

Syntheses and Properties of PI/Clay Hybrids

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ABSTRACT: A new organomontmorillonite (CM) for PI hybrids has been developed by ion-exchange reaction of cetyl pyridium chloride with Na⁺ montmorillonite (MMT). Polyimide/clay hybrids have been synthesized by employing two methods. Method I is by first blending a dimethylacetamide (DMAC) solution of 4,4'-oxydianiline diamine (ODA) with a DMAC dispersion of CM before adding pyromellitic dianhydride (PMDA). Method II is by blending a DMAC solution of poly(amic acid) with a DMAC dispersion of CM. Tensile, thermal, dielectric, and water-absorption properties of hybrids prepared by these two methods have been studied in detail. Results show that these properties depend on the clay type (organophilic or not), clay concentration, and the method to synthesis hybrids. The CM concentration of 3 wt % in the hybrid by Method II results in optimum properties in tensile strength, modulus, elongation, coefficient of thermal expansion (CTE), and water absorption. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1902–1910, 2001

Key words: nanocomposite; polyimide/clay hybrid; coefficient of thermal expansion; dielectric property

INTRODUCTION

Hybrids, made up of polyimides (PIs) and inorganic materials, are a vital subject of current research because various PIs are widely used as high performance polymers in advanced technologies such as microelectronics and aerospace.^{1–10} In addition, PI hybrids are often able to overcome severe thermal and mechanical stress concentration and associated reliability problems produced by the mismatch in coefficient of thermal expansion (CTE) and modulus between polymers, ceramics, or metals.^{11–18} These improvements enable PIs to meet some ultimate requirements in demanding applications such as highly rapid speed-up circuits and complex multilayer devices.

In addition, the resulting hybrids, known also as ceramers, have higher thermal stability, lower moisture absorption, higher hardness, better barrier resistance, and superior scratch resistance compared to the neat PIs. Therefore, the PI ceramers have attracted enormous interest in the field of hybrids.

Intercalation of polymer with clay has been an effective method to prepare polyimide hybrids. With 2 wt % addition of the montmorillonite (MMT) in PI, the permeability coefficients of H₂, O₂, and water vapor have been reduced to less than half of these of the pristine PI, and the CTE is lowered to 90% of the neat PI.¹⁷ However, at present, little is known about the mechanical and dielectric properties of the PI/clay hybrids and their relationship.

In this article, a quaternary pyridine ammonium (R₄N⁺) salt, cetyl pyridium chloride (CPC), has been chosen as the intercalant. Two synthesis methods are employed in preparing PI/clay hybrids. The effect of clay content and synthesis

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method on resulted properties of hybrids are investigated in detail.

EXPERIMENTAL

Materials

Montmorillonite "Kunipia F," a sodium montmorillonite (MMT) with cation exchange capacity of ca 115 meq/100 g, was obtained from the Kunimine Ind. Co. of Japan. CPC was supplied by Sigma of Japan, with a purity greater than 99%, and was used as received. The ultrapure (99.5%) pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were purchased from Chriskev Inc. of the USA. The *N,N'*-dimethylacetamide (DMAC) purchased from Aldrich Chemical, Milwaukee, WI, was dehydrated by distillation and stored under molecular sieves.

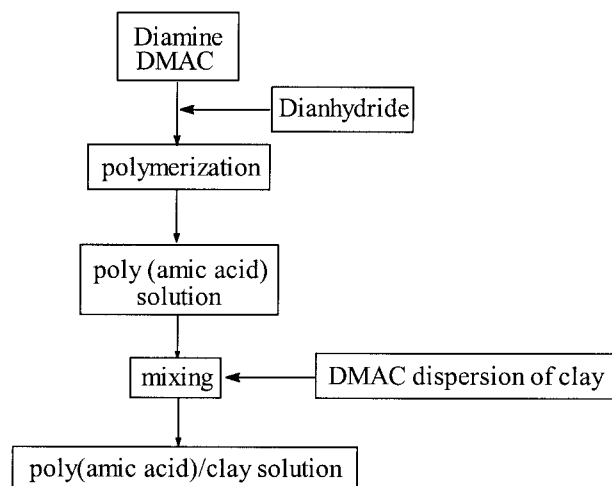
Preparation of Organophilic Montmorillonite

One gram of MMT was added into 50 mL water until the MMT was well dispersed in the water; equal molar CPC was added to the solutions, and the mixture was stirred vigorously for 24 h. The resulting organoclay was collected by filtration and washed with deionized water for several times until no Cl^- was detected by AgNO_3 , which is designated as organophilic montmorillonite (CM).

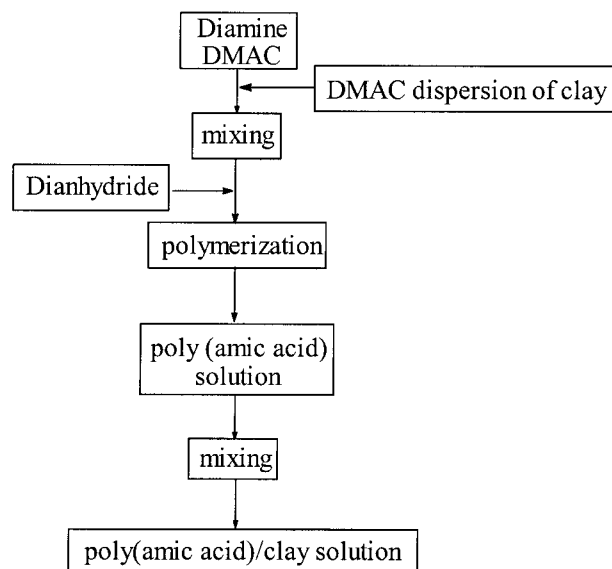
Preparation of Poly(amic acid)/Clay

Two routes were used to synthesize the poly(amic acid)/clay mixture, as shown by the flow charts in Scheme I.

Examples to prepare DMAC solution of poly(amic acid)/clay containing 1 wt % clay by two methods are given as follows: a mixture of 0.1381 g of CM and 5.77 mL DMAC was stirred vigorously at 90°C for 24 h to yield the DMAC dispersion of MMT. Method I: the ODA (6.508 g, 0.0325 mol) was dissolved in 58.23 mL DMAC. The above-prepared DMAC dispersion of MMT was put into the solution and continuously stirred at room temperature for another 24 h. PMDA (7.16 g, 0.0328 mol) was then added into the reaction mixture under nitrogen atmosphere and stirred at room temperature for 8 h, yielding a 16 wt % DMAC solution of poly(amic acid). Method II: ODA (6.5085, 0.0325 mol) was first dissolved in 58.23 mL DMAC. PMDA (7.16 g, 0.0328 mol) was then added into the reaction mixture under a



(a) Method I



(b) Method II

Scheme I Synthesis of poly(amic acid)/clay.

nitrogen atmosphere and stirred at room temperature for 4 h. The DMAC solution of MMT was added into the mixture and stirred vigorously at 30°C for 4 h to yield a 16 wt % DMAC solution of poly(amic acid).

Preparation of PI/Clay Hybrid Films

The obtained DMAC solution of poly(amic acid)/clay was coated by a doctor blade on a glass plate

Table I The Codes of Various Hybrids

Code	Clay Type	Clay Content in Hybrid (wt %)	Preparation Method
M1I	MMT	1	I
M1II	MMT	1	II
M3I	MMT	3	I
M3II	MMT	3	II
CM1I	CM	1	I
CM1II	CM	1	II
CM3I	CM	3	I
CM3II	CM	3	II
CM5I	CM	5	I
CM5II	CM	5	II
CM10I	CM	10	I
CM10II	CM	10	II

using an automatic film applicator at a rate of 0.34 mm/min, and subsequently heated at 60, 80, 100, 150, 200, and 300°C for 1 h under a nitrogen atmosphere. The film was then peeled off from the glass plate to obtain the PI/clay hybrid film with a thickness of $26 \pm 2 \mu\text{m}$ (for measurements of mechanical and thermal properties) or $160 \pm 2 \mu\text{m}$ (for tests on dielectric properties and water absorption). The codes of various hybrids with different formulations and preparing methods are listed in Table I.

Characterizations

FTIR measurement was made using a Nicolet Avatar 320 Fourier Transform Infrared Spectrophotometer. For all infrared spectra, 32 coadded scans were collected with a spectral resolution of 2 cm^{-1} . Wide-angle diffraction (WAXD) experiments were conducted on a Rigaku X-ray Diffractometer using Cu-K α radiation. It was operated at 50 kV, 250 mA, with a scan speed of 2.00 deg/min. The water absorption property of the sample was measured by immersing the specimen in water at 60°C for 48 h by following the ASTM D570-81. The coefficient of thermal expansion (CTE), parallel to the film surface direction, was measured in an extension mode using a TMA 2940 Thermo-mechanical Analyzer (Du Pont) with a force of 0.05 N. Tensile properties of the cured film at room temperature were measured using a Micro-Computer Universal Materials Tester Model-HT-8116 (Hung Ta Instrument Co., Ltd, Taiwan). Film samples of 150 mm long, 25.4 mm wide, and $26 \pm 2 \mu\text{m}$ thick were cut from free film. The gauge length was 110 mm, and the crosshead

speed was controlled at 10 mm/min. Dielectric constant and dielectric loss of the film at room temperature were measured by a DEA 2970 Dielectric Analyzer (Du Pont). The thermal gravimetric analysis (TGA) was conducted on a TGA 2950 (Du Pont) Thermogravimetric Analyzer under a flowing nitrogen atmosphere at a heating rate of 10°C/min. Transmission electron microscope (TEM) photographs of the PI/clay hybrid was taken on a JEOL-200FX (Japan) Transmission Electron Microscope, and its accelerated voltage was 200 kV. The sample for TEM observation was prepared by placing the PI/clay film into an epoxy capsule and then cured the epoxy at 80°C for 10 h in an oven. Then the cured epoxy containing PI/clay hybrid film was microtomed with a Leica Ultracut Uet into 90 nm-thick slices and deposited on a 200 mesh copper net for TEM observation. The UV-Vis absorption spectrum was measured with a DU 520 General Purpose UV-Vis Spectrophotometer from Beckman Instruments, Inc., USA.

RESULTS AND DISCUSSION

Intercalation of MMT with CPC

Figure 1(a) and 1(b) shows the X-ray diffraction patterns for the dried MMT and CM. Upon inter-

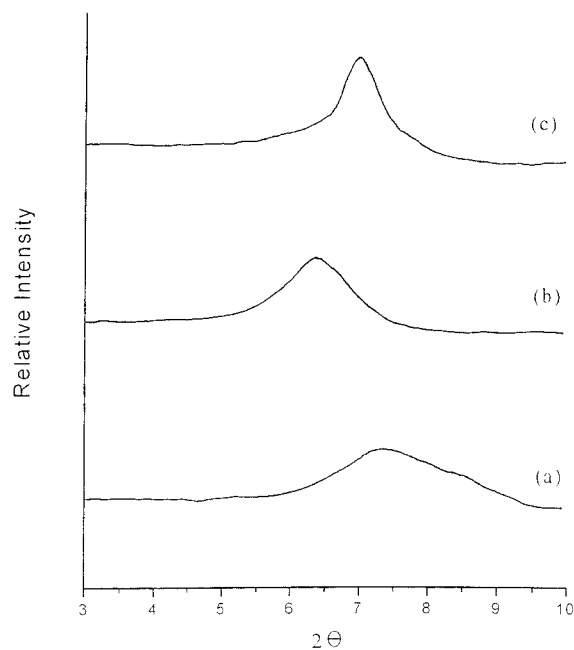


Figure 1 WAXD patterns of MMT (a), CM (b), and CM at 300°C for 2 h (c).

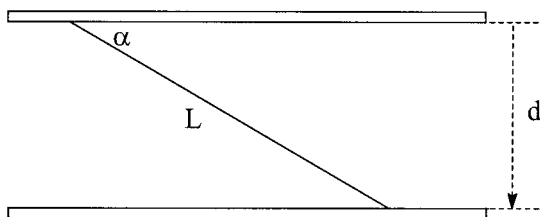


Figure 2 Model of CPC molecule between layers of montmorillonite.

calation, the basal spacing expands from 12 to 22 Å, indicating the incorporation of the large surfactant molecules.

The molecular length of CPC, calculated by constructing the completely structure space filling (CPK) model, is 22.945 Å. Comparing the sum of the calculated molecular length and a silicate layer with the observed basal spacing, it can be estimated that the CPC exists diagonally in the silicate layers of MMT (Fig. 2). The angle of CPC slant to the MMT layer, α , can be calculated by the following equation:

$$\sin \alpha = (d - 10)/L, \quad \alpha = 31.442^\circ$$

where L is the molecular length of the CPC, d is the basal spacing.

To obtain complementary evidence for the intercalation of CPC into the silicate lattice, FTIR spectra were recorded in the region of 400–4000 cm^{-1} . Figure 3 gives the IR spectra of MMT, CPC, and CM. The spectrum of CM contains the characteristic bands of MMT and CPC. Bands at 1092 and 1039 cm^{-1} are the typical bands of MMT, while those near 2850 and 2900 cm^{-1} are the characteristic bands of the symmetric and asym-

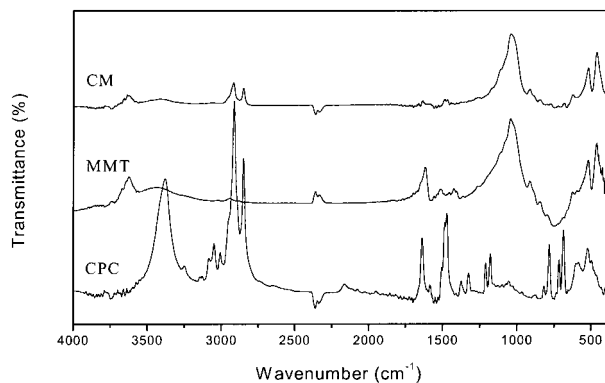


Figure 3 FTIR spectra of CPC, MMT, and CM.

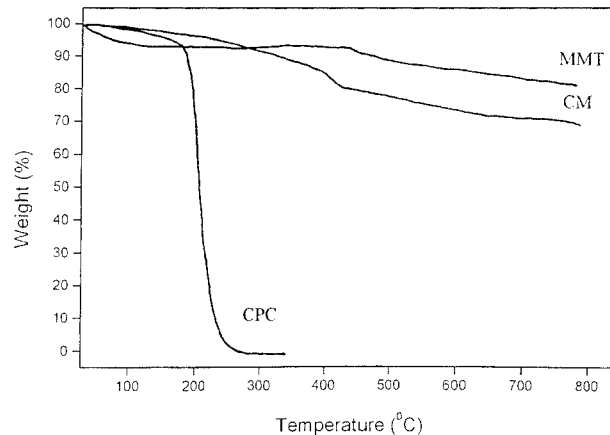


Figure 4 TGA curves of CPC, MMT, and CM.

metric stretching vibrations of methylene groups from the CPC.

The synthesis of PI can be divided into two steps. First is the formation of poly(amic acid), and the second is imidization of poly(amic acid), which should proceed to completion at a temperature higher than 300°C. Therefore, the thermal stability of organophilic MMT is very important, because it determines the thermal stability of hybrids and the dispersion of MMT in PI matrix.

The thermal stability is demonstrated by the TGA (Fig. 4). From the characteristic temperatures in TGA curves (Table II), it can be seen that the initial decomposition temperatures of CPC and CM are 182.4 and 251.1°C, respectively. In addition, the char yield of CPC at 249.4°C is 0%. However, when CPC is ionic bonded with MMT, it will not completely degrade at 250°C, or even at 600°C. This can be proven by comparing the sum of the weight of CPC in CM at 25°C (28.11 wt %) and its char yield (Y_c) at 600°C (Table II). In addition, the X-ray diffraction pattern of CM at 300°C for 2 h shows that its basal spacing is 13.75 Å, greater than that of MMT [Fig. 1(c) vs. Fig. 1(a)].

Table II Characteristic Temperatures and Char Yields from TGA Curves

	CPC	MMT	CM
T _{id} (5 wt %), °C	182.4	—	251.3
Y _c , (249.4°C), %	0	93.8	95.1
Y _c , (600°C), %	—	87.5	76.9
Y _c , (800°C), %	—	81.5	68.0

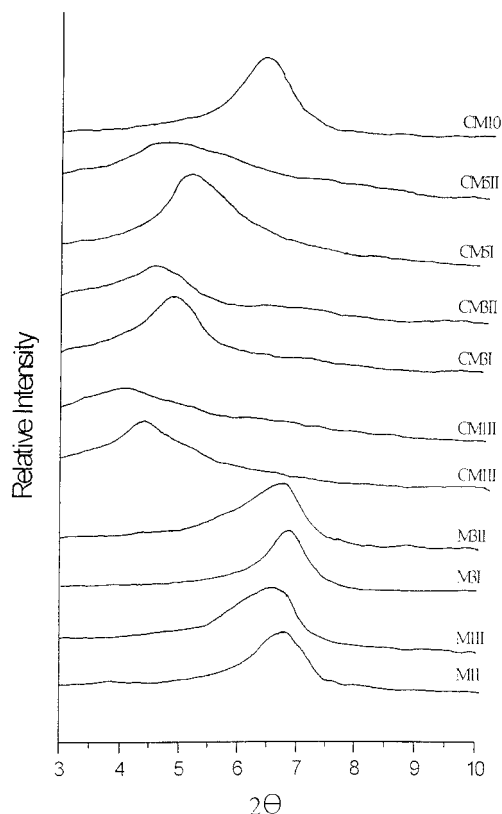


Figure 5 WAXD patterns of PI/clay hybrids.

Dispersion of Clay in the PI Matrix

Figure 5 shows X-ray patterns of various PI/clay hybrids. In general, the basal spacing of the sample prepared by Method II is slightly larger than that by Method I. The basal spacing is greatly influenced by the clay loading. The basal spacing decreases when the clay loading is increased. The basal spacing (001) of the clay in these composites ranges from 22 to 14 Å when the concentration of the organoclay is from 1 to 10 wt %. To further characterize the texture of hybrids prepared in the present work, TEM images obtained on thin sections of the PI/clay hybrids are shown in Figure 6. These clay aggregates are randomly distributed in the PI matrix in the range of 30–1200 Å, with the layers separated by about 16–25 Å, which is close to the result from WAXD for a typical intercalated phase. Therefore, a major fraction of the clay is indeed embedded in the polymer matrix as ordered intercalates, rather than as a completely exfoliated arrangement of single layers. As would be expected, this lamella of clays is dispersed evenly in the PI matrix along the direction of casting poly(amic acid) solution in preparing the hybrid film.

Although the hybrid contains 5 wt % CM, the hybrid film is still as transparent as the neat PI. Its transmittance at 660 nm is as high as 99.78%, similar to that of the neat PI. This fact is explained by the fine dispersion of the CM in the PI matrix at a size smaller than the wavelength of visible light.

Properties of PI/CM Hybrids

Tensile Properties

As we know, the PI film is usually prepared by casting or spin-coating the poly(amic acid) precursor solution on an essentially planar substrate, and therefore, residual stress is developed in the film due to the mismatch of the CTE between the film and the substrate. In general, the development of the residual stress, more or less, is unavoidable in the process in preparing the film. The residual stress built into a PI film may cause the film to crack, or initiate destruction of the semiconductor device. In developing PI systems, close attention must, therefore, be paid to the resulting mechanical properties of the material.

The tensile properties (strength, modulus, and elongation) with clay loading are shown in Figure 7(a) to 7(c). Tensile properties of hybrids made up of PI and CM, regardless of routes employed, are substantially higher than those of the pristine PI. However, when the CM content is greater than 3 wt %, the tensile properties of hybrids start to decrease. It appears that 3 wt % of CM in the hybrid is the optimum content to achieve most property improvement.

Figure 7 also indicates that the synthesis method has great influence on tensile properties of the hybrids. Based on the same CM content in hybrids, the hybrid prepared by Method II has higher tensile strength, higher modulus, and lower elongation than those from Method I. The poly(amic acid) prepared by Method II may possess higher molecular weight than that by Method I. It has been reported that a higher molecular weight poly(amic acid) can be produced by using higher concentrations of monomers.¹⁹ In the present work, the monomer concentration in Method II is higher than that in Method I, and thus a higher molecular weight of the poly(amic acid) by Method II is expected.

Dielectric Properties

Lower dielectric constant is one of the most desirable properties for next generation electronic de-

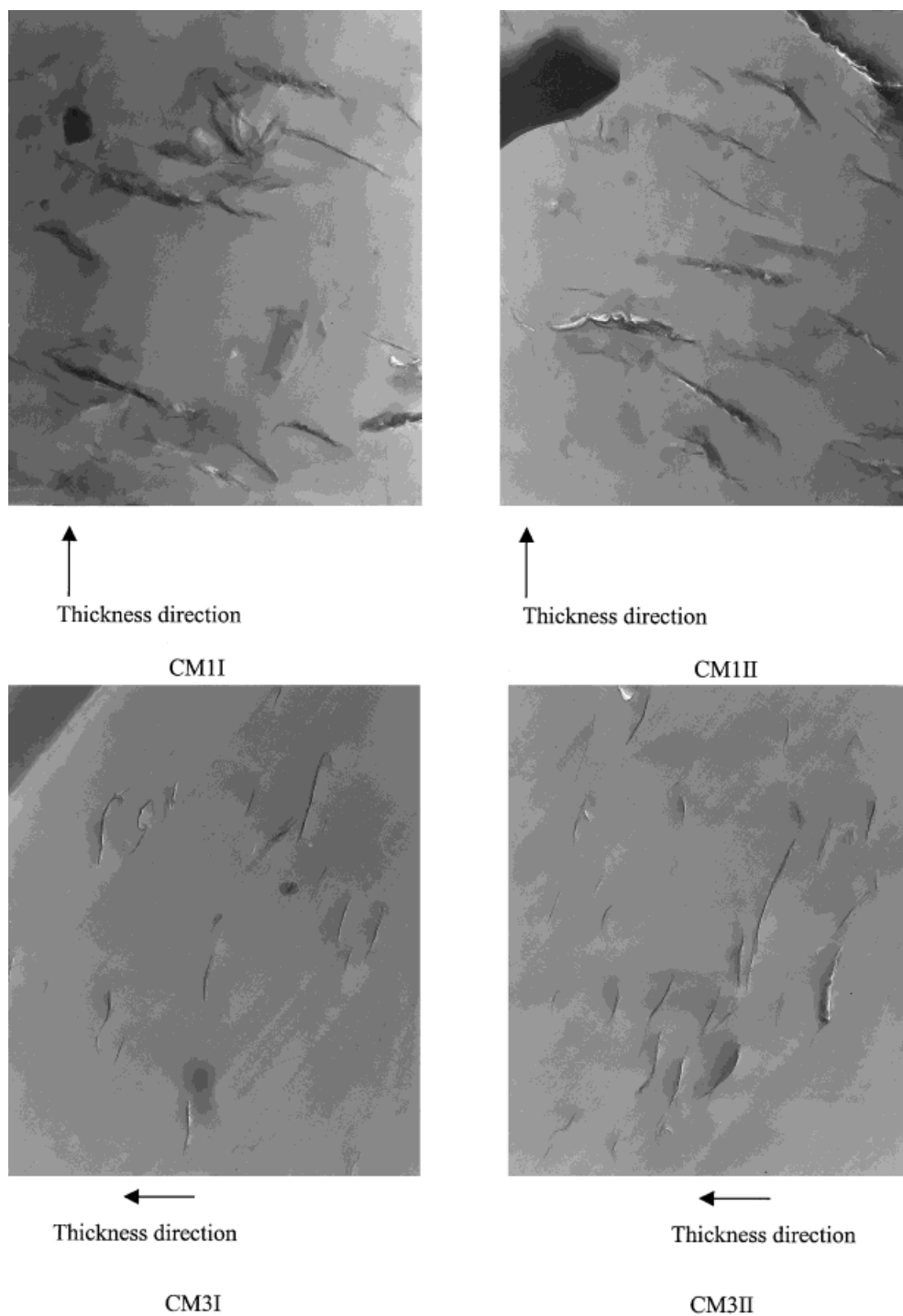


Figure 6 TEM images ($\times 20$ k) of various hybrids (1 mm = 200 nm).

vices. Figure 8(a) gives the dielectric constant of hybrids vs. frequency. Except for hybrids of M3I, CM5I, and CM10I, the rest have lower dielectric constant than the neat PI at all tested frequencies. In addition, they show a nearly constant dielectric constant over a broad range of frequen-

cies. The reduction in dielectric constants can be explained in terms of the reduction in the freedom of orientation of the clay unit and main-chain flexibility of the PI matrix. The former can be attributed to the presence of PI chains within the interlayer space of the clay silicate structure that

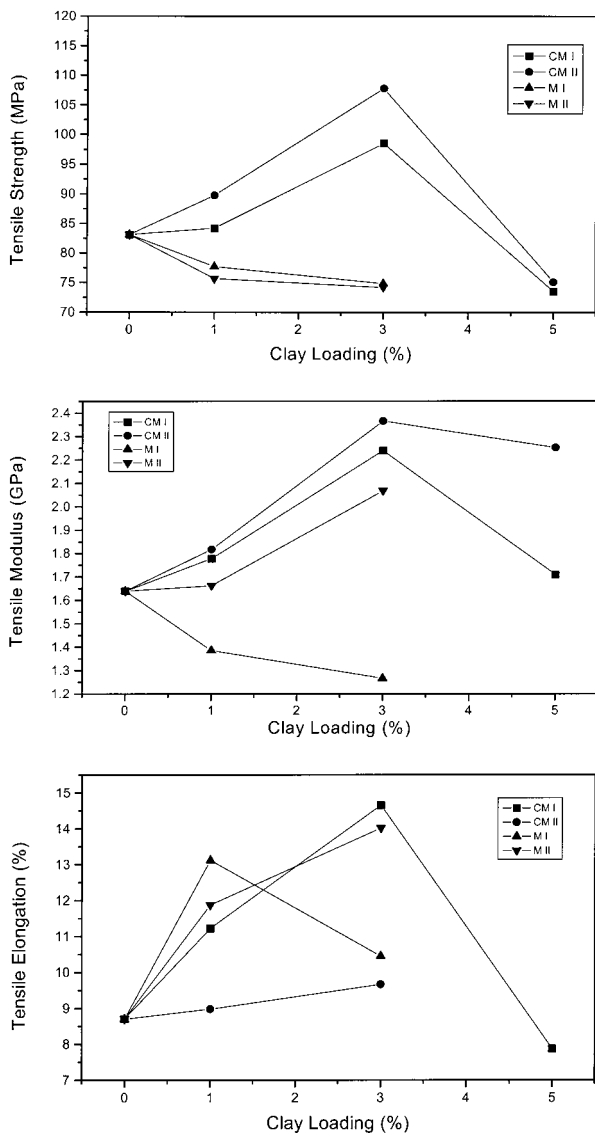


Figure 7 Tensile strength (a), modulus (b), and elongation (c) of hybrids with various levels of clay.

tends to increase the internal friction and the volume of the rotating unit. The latter can be attributed to the presence of the silicate lamellae preventing the main-chain flexibility of PI molecules. Therefore, the extent of dielectric constant reduction depends on how well clay is dispersed in the PI matrix. For two hybrids with the same clay loading, the one prepared by Method II has lower dielectric constant than the one prepared by Method I. This observed difference may come from different PI molecular weights because the observation that higher molecular weight PI leads to lower dielectric constant has been previously reported.²⁰

The value of dielectric loss ($\tan \delta$) can be controlled chemically or physically. The former involves the design and synthesis of polymers, while the latter comes from effects of plasticization, molecular weight, and morphology. In the present work, both aspects are important. Interfacial polarization has been proved to be the prime polarization in the range of 3–20 kHz and for those below 65 Hz.^{21,22} Elimination of impurities and structural heterogeneity is essential to maintain low dielectric loss. The increase of the amount of clay in hybrid composition results in higher heterogeneity, and therefore, causes higher $\tan \delta$, as shown in Figure 8(b). Except for M1II and CM1II, essentially all the other hybrids have higher dielectric loss than the neat PI.

Coefficient of Thermal Expansion (CTE)

Reducing the high CTE of the pristine PI to match the relatively lower CTE of silica or metal such as copper is one main object of this research. Clay with stacked silicate sheets has a substantially lower CTE than that of the PI. Therefore, the CTE of the polyimide/clay hybrid is expected to be lower than that of the neat PI. Figure 9 shows

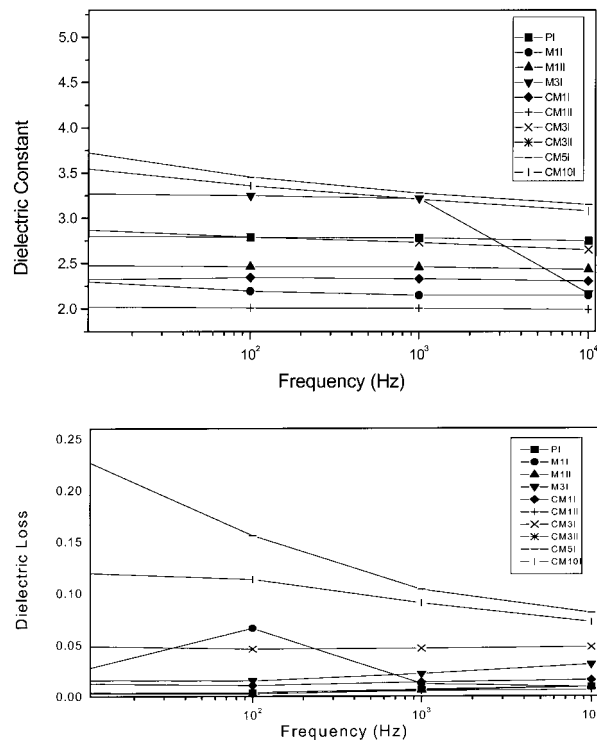


Figure 8 Dependence of dielectric constant (a) and loss (b) of hybrids with various levels of clay on frequency.

CTEs of various types clay/PI hybrids measured at 100°C. Essentially all PI/clay hybrids possess lower CTE than that of the pristine PI. The hybrid with organophilic MMT is more efficient to reduce the CTE than that of the untreated MMT. The extent of CTE reduction depends on the clay dispersion and the amount of PT intercalation within the MMT. When the content of the CM in the hybrid is increased, the resulted CTE decreases. When the contents of CM in the hybrids are 1, 3, 5, and 10 wt %, the corresponding CTE of hybrids are about 88, 74, 71, and 54% of the pristine PI, respectively. At equal clay content, hybrids prepared by Method I and Method II result in about same CTE.

Water Absorption

In addition to the requirements for low CTE and low dielectric constant, low moisture absorption is also critical for a polymer to be used in microelectronics. It is well known that a polymer matrix containing more polar groups tends to have higher water sorptive affinity. However, the accessibility of the polar groups and the relative strength of the water–water interaction vs. the water–polymer interaction are both important.²³ Clay containing stacked silicate sheets tends to reduce the accessibility of the polar groups of the PI. Therefore, a better clay dispersion should possess lower water absorption. As would be expected, essentially all the hybrids prepared have lower water absorption than the neat PI, as shown in Figure 10. At the same level of CM, hybrids prepared by the Method II have lower water absorption than those by the Method I.

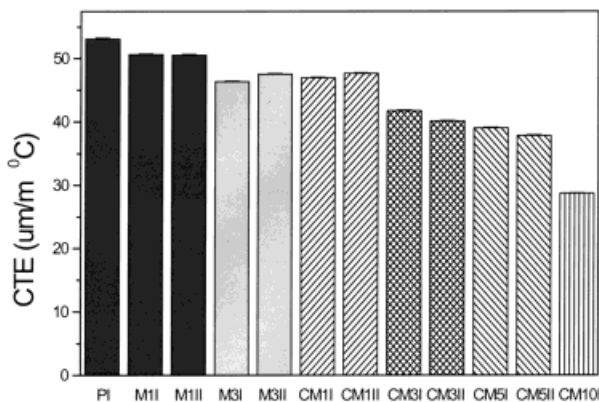


Figure 9 Coefficient of thermal expansion of various hybrids.

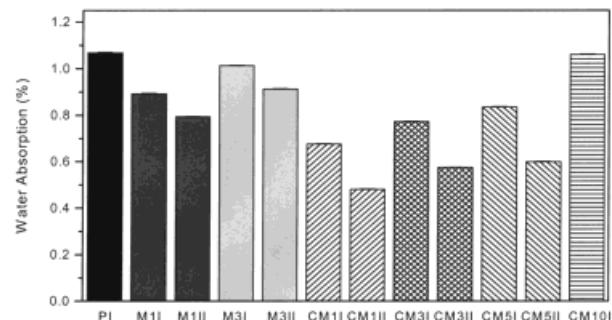


Figure 10 Water absorption of various hybrids.

CONCLUSIONS

A quaternary pyridine ammonium, cetyl pyridum chloride (CPC), has been used to develop a new organophilic montmorillonite (CM) in preparing PI/clay hybrids. PI/MMT and PI/CM hybrids with different clay contents ranging from 1 to 10 wt % have been synthesized by employing two different methods. Method I involved blending a dimethylacetamide (DMAC) solution of 4,4'-oxydianiline diamine (ODA) with a DMAC dispersion of CM before adding pyromellitic dianhydride (PMDA). Method II is by blending a DMAC solution of poly(amic acid) with a DMAC dispersion of CM. Tensile, thermal, dielectric, and water absorption properties of hybrids prepared by these two methods have been studied in detail. Results show that these properties are dependent on the clay type (organophilic or not), clay concentration, and the synthesis method. A 3 wt % CM concentration in the hybrid by Method II results in optimum overall properties in terms of tensile strength, modulus, elongation, coefficient of thermal expansion (CTE), and water absorption.

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