

# Colorless Polyimide Nanocomposite Films: Thermomechanical Properties, Morphology, and Optical Transparency

Hyo-Seong Jin, Jin-Hae Chang

Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi 730-701, Korea

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**ABSTRACT:** Polyimide (PI)/organoclay hybrid films were prepared by the solution intercalation method, using dodecyltriphenylphosphonium-mica ( $C_{12}$ PPh-Mica) as the organoclay. The variations with organoclay content of the thermomechanical properties, morphology, and optical transparency of the hybrids were examined for concentrations from 0 to 1.0 wt %. For low clay contents ( $\leq 0.5$  wt %), the clay particles are better dispersed in the matrix polymer, without the formation of large agglomerates of particles, than they are for high clay contents. However, agglomerated structures form and become denser in the PI matrix for clay contents  $\geq 0.75$  wt %. This is in agreement with the observed trends in the thermomechanical properties

and the optical transparency, which worsen drastically when the clay content of the  $C_{12}$ PPh-Mica/PI hybrids reaches 0.75 wt %. However, when the amount of organoclay in the hybrid is 0.75 wt %, the initial modulus of the hybrid film is at its maximum value. The PI hybrid films were found to exhibit excellent optical transparencies and to be almost colorless. It was found, however, that the transparency decreases slightly with increases in the organoclay content because of agglomeration of the clay particles. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 109–117, 2008

**Key words:** colorless polyimide; organoclay; nanocomposites

## INTRODUCTION

Despite its poor processability and solubility in common solvents, polyimide (PI) is used widely in various industries. Aromatic PIs are highly resistant to solvents, exhibit excellent mechanical properties, excellent thermal and thermo-oxidative stabilities, and have low densities.<sup>1–6</sup>

Lightly colored PIs can be prepared from dianhydride and diamine monomers with substituted fluorine moieties in their side groups. It has been shown that lightly colored or colorless PIs have better solubility, thermal stability, and optical transparency than traditional PIs, but have inferior moisture absorption and color intensity.<sup>7–10</sup> Optically transparent PI films have in particular been widely used in electro-optical devices and semiconductor applications.<sup>11–14</sup>

Organic/inorganic hybrids have generated substantial recent interest because of their desirable organic and inorganic characteristics and their resulting potential as single molecular scale composites, as well as the new properties arising from the interac-

tions between the two components.<sup>15–17</sup> By introducing a few weight percent of an inorganic clay into the polymer matrix, the resulting nanoscaled composites have been found to exhibit significant improvements in many properties over those of the polymer matrix, such as in their mechanical and thermal properties, and in their flame retardance.<sup>18–20</sup>

In our previous paper,<sup>21</sup> we demonstrated that large improvements in the thermomechanical properties of PI nanocomposites can be achieved by the addition of an organoclay. This enhancement of the thermomechanical properties can be satisfactorily explained in terms of the effective dispersion of the clay in the nanocomposites that results from the large aspect ratio of the clay particles.

In this study, we investigated the synthesis of an aromatic precursor polymer bearing trifluoromethyl-substituted benzene in its side groups and the thermal cyclization of this precursor to produce a colorless PI. Our approach is based on the reaction of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and bis(3-aminophenyl) sulfone (APS), which is a precursor of colorless PIs. We synthesized PI/organoclay hybrid films containing the organoclay  $C_{12}$ PPh-Mica by using a solution intercalation method. This paper discusses the variations of the thermomechanical and optical properties and the morphology of the colorless PI hybrid films with organoclay content.

Correspondence to: Jin-Hae Chang (changjinhae@hanmail.net).

TABLE I  
Intercalation Conditions of Polyimide Hybrid Films

Sample	Temp (°C)/time (h)/pressure (Torr)
PAA	0/1/760 → 0/2/760 → 25/13/760 → 25/25/760 → 50/2/760 → 80/1/1
PI	110/0.5/760 → 140/0.5/760 → 170/0.5/760 → 195/0.85/760 → 220/0.85/760 → 235/2/760

## EXPERIMENTAL

### Materials

The source clay, Kunipia-F (Na<sup>+</sup>-Mica), was obtained from Kunimine Co. By screening the Na<sup>+</sup>-Mica with a 325-mesh sieve to remove impurities, we obtained a clay with a cationic exchange capacity of 119 meq/100 g. All reagents were purchased from TCI and Aldrich Chemical Co. Commercially available solvents were purified by distillation. 6FDA and APS 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 the organoclay and the colorless PI hybrid films

The organically modified mica used in this study was synthesized via the ion exchange reaction between Na<sup>+</sup>-Mica and dodecyltriphenylphosphonium chloride (C<sub>12</sub>PPh-Cl<sup>-</sup>). This organophilic mica was obtained with a multi-step procedure,<sup>22</sup> and is denoted C<sub>12</sub>PPh-Mica.

Poly(amic acid) (PAA) was synthesized from 6FDA and APS in DMAc with a low temperature method.<sup>23</sup> 4.60 g (1.85 × 10<sup>-2</sup> mol) of APS and 30 mL of DMAc were placed in a 250 mL three-necked flask. This mixture was stirred at 0°C for 30 min under a nitrogen atmosphere. 8.23 g (1.85 × 10<sup>-2</sup> mol) of 6FDA in 40 mL DMAc was added to the solution. The solution was stirred vigorously at 0°C for 2 h, and then at room temperature for 13 h, yielding a 15.5 wt % DMAc solution of PAA.

Since the synthetic procedures for the various polymer/organoclay nanocomposites with differing C<sub>12</sub>PPh-Mica contents were the same, only one procedure, that for the preparation of PI/C<sub>12</sub>PPh-Mica (0.5 wt %), is described here. A mixture of 20 mL of the DMAc dispersion of 0.064 g C<sub>12</sub>PPh-Mica, 13 g of PAA solution, and excess DMAc (20 mL) was stirred vigorously at room temperature for 24 h. The solution was cast onto glass plates, and the solvent was evaporated in a vacuum at 50°C for 2 h and at 80°C for 1 h. The resulting films were then thermally treated at various heat treatment temperatures to promote heterocyclization.<sup>24-26</sup> No fixed tools were

used in the orientation of the glass plate during heat treatment since orientation does influence some characteristics of film specimens, such as tensile properties and morphology. Table I summarizes the intercalation conditions employed for the preparation of each hybrid film.

The PIs are soluble in DMAc, which was used in the measurement of solution viscosity. The inherent viscosities of the resulting PI hybrid films in DMAc (see Table II) were found to range from 0.47 to 0.60 dL/g, measured at a concentration of 0.1 g/dL at 30°C. Considering the fact that the clay contents excluded out of the hybrid sample, these numbers can be regarded as being constant. The chemical structures relevant to the synthetic route are shown in Scheme 1.

### Characterization

Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Rigaku (D/Max-IIIb) X-ray diffractometer, using Ni-filtered Cu-Kα radiation. The scanning rate was 2°/min over a range of 2θ = 2–12°. A differential scanning calorimeter (DSC S-650) and a thermogravimetric analyzer (TGA-1000) were used on a SCINCO instrument with a heating rate of 20°C/min.

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 with dimensions of 5 × 70 mm. Averages of at least ten individual determinations were used. The experi-

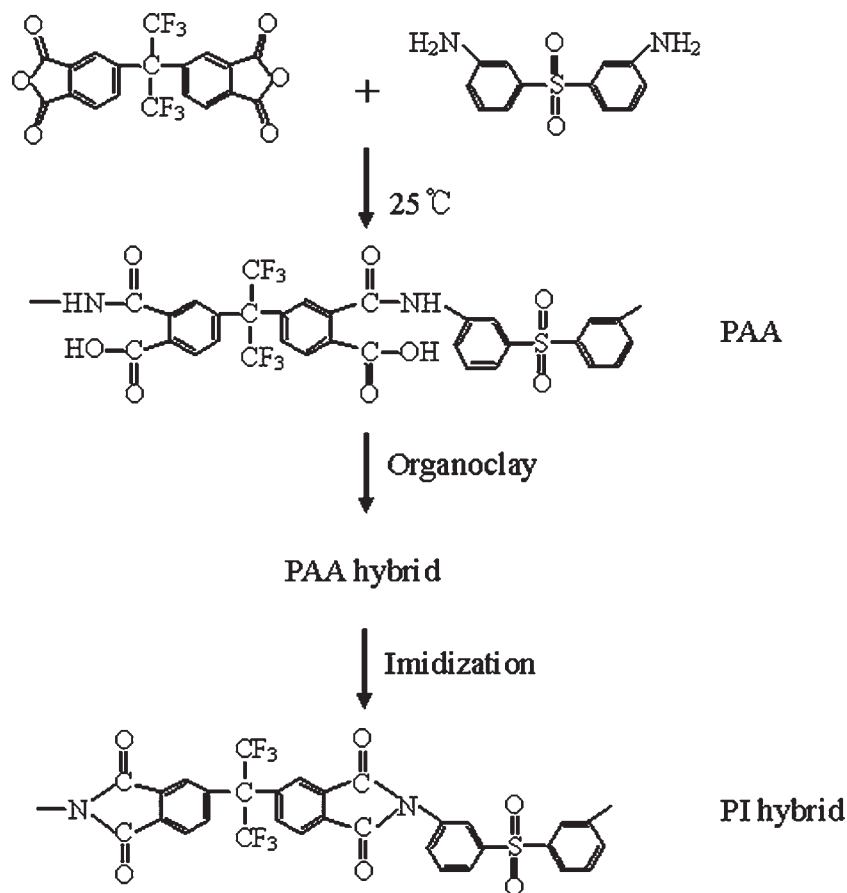
TABLE II  
Thermal Properties of Polyimide Hybrid Films

Organoclay (wt %)	I. V. <sup>a</sup>	T <sub>g</sub> (°C)	T <sub>D</sub> <sup>ib</sup> (°C)	w <sub>tR</sub> <sup>800c</sup> (%)
0 (pure PI)	0.47	198	496	54
0.25	0.52	196	506	54
0.50	0.60	197	519	53
0.75	0.57	196	517	54
1.00	0.53	197	513	54

<sup>a</sup> Inherent viscosities were measured at 30 °C by using 0.1 g/100 mL solution in a *N,N*-Dimethylacetamide.

<sup>b</sup> At a 2% initial weight-loss temperature.

<sup>c</sup> Weight percent of residue at 800 °C.



**Scheme 1** Synthesis of colorless PI nanocomposites.

mental uncertainties in tensile strength and modulus were  $\pm 1$  MPa and  $\pm 0.05$  GPa respectively.

The morphologies of the fractured surfaces of the extrusion samples were investigated using a Hitachi S-2400 scanning electron microscope. The fractured surfaces were sputter-coated with gold using an SPI Sputter Coater for enhanced conductivity. TEM photographs of ultrathin sections of the PI/ $C_{12}$ PPh-Mica hybrid films were obtained with an Leo 912 OMEGA transmission electron microscope using an acceleration voltage of 120 kV at the Korea Basic Science Institute.

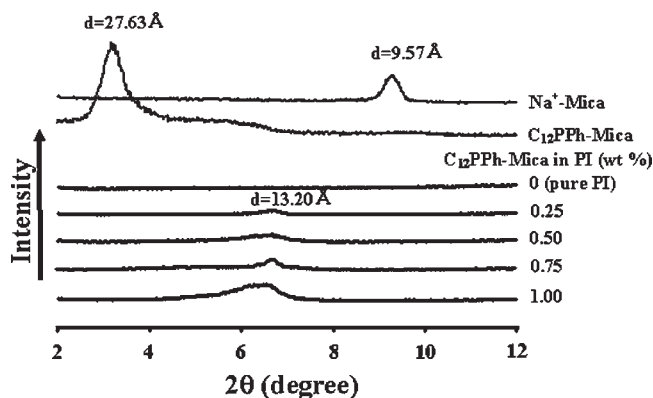
The color intensity of the polymer films was evaluated with a Minolta spectrophotometer (Model CM-3500 days). The measurements were obtained for 80  $\mu\text{m}$  thick films. Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded on a SCINCO S-1130.

## RESULTS AND DISCUSSION

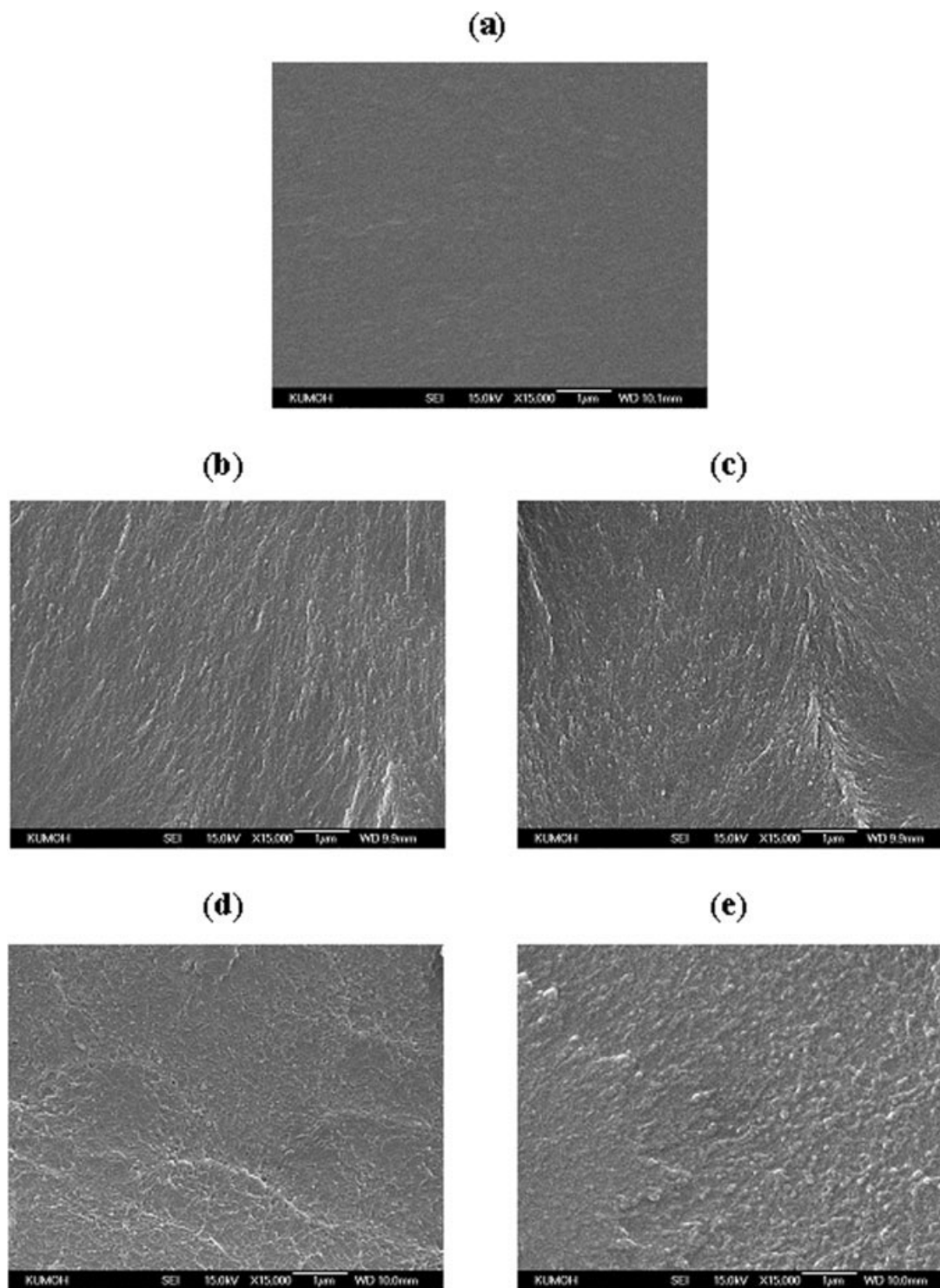
### XRD

The X-ray scattering intensities of the pristine clay, organoclay, and PI hybrid films with various clay contents are shown in Figure 1. The measured

$d_{001}$ -spacing of  $\text{Na}^+$ -Mica was 9.57  $\text{\AA}$  ( $2\theta = 9.23^\circ$ ). After cation exchange between  $\text{Na}^+$ -Mica and dodecyltriphenylphosphonium chloride ( $C_{12}\text{PPh-Cl}^-$ ), the  $d_{001}$ -spacing was found to be 27.63  $\text{\AA}$  ( $2\theta = 3.19^\circ$ ). It appears that  $\text{Na}^+$  is replaced by  $C_{12}\text{PPh-Cl}^-$  during the organic modification and that the  $C_{12}\text{PPh-Mica}$  prepared in this study is well dispersed in DMAc. In general, a larger interlayer spacing should assist the intercalation of the polymer chains. It should also



**Figure 1** XRD patterns of  $\text{Na}^+$ -Mica,  $C_{12}\text{PPh-Mica}$ , and PI hybrids with various organoclay contents.



**Figure 2** SEM photographs of PI/C<sub>12</sub>PPh-Mica hybrids containing (a) 0 (pure PI), (b) 0.25, (c) 0.50, (d) 0.75, and (e) 1.0 wt % of C<sub>12</sub>PPh-Mica.

lead to easier dissociation of the clay, which results in hybrids with better clay dispersion.<sup>27,28</sup>

For the PIs containing up to 0.50 wt % organoclay content, only a slight peak at  $d = 13.20 \text{ \AA}$  was present in the XRD results for the cast films. A substantial increase in the intensities of the XRD peaks was

observed for increases in the clay loading from 0.50 to 1.0 wt %, which suggests that the dispersion is better at a lower clay loading than at a higher clay loading. The presence of this peak indicates that there are partially intercalated organoclay layers dispersed in the PI. This shift from 27.63 to 13.20  $\text{\AA}$  in

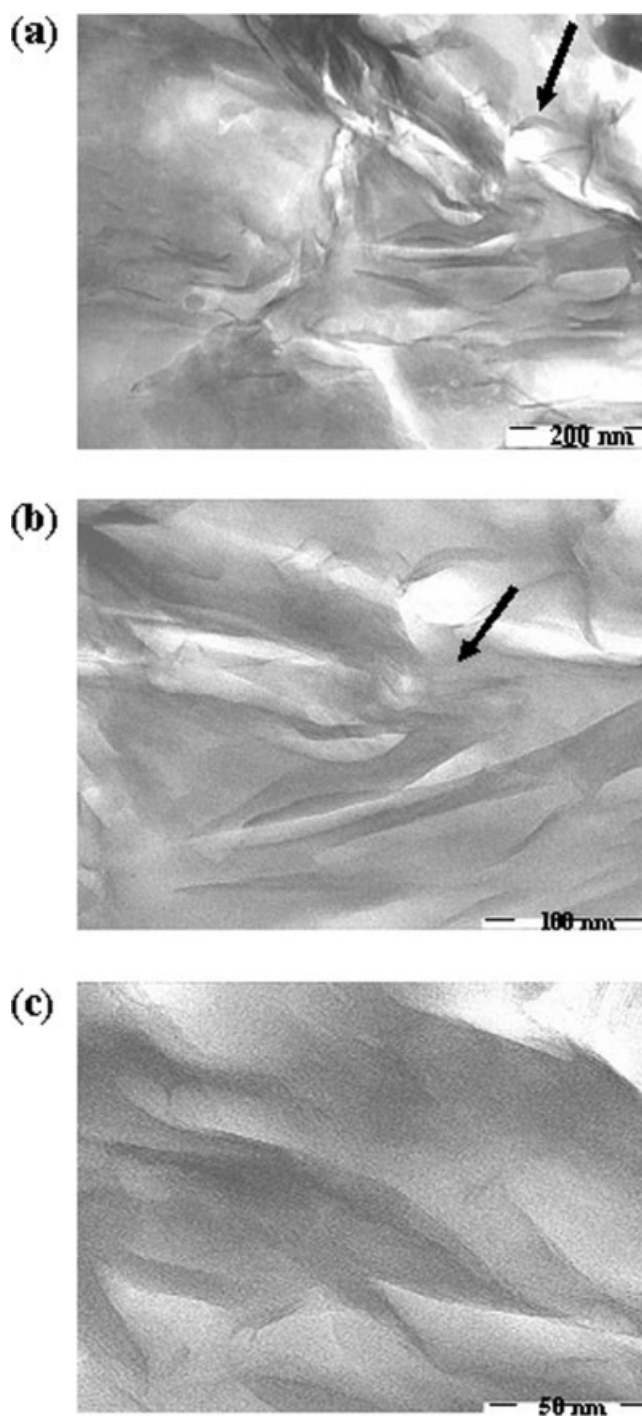
the  $d$ -spacing of the C<sub>12</sub>PPh-Mica layers after imidization can be explained by the squeezing of the clay layers by the PAA molecules outside the mica layers during the imidization solvent removal process, which reduces the spacing between the clay layers. This also implies that there is no large quantity of exfoliated organoclay in the PI, and the organoclay is present in the form of an intercalated layer structure as a result of the dehydration of the PI.

Although XRD is very useful for measuring the  $d$ -spacing of ordered immiscible and ordered intercalated polymer nanocomposites, it is not adequate for the analysis of disordered and exfoliated materials.<sup>29,30</sup> Electron microscopy provides the principal evidence in our study for the formation of the nanocomposites.

### Morphology

The morphologies of hybrid films containing up to 1.0 wt % C<sub>12</sub>PPh-Mica in a PI matrix were examined by observing their fracture surfaces with scanning electron microscopy (SEM), and the results are shown in Figure 2. Figure 2 shows that clay phases formed in the hybrid films as a result of increasing the organoclay content from 0 to 1.0 wt %. The PI hybrid films containing 0.25 and 0.50 wt % C<sub>12</sub>PPh-Mica were found to have morphologies consisting of clay domains, 80–100 nm in size, well dispersed in a continuous PI phase (see Figs. 2(b) and (c)). Figure 2(d) shows micrographs of the 0.75 wt % C<sub>12</sub>PPh-Mica/PI hybrid film, which contains clay phase 150–200 nm in diameter. There are voids and some deformed regions in the 1.0 wt % C<sub>12</sub>PPh-Mica/PI hybrid film in Figure 2(e), which may be attributed to the coarseness of the fractured surface. However, the fractured surfaces were found to be more deformed when the hybrid films contained more clay, which is probably a consequence of the agglomeration of clay particles. When the clay content was increased above 0.75 wt %, the presence of agglomerated clay particles due to increasing clay content was observed in the PI hybrids. This is in agreement with the thermomechanical property trends that are discussed in the next section: the thermomechanical properties and optical transparency worsen drastically when the PI/C<sub>12</sub>PPh-Mica clay content reaches 0.75 wt % (see Tables II–IV).

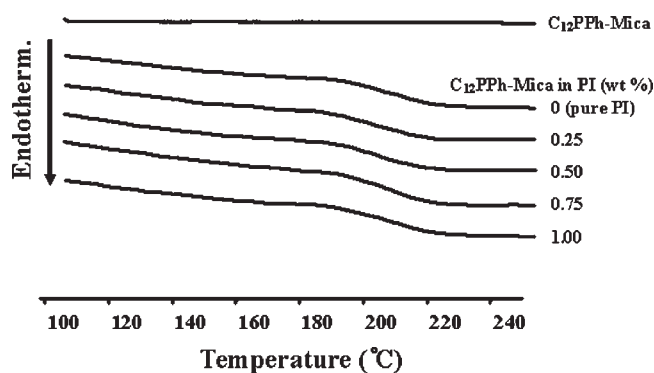
To examine the dispersion of the clay layers in the hybrid films in more detail, we carried out TEM studies. Typical TEM photographs at various magnifications of a 0.5 wt % hybrid film are shown in Figure 3. The dark lines are the intersections of the 1 nm thick sheet layers. Figure 3 shows that the organoclay is somewhat dispersed in the polymer matrix at all magnification levels, although some of



**Figure 3** TEM micrographs of 0.5 wt % C<sub>12</sub>PPh-Mica in PI hybrid films increasing the magnification levels from (a) to (c).

the clays are agglomerated at size levels greater than approximately 20 nm.

We conclude that for low clay contents ( $\leq 0.5$  wt %) the clay particles are better dispersed in the matrix polymer, without a large agglomeration of particles, than they are for high clay contents; agglomerated structures form and become denser in the PI matrix



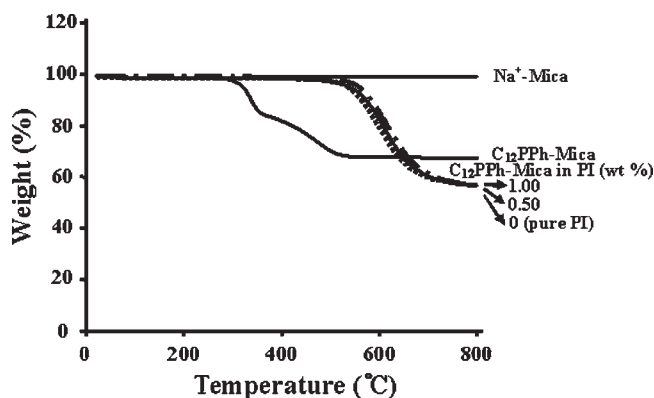
**Figure 4** DSC thermograms of  $C_{12}PPh$ -Mica and PI hybrids with various organoclay contents.

for clay contents above 0.75 wt %. This is consistent with the XRD and SEM results shown in Figures 1 and 2 respectively.

### Thermal behavior

The DSC traces of the organoclay, pure PI, and PI hybrid films are shown in Figure 4. The DSC thermograms show that the glass transition temperatures ( $T_g$ ) of the PI hybrids are virtually constant for organoclay loadings in the range 0.25–1.0 wt %. Thus the effects of small amounts of dispersed clay layers on the free volume of the PIs are not significant, and the glass transition temperatures of the PI hybrids are not affected by increases in the organoclay loading. The thermal properties of the PI hybrid films with various  $C_{12}PPh$ -Mica contents are listed in Table II.

The results of the thermal gravimetric analyses (TGA) for pure PI and PI hybrid films with 0.25–1.0 wt % organoclay are shown in Table II and Figure 5. The TGA curves in Figure 5 indicate that the samples undergo no weight loss below 100°C,



**Figure 5** TGA thermograms of  $Na^+$ -Mica,  $C_{12}PPh$ -Mica, and PI hybrids with various organoclay contents.

**TABLE III**  
Tensile Properties of Polyimide Hybrid Films

Organoclay (wt %)	Ult. Str. (MPa)	Ini. Mod. (GPa)	E. B. <sup>a</sup> (%)
0 (pure PI)	87	2.62	5
0.25	90	3.01	3
0.50	103	3.16	4
0.75	85	3.41	3
1.00	84	3.11	3

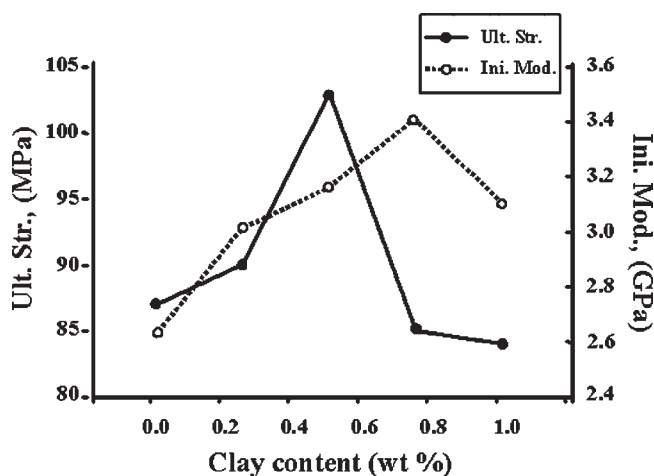
<sup>a</sup> Elongation percent at break.

and thus there is no water in the samples. The TGA curves of PI and its hybrids are nearly the same until about 400°C. Above this temperature, the initial thermal degradation temperature ( $T_D^i$ ) varies with the organoclay loading of the hybrids. Table II summarizes the  $T_D^i$  of the PI hybrids (at 2% weight loss), which increase with the amount of organoclay. The  $T_D^i$  of the PI hybrids vary between 496 and 519°C with increases in the clay content from 0 to 1.0 wt %; the largest increase in  $T_D^i$  with respect to that of pure PI is 23°C, for 0.50 wt %  $C_{12}PPh$ -Mica/PI. The addition of clay enhances the initial decomposition temperatures because of its action as an insulator and as a mass-transport barrier to the volatile products generated during decomposition.<sup>31–33</sup> When the organoclay content is 1.0 wt %, the value of  $T_D^i$  is 513°C. This decrease in  $T_D^i$  is probably due to some agglomeration of the filler particles above a critical organoclay content, which is consistent with the XRD and SEM results shown in Figures 1 and 2 respectively. In contrast to the trend in the thermal properties, the weight of the residue at 800°C was found to be fairly constant for clay loadings between 0 and 1.0 wt %, ranging from 53 to 54% as shown in Table II.

We conclude from the above results that the introduction of inorganic components into organic polymers can improve their thermal stability, and that these improvements occur because clays have good thermal stability.

### Mechanical properties

The mechanical tensile properties of PI hybrid films with various filler contents are shown in Table III. The strength and modulus values were found to be enhanced with respect to those of PI for filler contents up to a critical content, with inferior values above that content. It appears that there is a critical amount of filler beyond which the filler's reinforcing capacity diminishes. For example, the strength of the 0.50 wt %  $C_{12}PPh$ -Mica hybrid film is 103 MPa (see Table III), which is about 20% higher than that of pure PI (87 MPa). When the organoclay content is



**Figure 6** Effect of the clay loading on the ultimate strength and initial modulus of the PI hybrid films.

1.0 wt %, the strength is 84 MPa. This decrease in the ultimate tensile strength is mainly due to the agglomeration of filler particles above a critical organoclay content.<sup>34,35</sup>

A similar trend was observed for the initial modulus. The value of the initial modulus increases from 2.62 to 3.41 GPa with increases in the C<sub>12</sub>PPh-Mica content up to 0.75 wt % and is lower (3.11 GPa) for 1.0 wt % organoclay content. The variations of the ultimate strength and the initial modulus with filler content are shown in Figure 6. These enhancements of the tensile properties of PI are ascribed to the resistance exerted by the clay, and to the orientation and aspect ratio of the clay layers.<sup>36–38</sup> In short, the reinforcing effect does not obey a rule of mixtures in this system. Similar results have previously been obtained with other polymer nanocomposites.<sup>37</sup>

The elongation at breakage of the hybrid films was found to be virtually unchanged by variation in the organoclay content, i.e., it varied from 3 to 5% as the organoclay content was increased from 0 to 1.0 wt %. This result is characteristic of materials reinforced with stiff inorganic materials.

### Optical transparency

The films prepared with the solvent casting process are almost colorless, and their levels of transparency vary with increases in the organoclay content from 0.25 to 1.0 wt %, as shown in Table IV. The  $b^*$  value of a pure PI film was found to be 1.49 and its degree of colorlessness to be almost the same as that of aliphatic poly(methyl methacrylate).<sup>39</sup> The values of  $b^*$  were found to increase with increases in the organoclay content, probably because of agglomeration of the clay particles. For example,  $b^*$  increases from 3.35 to 5.26 with increases in the organoclay content from 0.25 to 1.0 wt %. These values of  $b^*$  are significantly lower than those of conventional aromatic PI films such as Kapton 200KN.

The transparency decreases slightly with increases in the organoclay content. The hybrid film containing 1.0 wt % C<sub>12</sub>PPh-Mica is slightly more yellow than the 0.25–0.75 wt % films (see Figs. 7(b)–(d)), but there is still no problem with reading a letter through the film (see Fig. 7(e)). Because the levels of transparency are not affected significantly by increases in the organoclay content from 0 to 1.0 wt %, as shown in Figure 7, there is little difference between the optical transparencies of the samples. Moreover, since the hybrid films have phase domains smaller than the wavelengths of visible light (i.e., 400–800 nm), the materials are transparent even for clay loadings up to 1.0 wt %.<sup>19,21</sup>

The color intensities can be elucidated from the cut-off wavelengths ( $\lambda_o$ ) of the UV–vis absorption spectra. Figure 8 shows the UV–vis spectra of the PI hybrid films. The values for the PI hybrid films were recorded in the range 272–286 nm for organoclay contents from 0 to 1.0 wt %. The PI hybrid films containing up to 0.50 wt % C<sub>12</sub>PPh-Mica exhibit the highest transmittance and lower  $\lambda_o$  than the other hybrid films. The lightest colored pure PI could be explained the shortest  $\lambda_o$  because the presence of the CF<sub>3</sub> groups in the monomers significantly reduces charge transfer complex formation and the intermolecular interactions,<sup>39,40</sup> and the superior transparency of these 6FDA-based PIs may be due to the limited electronic

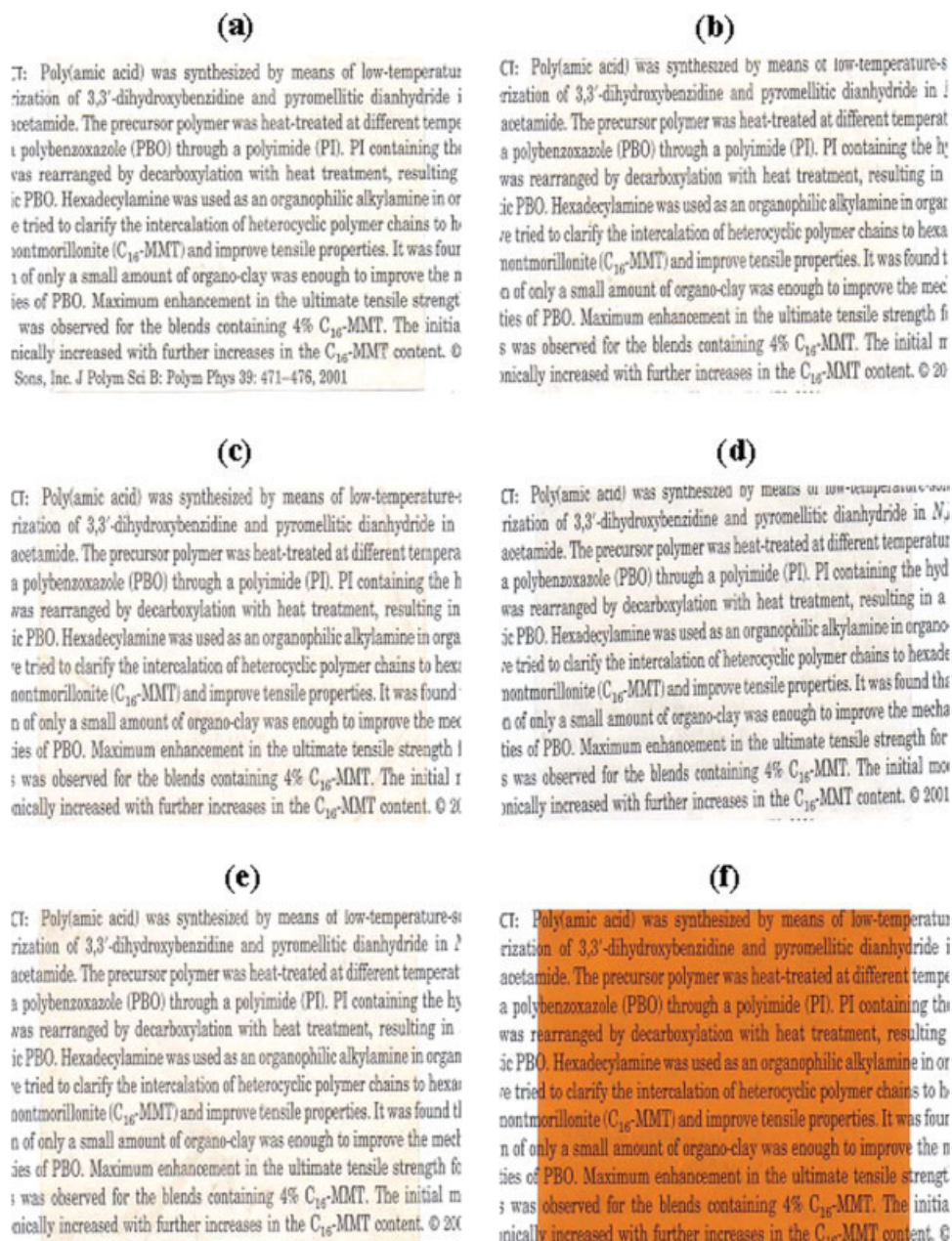
**TABLE IV**  
Color Coordinates of Polyimide Hybrid Films

Organoclay (wt %)	Film thickness ( $\mu\text{m}$ )	L <sup>a</sup> (White-black)	a <sup>*b</sup> (Red-green)	b <sup>*c</sup> (Yellow-blue)
0 (pure PI)	80	89.72	–1.25	1.49
0.25	78	88.19	–1.24	3.35
0.50	78	86.34	–1.09	3.66
0.75	81	84.49	–0.80	4.62
1.00	77	85.46	–1.08	5.26
Kapton <sup>®</sup> 200KN	50	65.50	12.27	44.69

<sup>a</sup> An L of 100 is white, and 0 is black.

<sup>b</sup> A positive a\* of indicates red, and a negative a\* indicates green.

<sup>c</sup> A positive b\* of indicates yellow, and a negative b\* indicates blue.



**Figure 7** Photographs of PI/organoclay hybrid films containing (a) 0 (pure PI), (b) 0.25, (c) 0.50, (d) 0.75, and (e) 1.0 wt % of C<sub>12</sub>PPh-Mica. Kapton® 200KN was shown in (f) as a reference. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

conjugation along their backbones.<sup>41,42</sup> However, the values of  $\lambda_o$  were found to increase with linear increases in the organoclay content, which is due to agglomeration of the clay particles. The values of  $\lambda_o$  were found to vary in the range 275–284 nm with increases in the C<sub>12</sub>PPh-Mica content from 0.50 to 1.0 wt %. Evidence for clay agglomeration was found with XRD and SEM, as shown in Figures 1 and 2.

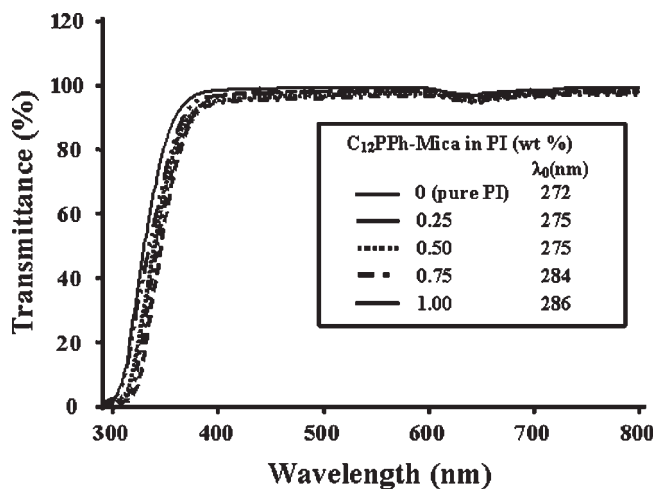
## CONCLUSIONS

We synthesized PI/organoclay hybrid films using C<sub>12</sub>PPh-Mica as an organoclay with a solution inter-

calation method based on the reaction of 6FDA and APS, which is a precursor of colorless PIs. The present study investigated the dependence of the thermomechanical and optical properties of the PI/organoclay hybrid films on their organoclay content. The XRD and electron microscopy studies indicated that the as-prepared PI hybrid films are nanocomposite materials. In addition, the SEM and TEM studies confirmed that the organoclays are intercalated, and revealed some agglomeration of the clay particles within the polymer matrix.

The thermomechanical properties of the nanocomposites were found to improve with increases in the





**Figure 8** UV-vis transmittance (%) of PI hybrid films with various organoclay contents.

organoclay loading up to a critical loading. The results of the electron microscopic analyses indicated that for clay loadings below 0.5 wt %, the clay particles are dispersed in the polymer matrix without substantial agglomeration. On increases in the clay content to 0.75 wt % and above; however, it was found that a denser agglomerated structure forms in the polymer matrix. For this hybrid system, the largest improvements in the thermal stability and ultimate strength were found for a C<sub>12</sub>PPh-Mica loading of only 0.5 wt %.

The values of  $b^*$  were found to vary from 1.49 to 5.26 with increases in the organoclay content from 0 to 1.0 wt %. The transparency only decreases slightly with increases in the organoclay content. The UV-vis measurements showed that the PI hybrid films have excellent transparency. The superior properties of these colorless PI hybrid films may be useful in many electronic applications, as well as in conventional composite fields.

## References

- Yokota, R.; Horiuchi, R.; Koichi, M.; Soma, H.; Mita, I. *J Polym Sci Polym Lett Ed* 1988, 49, 215.
- Feger, C.; Khojasteh, M. M.; Htoo, M. S.; *Advances in Polyimide Science and Technology*; Technomic: Lancaster, PA, (1993).
- Akinseye, T. D.; Harruna, I.; Bota, K. B. *Polymer* 1997, 38, 2507.
- Moy, T. M.; McGrath, J. E. *J Polym Sci Part A: Polym Chem Ed* 1903, 1988, 32.
- Ueda, M.; Nakayama, T. *Macromolecules* 1996, 29, 6427.
- Yano, K.; Usuki, A.; Okada, A. *J Polym Sci Part A: Polym Chem Ed* 1997, 35, 2289.
- Misra, A. C.; Tesoro, G.; Hougham, G.; Pendarkar, S. M. *Polymer* 1992, 33, 1078.
- Yang, C. P.; Chen, Y. C. *J Appl Polym Sci* 2005, 96, 2399.
- Matsuura, T.; Hakuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* 1991, 24, 5001.
- Park, S. H.; Kim, K. J.; So, W. W.; Moon, S. J.; Lee, S. B. *Macromol Res* 2003, 11, 157.
- Dupont, B. S.; Bilow, N. US Pat 4,592,925 (1986).
- Landis, A. L.; Naselow, A. B. US Pat 4,645,824 (1987).
- Higashi, K.; Noda, Y. Eur Pat 240249 (1986).
- Matsuura, T.; Ando, S.; Sasaki, S.; Yamamoto, F. *Electron Lett* 1993, 29, 2107.
- Pinnavaia, T. J.; Beall, G. W. *Polymer-Clay Nanocomposites*; Wiley: New York, 2001.
- Imai, Y.; Nishimura, S.; Abe, E.; Tateyama, H.; Abiko, A.; Yamaguchi, A.; Aoyama, T.; Taguchi, H. *Chem Mater* 2002, 14, 477.
- Lagaly, G. *Appl Clay Sci* 1999, 15, 1.
- Usuki, A.; Koiwai, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Appl Polym Sci* 1995, 55, 119.
- Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem Ed* 1993, 31, 2493.
- Osman, M. A.; Mittal, V.; Morbidelli, M.; Suter, U. W. *Macromolecules* 2003, 36, 9851.
- Chang, J.-H.; Park, D. K.; Ihn, K. J. *J Appl Polym Sci* 2002, 84, 2294.
- Chang, J.-H.; Kim, S. J.; Joo, Y. L.; Im, S. *Polymer* 2004, 45, 919.
- Chang, J.-H.; Park, K. M. *Eur Polym Mater* 2000, 36, 2185.
- Chang, J.-H.; Park, K. M. *Polym Eng Sci* 2001, 41, 2226.
- Petrovic, X. S.; Javni, I.; Waddong, A.; Banhegyi, G. J. *J Appl Polym Sci* 2000, 76, 133.
- Zhu, Z. K.; Yang, Y.; Yin, J.; Wang, X. Y.; Ke, Y. C.; Qi, Z. N. *J Appl Polym Sci* 1999, 3, 2063.
- Hsiao, S. H.; Liou, G. S.; Chang, L. M. *J Appl Polym Sci* 2001, 80, 2067.
- Ke, Y.; Lu, J.; Yi, X.; Zhao, J.; Qi, Z. *J Appl Polym Sci* 2000, 78, 808.
- Morgan, A. B.; Gilman, J. W. *J Appl Polym Sci* 2003, 87, 1329.
- Davis, C. H.; Mathias, L. J.; Gilman, J. W.; Schiraldi, D. A.; Shields, J. R.; Trulove, P.; Sutto, T. E.; Delong, H. C. *J Polym Sci Part B: Polym Phys Ed* 2002, 40, 2661.
- Fornes, T. D.; Yoon, P. J.; Hunter, D. L.; Keskkula, H.; Paul, D. R. *Polymer* 2002, 43, 5915.
- Fischer, H. R.; Gielgens, L. H.; Koster, T. P. M. *Acta Polym* 1999, 50, 122.
- Wen, J.; Wikes, G. L. *Chem Mater* 1996, 8, 1667.
- Chang, J.-H.; Park, D. K.; Ihn, K. J. *J Polym Sci Part B: Polym Phys Ed* 2001, 39, 471.
- Chang, J.-H.; Park, K. M.; Cho, D.; Yang, H. S.; Ihn, K. *J Polym Eng Sci* 2001, 41, 1514.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1998, 8, 1185.
- Chen, L.; Wong, S. C. *J Appl Polym Sci* 2003, 88, 3298.
- Zhang, Q.; Fu, Q.; Jiang, L. X.; Lei, Y. *Polym Int* 2000, 49, 1561.
- Yang, C. P.; Su, Y. Y. *Polymer* 2005, 46, 5778.
- Yang, C. P.; Chen, R. S.; Chen, K. H. *J Polym Sci Part A: Polym Chem Ed* 2003, 41, 922.
- Li, F.; Fang, S.; Ge, J. J.; Honigfort, P. S.; Chen, J. C.; Harris, F. W.; Cheng, S. Z. D. *Polymer* 1999, 27, 5964.
- Ma, S. L.; Kim, Y. S.; Lee, J. H.; Kim, J. S.; Kim, I.; Won, J. C. *Polymer (Korea)* 2005, 29, 204.