure 7** Translucency of PI/C<sub>16</sub>-MMT hybrid films as a function of organoclay loading.

must be perfectly translucent so as to reduce light scattering and obtain high values of translucency and optical purity. To prevent light scattering, the dispersed phase should have an average size inferior to the visible light wavelength<sup>12</sup> (i.e., 400–800 nm).

Nanocomposite films are made of clay nanoparticles dispersed in a PI polymer matrix. The films, prepared by the solvent-casting process, are light brown in color, but highly translucent, and levels of translucency are not affected by increasing the C<sub>16</sub>-MMT content from 0 to 4 wt %, as shown in Figure 7. Because nanocomposites may have phase domains smaller than the wavelength of light, the materials may be translucent. The translucency of the nanocomposites comes from the nanoscale dispersion of the clay particles in the matrix polymer. The translucency, however, decreased with increases of the content of organoclay resulting from agglomeration of the clay particles. Compared to the films of 1–4 wt %, the film containing 8 wt % C<sub>16</sub>-MMT was shown to be slightly darker brown in Figure 7 (no such indications could be observed in this figure because of the printing process).

## CONCLUSIONS

We prepared and characterized heterocyclic polymer/hexadecylamine–MMT nanocomposites. The XRD and TEM of PI hybrids were in support of the formation of nanocomposite materials. The thermal stability and mechanical property of the nanocomposite were improved with organoclay content. From the permeability results, it becomes evident that the mass transfer process for the respective penetrants is highly dependent on the clay loading level and exhibits a nonlinear dependency. Overall, it was found that additions of small amounts of C<sub>16</sub>-MMT were enough to improve the properties of PI.

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## REFERENCES

1. Sroog, C. E. *Prog Polym Sci* 1991, 16, 561.
2. Mittal, K. L. *Polyimides: Synthesis, Characterization, and Applications*; Plenum Press: New York, 1984.

3. Feger, C.; Khojasteh, M. M.; Htoo, M. S. *Advances in Polyimide Science and Technology*; Technomic: Lancaster, PA, 1993.
4. So, Y. H.; Heeschen, J. P. *J Org Chem* 1997, 62, 3552.
5. Wolfe, J. F.; Arnold, F. E. *Macromolecules* 1981, 14, 909.
6. Huang, S. J.; Hoyt, A. E. *Trends Polym Sci* 1995, 3, 262.
7. Ballauff, M. *Angew Chem Int Ed Engl* 1989, 28, 253.
8. Tamai, S.; Yamashita, W.; Yamaguchi, A. *J Polym Sci Part A: Polym Chem* 1998, 36, 971.
9. Kim, K.; Ree, M. *J Polym Sci Part A: Polym Chem* 1998, 36, 1755.
10. Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem Mater* 1995, 7, 2145.
11. Usuki, A.; Koiwai, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Appl Polym Sci* 1995, 55, 119.
12. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 2493.
13. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. *Macromolecules* 1995, 28, 8080.
14. Lee, D. C.; Jang, L. W. *J Appl Polym Sci* 1996, 61, 11179.
15. Chang, J.-H.; Park, K. M. *Polym Eng Sci* 2001, 41, 1514.
16. Tullose, G. L.; Mathias, L. J. *Polymer* 1999, 40, 3463.
17. Tullose, G. L.; Powers, J. M.; Jeskey, S. J.; Mathias, L. J. *Macromolecules* 1999, 32, 3598.
18. Yang, Y.; Zhu, Z.; Yin, J.; Wang, X.; Qi, Z. *Polymer* 1999, 40, 4407.
19. Chang, J.-H.; Park, K. M. *Eur Polym J* 2000, 36, 2185.
20. Yano, K.; Usuki, A.; Okada, A. *J Polym Sci Part A: Polym Chem* 1997, 35, 2289.
21. Petrovic, X. S.; Javni, I.; Waddong, A.; Banhegyi, G. J. *J Appl Polym Sci* 2000, 76, 133.
22. Zhu, Z. K.; Yang, Y.; Yin, J.; Wang, X. Y.; Ke, Y. C.; Qi, Z. N. *J Appl Polym Sci* 1999, 3, 2063.
23. Ward, W. J.; Gaines, G. L.; Alger, M. M.; Stanley, T. J. *J Membr Sci* 1991, 55, 173.
24. Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 573.
25. LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl Clay Sci* 1999, 15, 11.