

Synthesis and Properties of Polyimide (Containing Naphthalene) Nanocomposites with Organo-Modified Montmorillonites

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ABSTRACT: 2,7-Bis(4-aminophenoxy) naphthalene (BAPN), a naphthalene-containing diamine, was synthesized and polymerized with a 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) to obtain a polyimide (PI) via thermal imidization. To enhance the thermal and mechanical properties of the polymer, PI–Montmorillonite (MMT) nanocomposites were prepared from a DMAc solution of poly(amic acid) and a DMAc dispersion of MMT, which were organo-modified with various amounts of *n*-dodecylamine (DOA) or cetylpyridium chloride (CPC). FTIR, XRD, and TEM (transmission electron microscopy) were used to verify the incorporation of the modifying agents into the clay structure and the intercalation of the organoclay into the PI matrix. Results demonstrated that the introduction of a small amount of MMT (up to 5%) led to the improvement in thermal stability and mechanical properties of

PI. The decomposition temperature of 5% weight loss ($T_{d,5\%}$) in N_2 was increased by 46 and 36°C in comparison with pristine PI for the organoclay content of 5% with DOA and CPC, respectively. The nanocomposites were simultaneously strengthened and toughened. The dielectric constant, CTE, and water absorption were decreased. However, at higher organoclay contents (5–10%), these properties were reduced because the organoclay was poorly dispersed and resulted in aggregate formation. The effects of different organo-modifiers on the properties of PI–MMT nanocomposite were also studied; the results showed that DOA was comparable with CPC. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2966–2972, 2006

Key words: polyimide; naphthalene; organoclay; nanocomposites; montmorillonite

INTRODUCTION

Polyimides (PIs) are versatile engineering polymers that have been widely used in many electronic applications because of their outstanding thermal stability, mechanical properties, and low dielectric constant. However, PIs are difficult to process because of their infusibility and their insolubility in most organic solvents.¹ The search for new PIs or PI hybrids with other organic or inorganic materials to improve processability, high glass transition temperatures (T_g), and mechanical properties has received significant attention from research communities over the past few years.² It is expected that polymer/inorganic hybrids or nanocomposite materials would exhibit unique, characteristic, and combined properties of both inorganic (retention of mechanical properties at high temperature and low thermal expansion) and organic polymer (toughness, ductility, and processability).³

When developing such PI hybrids, it is understood that the structural rigidity of dianhydrides contributes

to the increase of T_g in 300–400°C range. However, there are no suitable fabrication methods available to process such high T_g materials. Because of these limitations, many researchers have focused their attention on modification of the backbone structures of PIs. An approach, such as the incorporation of a flexible ether linkage and *meta*-oriented phenylene groups into the polymer backbone, has led to an increase in polymer chain flexibility and solubility of PIs, but has also lowered the effective upper use temperature of these polymers.⁴ To improve the heat resistance of this type of PI, few PIs containing naphthalene group have been developed.^{5,6} On the other hand, to enhance the thermal stability, mechanical strength, and electrical properties of polyimides, PI/clay hybrids have been under extensive study.^{7–18} Intercalation of polymers with clay has proved to be an effective method to prepare PI composites.⁷ Montmorillonite (MMT) is one of the most often used clay.¹⁰ MMT has a very high aspect ratio and is composed of silicate sheets about 1 nm thick with adsorbed exchangeable alkali or alkaline earth cations. Before the preparation of PI/MMT composites, modification is generally required. The alkali or alkaline earth ions of the hydrophilic MMT clay surface should be ion exchanged by the organic cations to provide a hydrophobic surface.¹² The commonly used agents are long carbon-chain alkyl ammo-

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nium salts, such as *n*-dodecylamine (DOA),^{8,12,13} In some studies, cetylpyridium chloride (CPC) was used as modifier instead.¹⁴

To prepare a new PI-MMT nanocomposite, we synthesized a diamine, 2,7-bis(4-aminophenoxy) naphthalene (BAPN), and polymerized it with 3,3',4,4'-benzophenonetetra carboxylic dianhydride (BTDA) to obtain a PI containing naphthalene. To improve the thermal and mechanical properties of this polyimide with ether linkages, we incorporated various amounts of organo-modified MMT to prepare PI-MMT nanocomposites. FTIR, XRD, and TEM (transmission electron microscopy) were used to identify the incorporation of the modifying agents into the clay structure and the intercalation of the organoclay into the PI matrix. TGA, DSC, and TMA were used to measure the thermal properties. The effects of different organic modifiers, DOA and CPC, on the thermal and mechanical properties, moisture absorption, and dielectric constant of PI-MMT hybrids were investigated.

EXPERIMENTAL

Materials

2,7-Dihydroxynaphthalene (Acros), *p*-chlorobenzene (Fluka), potassium carbonate (Fluka), hydrazine monohydrate (Kanto, Japan), 10% palladium on activated carbon (Acros), *N,N*-dimethyl acetamide (DMAc; Tedia), *n*-dodecylamine (Acros), and cetylpyridium chloride (Acros) were used as received without further purification. Kunipia F (Na-Montmorillonite) clay with cation exchange capacity of 119 meq/100 g was received from Kunimine Industries Co., Ltd. (Japan). 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA; Acros) was recrystallized from acetic anhydride to achieve the required purity.

Synthesis of 2,7-bis(4-aminophenoxy)naphthalene diamine

BAPN was prepared according to a procedure described in the literature.⁵ 2,7-Dihydroxynaphthalene was reacted with *p*-chloronitrobenzene via aromatic nucleophilic substitution in the presence of potassium carbonate. The resulting dinitro compound was subsequently reduced with hydrazine as the reducing agent and palladium as the catalyst to produce the diamine compound BAPN. M.p. 170–172°C.

IR (KBr) (cm^{-1}) 3395, 3444 (Ar-NH₂), 1220 (C—O—C str). ¹H-NMR (DMSO-*d*₆) δ 7.77 (2H, Hc), 7.06 (2H, Hb), 6.95 (2H, Ha), 6.82 (4H, Hd), 6.63 (4H, He), 5.0 (4H, NH₂). Elemental analysis: Anal. Calcd for C₂₂H₁₈N₂O₂ (%): C, 77.19; H, 5.26; N, 8.19. Found (%): C, 77.20; H, 5.26; N, 8.18. These results are comparable with literature data.⁵

Preparation of organophilic MMT clay

The organic clay was prepared by a cationic exchange reaction between the sodium cations on MMT surface and organic cations of intercalating agents. We have modified the procedure reported by Yano et al.⁸ in this investigation.

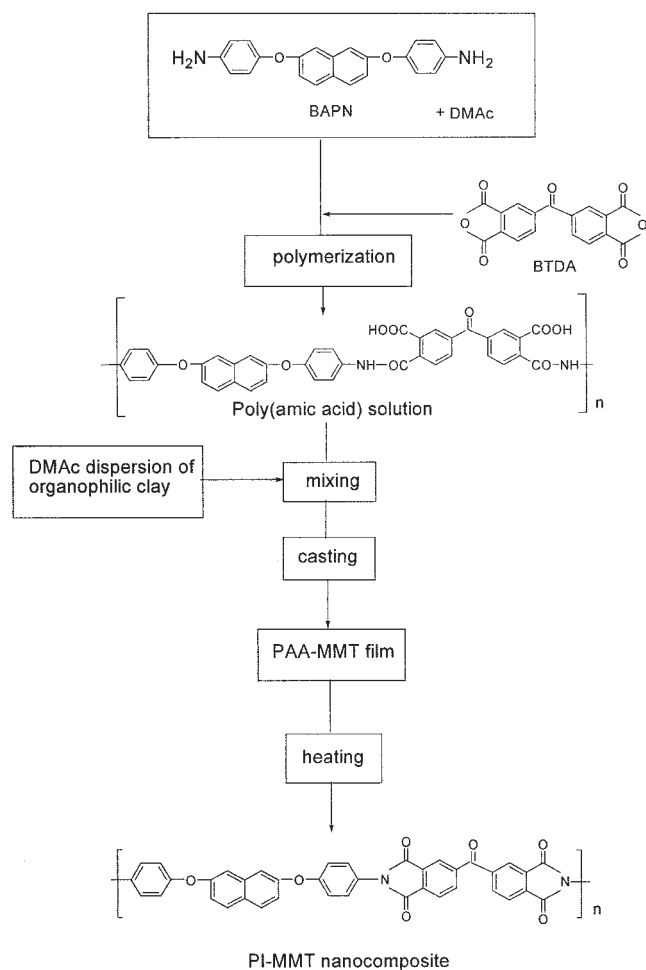
A mixture of 8.82 g DOA, 4.8 mL concentrated hydrochloric acid, and 100 mL distilled water was taken in a 500-mL beaker and heated to 80°C. Na-montmorillonite clay of 20 g was separately dispersed in 350 mL of deionized water at 80°C. The dispersion of MMT was added to the ammonium salt solution of DOA, and the mixture was stirred vigorously at 60°C for 12 h. The resulting organoclay was collected by filtration and washed with deionized water several times until no Cl⁻ was detected by AgNO₃. The organophilic montmorillonite (which is designated as DOA-MMT) was then dried in a vacuum oven at 80°C for 24 h. The dry solid was ground into a fine powder and screened with a 325-mesh sieve and stored for further use.

A similar procedure was utilized in the preparation of MMT modified with CPC (designated as CPC-MMT).

Preparation of PI-clay nanocomposite films

Most of the PI-clay nanocomposites were prepared by a two-stage process: poly(amic acid) (PAA) was first synthesized from dianhydride and diamine, then organophilic clay was added to prepare the composite.⁸ A flow chart for the preparation of PI-clay nanocomposite film is illustrated in Scheme 1. BAPN 11.3 g (0.033 mol) and DMAc 100 g were placed into a 500-mL three-neck flask under nitrogen purge. The mixture was stirred until the solution was clear. Equal molar amounts of solid BTDA were added to the BAPN solution to make a solution with a solid content of 18%. The reaction mixture was stirred for 1 h at room temperature to give a transparent yellow viscous solution of PAA. To prepare organophilic MMT in DMAc at different concentrations (1, 5, and 10%), various quantities of DOA-MMT or CPC-MMT were each added to DMAc and mixed for 12 h. The organoclay suspensions were then mixed with PAA to yield PAA-organoclay in DMAc. The final solid content of PAA in DMAc was 16%.

The PAA-organoclay solution was spread on a glass plate using a spin-coater, to control the film thickness. The films were thermally dried at 60°C for 8 h to remove most of the solvent in a forced air oven and subsequently heated at 100, 150, and 200°C for 1 h, and then at 300°C for 2 h in a nitrogen atmosphere to achieve fully imidization. The films were then cooled to room temperature and peeled off from the glass plate to obtain the PI-MMT hybrid films. Table I lists



Scheme 1. Synthesis of PI-MMT hybrids.

the codes of various hybrids with different formulations.

Characterization

Fourier transfer infrared (FTIR) spectra were measured on a Bio-rad FTS-40A spectrometer. $^1\text{H-NMR}$ spectra were obtained on a Bruker AMX-400 spectrometer with dimethyl sulfoxide ($\text{DMSO-}d_6$) as the solvent. Thermogravimetric analysis (TGA) was performed with a PerkinElmer TGA-7 thermal analyzer at a heating rate of $20^\circ\text{C}/\text{min}$ within the temperature range of $30\text{--}800^\circ\text{C}$. Differential scanning calorimetry (DSC) data were obtained by a PerkinElmer DSC-7. Samples of 5–10 mg were sealed in hermetic aluminum pans and scanned in the calorimeter at a heating rate of $20^\circ\text{C}/\text{min}$ in the range of $30\text{--}400^\circ\text{C}$ under N_2 atmosphere. The T_g values were measured as the change of the specific heat in the heat flow curves. X-ray diffractograms (XRD) were obtained at room temperature with film specimens about 0.2 mm thick on a Rigaku RINT 2000 instrument, using Ni-filtered $\text{Cu K}\alpha$ radiation (40 kV, 15 mA). The samples for TEM

study were prepared by placing PI-MMT films in an epoxy resin and curing the resin at 60°C for 48 h. The cured epoxies containing PI-MMT were microtomed with a diamond knife into $\sim 70\text{-nm}$ -thick slices and placed on a 200-mesh copper grid and examined with a Zeiss 10C TEM using an acceleration voltage of 80 kV. An Instron universal tester model 4467 was used to study the stress-strain behavior of the samples. The dielectric property of the polymer films was tested by the IM6 of ZAHNER-elektrik GmbH and Co. KG at a frequency of 1 kHz with AC amplitude of 5 mV rms. The in-plane coefficients of thermal expansion (CTE) were measured by a thermal mechanical analyzer (TMA) model 2940 from TA Instruments, at a heating rate of $5^\circ\text{C}/\text{min}$ in nitrogen under a force of 0.05 N. Water absorption was determined by immersing ~ 0.5 g of polymer films in 30°C water for 48 h, then measuring the weight difference before and after immersion.

RESULTS AND DISCUSSION

Synthesis of diamine and polyimide containing naphthalene

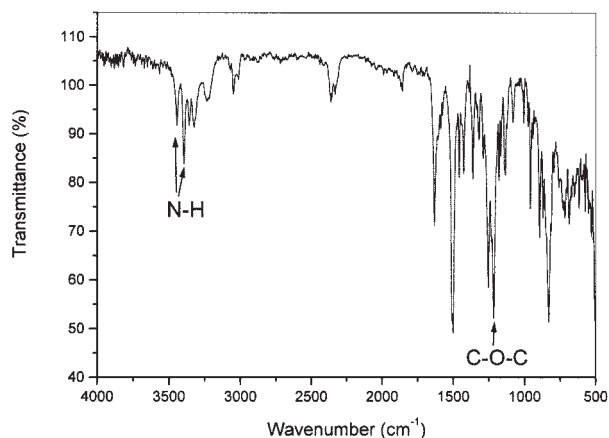
The diamine BAPN was synthesized from 2,7-dihydroxynaphthalene in two steps according to a well-established procedure. The structure of BAPN was confirmed by IR spectrum, $^1\text{H-NMR}$ spectrum and elemental analysis. The FTIR spectrum of BAPN is depicted in Figure 1(a). Absorption bands at 3444 and 3395 cm^{-1} are the result of asymmetric and symmetric stretching of the Ar-NH_2 . Absorption at 1220 cm^{-1} indicates C-O-C presence. Figure 1(b) shows the $^1\text{H-NMR}$ spectrum of BAPN. The signal at 5.0 ppm is peculiar to the amino group. All of the spectroscopic data obtained were in good agreement with the proposed structure.

The synthesis of PI can be divided into two steps. The first step is the formation of PAA, and the second being the imidization of PAA. The FTIR spectra of PAA and PI containing naphthalene are shown in Figure 2. It exhibits the characteristic absorption bands of amide and carboxyl groups at $1500\text{--}1730\text{ cm}^{-1}$ and $3240\text{--}3320\text{ cm}^{-1}$ regions disappeared and those of the

TABLE I
The Codes of Various PI-MMT Hybrids

Code	Clay type	Clay content (wt %)
PI	—	0
PI-DM ₁	DOA-MMT	1
PI-DM ₅	DOA-MMT	5
PI-DM ₁₀	DOA-MMT	10
PI-CM ₁	CPC-MMT	1
PI-CM ₅	CPC-MMT	5
PI-CM ₁₀	CPC-MMT	10

(a) FT-IR spectrum of BAPN



(b) ¹H NMR spectrum

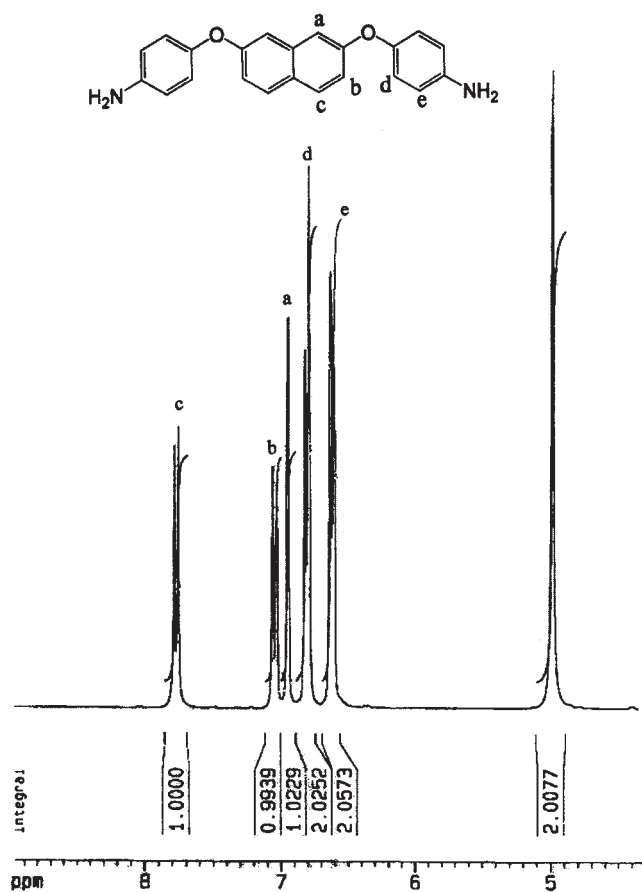


Figure 1 FTIR and ¹H-NMR spectra of BAPN.

imide group formed at 1780 and 1720 cm⁻¹ (asymmetric and symmetric C=O stretching), 1380 cm⁻¹ (C-N stretching), and 720 cm⁻¹ (tertiary amine).

Intercalation of MMT with DOA and CPC

Figure 3 shows the X-ray diffraction patterns for the dried MMT and organoclays modified by DOA and

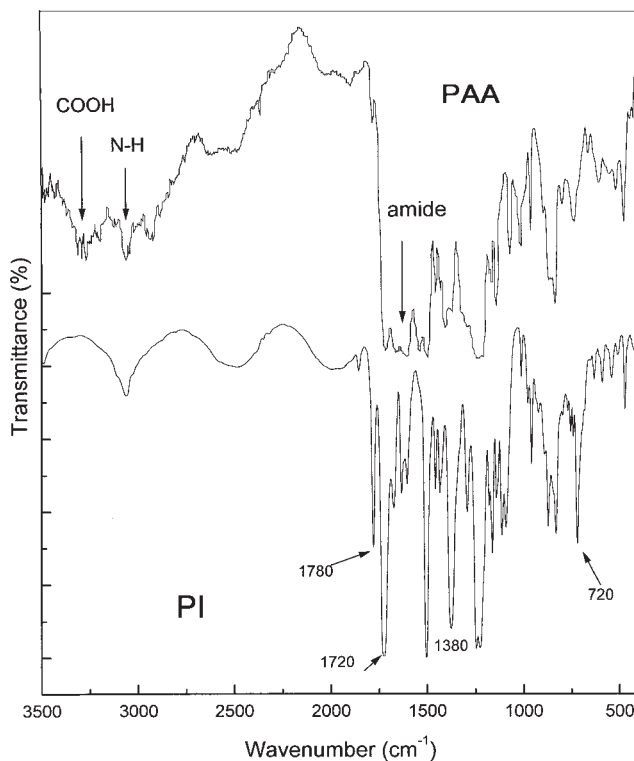


Figure 2 FTIR spectrum of PAA and PI.

CPC. The interlayer spacing of MMT ($2\theta = 7.08^\circ$, $d = 12.5 \text{ \AA}$) increased after surface treatment with DOA and CPC to 18.2 \AA ($2\theta = 4.86^\circ$) and 21.6 \AA ($2\theta = 4.08^\circ$), respectively. These results are comparable with other studies^{13,14} and confirm the expansion of silicate layers in the organophilic clay. The thermal stability is demonstrated by the TGA in Figure 4. The initial degradation temperatures of DOA-MMT and CPC-MMT in air were found to be much higher than the decomposition temperatures of DOA and CPC. This

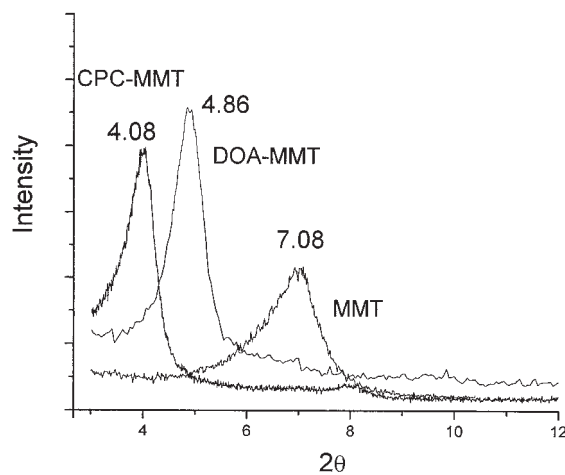


Figure 3 X-ray diffractograms of MMT and organoclays.

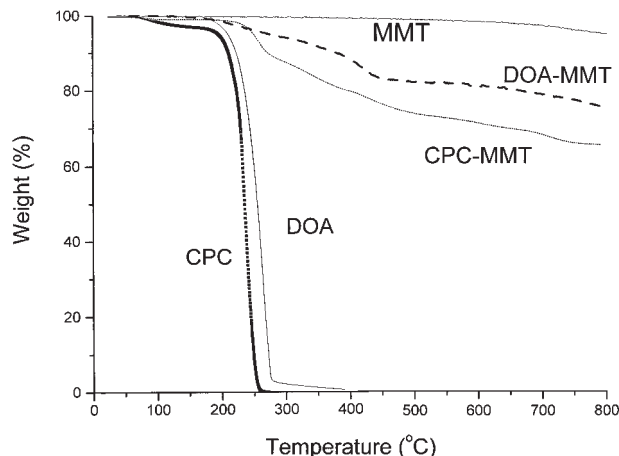


Figure 4 TGA curves of CPC, DOA, MMT, DOA-MMT, and CPC-MMT.

implies that dodecylammonium or cetylpyridium ions reacted with MMT.

Characterization of PI-MMT nanocomposites

IR spectroscopy

The IR spectra of organo-modified PI-MMT are illustrated in Figure 5. The spectra exhibited the characteristic absorption of both organic and inorganic groups. The intensity of the absorption bands at 3647, 2960, 1479, and 1086 cm^{-1} (associated with —OH stretching, C—H stretching of $\text{—CH}_2\text{—}$ chain, C—H bending, and Si—O stretching, respectively) increases as the organoclay content in PI increases.

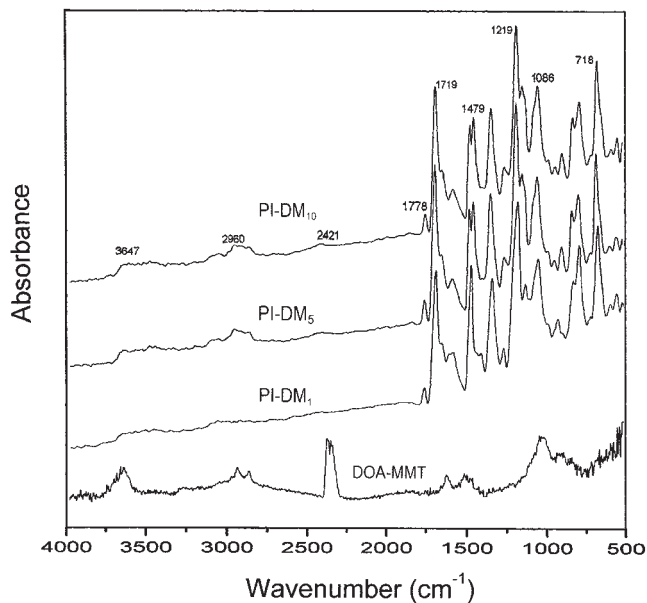


Figure 5 FTIR spectra of DOA-MMT, PI-DM₁, PI-DM₅, and PI-DM₁₀.

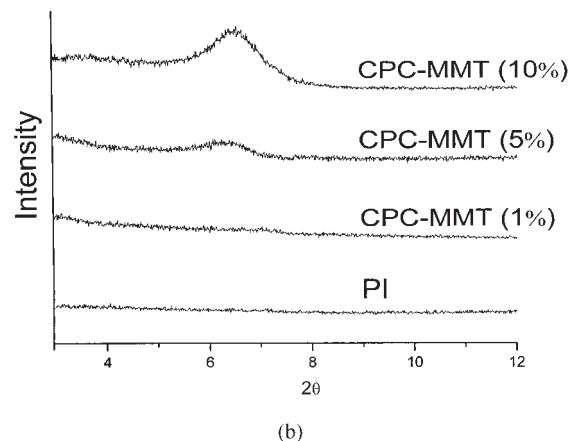
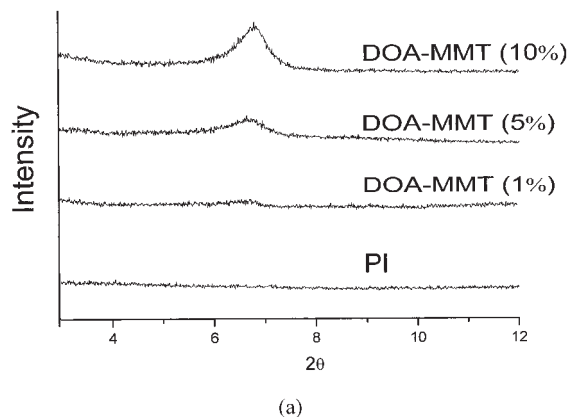


Figure 6 XRD patterns of PI-MMT hybrids as a function of organoclay loading.

MMT dispersion in PI matrix

The XRD curves of PI, PI-DM₁₋₁₀, and PI-CM₁₋₁₀ are shown in Figures 6(a) and 6(b). For PI-DM₁ and PI-CM₁, the curves show no peak, indicating that the peak corresponding to the basal spacing disappeared. This suggests that the organophilic clay in the nanocomposite dispersed homogeneously into the PI matrix. When the amount of organoclay was increased to 5%, there was a small peak at $2\theta = 6.7^\circ$ for PI-DM₅, indicating that there is a small amount of organoclay existing in the form of an intercalated layer structure. The shift of peaks might be attributed to the decomposition of organo-modifier. This can be explained by the loss of some dodecylamine molecules from the clay galleries in the presence of polyimide during imidization. Since ammonium salt is not stable at elevated temperature, it can decompose to form an amine. The amine is capable to react with PAA during imidization. When content of the organophilic clay increases, its density increases in the matrix such that the decomposed organophilic tactoids can form into aggregates.¹³ For PI-CM₅, similar situation was observed, with a small peak at $2\theta = 6.4^\circ$. In the future, other organic modifiers should be investigated. In Fig-



Figure 7 TEM micrograph of the cross section of PI-MMT.

ure 7, the TEM of PI-DM₅ reveals that individual silicate layers, along with several stacks, were found to be exfoliated in the PI matrix. The clay galleries at higher clay content could not always be effectively exfoliated into nanolayers, and some have remained as aggregates in the form of an intercalated layer structure.

Thermal properties

The thermal properties of the PI-MMT clay were evaluated by TGA and DSC, and the results are summarized in Table II. The temperatures of 5% weight loss ($T_{d,5\%}$) of these PI-clays stayed in the range of 556–606°C. They left more than 64% char yield at 800°C in a nitrogen atmosphere. The TGA data indicate that these PI-clays have fairly high thermal stability. T_g increased gradually with an increase in the organoclay content. The increase in the T_g can be attributed to the strong interaction between the polymer and layered silicate surfaces because of the nanometer size, which restricted segmental motion near the organic-inor-

TABLE II
Thermal Properties of PI-MMT Hybrids

Code	In nitrogen		In air	
	T_g (°C)	$T_{d,5\%}$ (°C)	$T_{d,5\%}$ (°C)	Char yield ^a
PI	284	560	556	0.2
PI-DM ₁	297	572	567	1.7
PI-DM ₅	300	606	601	5.8
PI-DM ₁₀	306	598	591	9.5
PI-CM ₁	285	571	557	1.3
PI-CM ₅	286	596	586	4.2
PI-CM ₁₀	295	594	578	9.1

^a Char yield: Residual wt % at 800°C.

TABLE III
Mechanical Properties of PI-MMT Hybrids

Code	Tensile strength (MPa)	Elongation at break (%)	Modulus (GPa)
PI	195	3.73	3.8
PI-DM ₁	252	2.15	3.9
PI-DM ₅	449	1.10	5.8
PI-DM ₁₀	248	0.62	4.0
PI-CM ₁	292	2.52	4.2
PI-CM ₅	418	1.44	6.4
PI-CM ₁₀	237	0.65	5.1

ganic interface.¹² The $T_{d,5\%}$ (in N₂) increased by 46 and 36°C in comparison with pristine PI for the organoclay content of 5% with DOA and CPC, respectively. This increase in the thermal stability may be caused by the “barrier effect” of the MMT layer structure, which hinders mobility of the small molecules produced during the thermal decomposition of the PI.¹¹ The effects of different organo-modifiers (DOA and CPC) on the thermal properties were comparable.

Mechanical properties

Table III summarizes the tensile properties of PI-MMT nanocomposite films. The improvement in the mechanical properties may result from the strong interface interaction between PI and organoclay. The increase in the modulus is ascribed to the reinforcement effect attained by the dispersion of the clay nanolayer into PI film.¹² When the organoclay content was lower, the interface between the exfoliated MMT sheets and PI could effectively reduce the formation of the shear zone, and the layer structure of MMT could also stop the development of cracks from the shear zone.¹⁶ PI could simultaneously be strengthened and toughened by the introduction of exfoliated organoclay. Hence, the elongation decreased with the increasing organoclay content. The introduction of organoclays caused tensile strength to initially increase and then decrease as shown in Figure 8. When the clay content exceeded 5%, both the tensile strength and the modulus were decreased, possibly because of the poor dispersion of organoclay in the PI matrix. This reduction of the mechanical properties can be attributed to the aggregation of the clay nanolayers. Therefore, the efficiency of clay to modify the mechanical properties of the polymer is primarily determined by the degree of its dispersion in PI matrix. The results agree with XRD data.

Dielectric constant

The dielectric strength is an important parameter for selecting an appropriate electrical insulation material.

The dielectric constant (as listed in Table IV) decreased with increasing amounts of dispersed organoclay. The decrease in dielectric constants might be attributed to the reduction in the freedom of orientation of the clay unit and main-chain flexibility of the PI matrix.¹⁴ The clay aggregation at high clay content (more than 5%) resulted in the increase of the dielectric constant. Therefore, the extent of dielectric constant reduction depends on how well the clay is dispersed.

Coefficient of thermal expansion

Clay consists of stacked silicate sheets of which CTE is much smaller than that of PI. Therefore, the CTE of PI-MMT hybrid is expected to be smaller than that of pristine PI (see Table IV). The extent of CTE reduction depends on the clay dispersion and the amount of intercalation within the MMT. The tendency is in accordance with the change of the dielectric constant.

Water absorption

In addition to the low dielectric constant and CTE requirements, low water absorption is also critical for a polymer to be used in microelectronics. The water absorption measurements are tabulated in Table IV. The PI-MMT nanocomposites show less water absorption than pristine PI. The stacking layers of clay can act as a barrier to water diffusion into the PI film. Therefore, better clay dispersion should possess lower water absorption.¹⁴ As Table IV demonstrates, a clay content of 10% results in a slight increase in the water absorption. This might be caused by the aggregation of silicates that produce a poor dispersion.

CONCLUSIONS

Both the XRD and TEM data indicate that the MMT clay was dispersed in the polymer matrix at a nano-

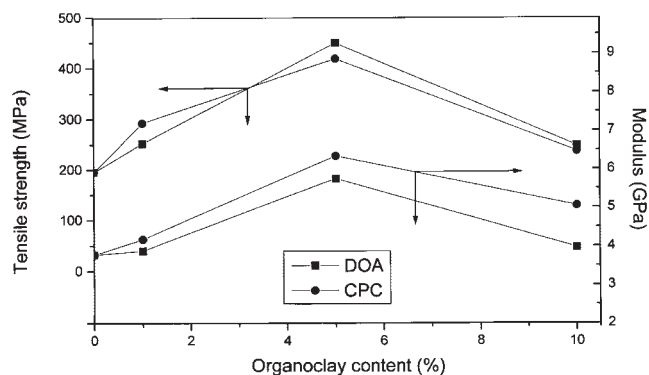


Figure 8 Mechanical properties at various organoclay contents.

TABLE IV
Physical Properties of PI-MMT Hybrids

Code	Dielectric constant	CTE (ppm/°C)	Water absorption (%)
PI	4.4	59	1.20
PI-DM ₁	3.9	55	0.52
PI-DM ₅	2.4	35	0.34
PI-DM ₁₀	2.8	45	0.36
PI-CM ₁	4.0	55	0.88
PI-CM ₅	3.1	48	0.85
PI-CM ₁₀	3.5	52	0.86

meter scale with the addition of a small amount of clay. The thermal stability and mechanical properties of the nanocomposites were improved with organoclay content up to 5%. The dielectric constant, CTE, and water absorption were decreased with the incorporation of MMT organoclay up to 5% loading. At a higher organoclay contents (5–10%), these properties were slightly reduced, possibly due to the poor dispersion of the organoclay resulting from the aggregation of silicates. In general, the properties of PI (containing naphthalene)-MMT nanocomposites modified by DOA-MMT were comparable with those treated by CPC-MMT.

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