

# Effect of Montmorillonite on Thermal and Moisture Absorption Properties of Polyimide of Different Chemical Structures

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**ABSTRACT:** The thermal properties and the moisture absorption of three types of polyimide/montmorillonite nanocomposite were investigated: 3,3',4,4'-biphenyltetracarboxylic dianhydride-4,4'-oxydianiline (BPDA-ODA); pyromellitic dianhydride-ODA (PMDA-ODA); and 3,3',4,4'-benzophenone tetracarboxylic dianhydride-ODA (BTDA-ODA). The inhibition effect on in-plane coefficients of thermal expansion (CTE) and moisture absorption of these polyimide nanocomposites by layered silicates from montmorillonite was found to decrease with the crystallinity in the pristine polyimides. The largest reduction, 30% in in-plane CTE occurred in the case of amorphous BTDA-ODA containing 5 wt % montmorillonite as compared with that of pure BTDA-ODA, while the reduction in in-plane CTE was 20% for the case of semicrystalline BPDA-ODA. The maximum reduction in moisture absorption, 43%, also took place for the case of 3/97 ODA-Mont/BTDA-ODA as compared with that of pure BTDA-ODA, whereas the semicrystalline 1/99 PPD-Mont/BPDA-ODA showed a 30% reduction as compared with that of pure BPDA-ODA. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1742–1747, 2001

**Key words:** montmorillonite; polyimide; nanocomposites; coefficients of thermal expansion; moisture absorption

## INTRODUCTION

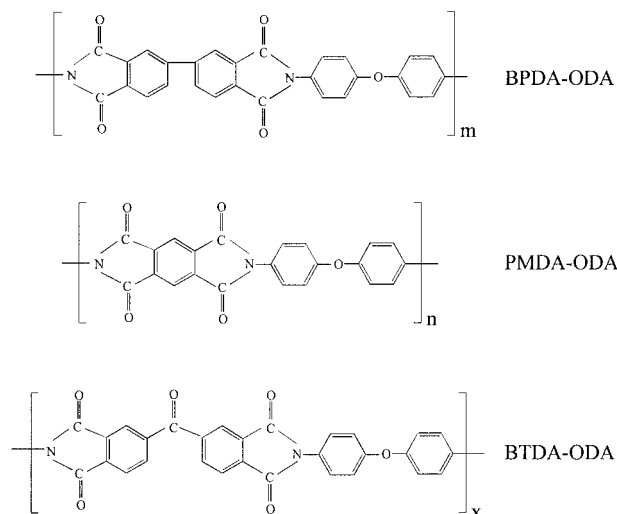
Polyimides are widely used as interlayer dielectrics and as packaging materials in the fabrication of microelectronic devices because of their good thermoxidative stability, high mechanical properties, excellent electrical properties, and superior chemical resistance.<sup>1–4</sup> In the microelectronic devices, large differences in the coefficients of thermal expansion (CTE) between polyimide and aluminum, copper, silicon, or silicon dioxide

could cause the devices to crack, peel, and bend, and high moisture absorption could damage the devices. Hence, the requirement of low CTE and low moisture absorption on polyimide was quite stringent. For these reasons, polyimides of various chemical structure have been developed, but new-structure polyimides sometimes have other ramifications. A case in point was the introduction of fluorine into the backbone of polyimide molecules,<sup>5–7</sup> but it led to poor mechanical properties.

Natural montmorillonite consisted of stacks of disklike silicate layers with a thickness about 1.0 nm and a diameter ~100 nm. The high-aspect-ratio, high-tensile-modulus, and low-thermal-expansion silicates were therefore an ideal candidate for reinforcing polyimide. Mont-

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**Figure 1** Schematic drawings of chemical structure of polyimide.

montmorillonite/polymer nanocomposites such as montmorillonite/nylon 6,<sup>8–10</sup> montmorillonite/epoxy,<sup>11–13</sup> montmorillonite/polystyrene,<sup>14</sup> and montmorillonite/polyurethane<sup>15–17</sup> has been developed in recent years. Montmorillonite/polyimide (pyromellitic dianhydride-4,4'-oxydianiline, PMDA-ODA) nanocomposites have also been formed by several research groups using different swelling agents.<sup>18–20</sup> In our previous study,<sup>21–23</sup> difunctional group swelling agents such as *p*-phenylenediamine (PPD) or 4,4'-oxydianiline (ODA) were used; the resultant montmorillonite/polyimide (PMDA-ODA) nanocomposites were thermally more stable and mechanically stronger than the pure polyimide. In this study, as an extension of previous ones, we would like to investigate the effect montmorillonite on the thermal properties and the moisture absorption of the polyimide of different chemical structures, from amorphous to semicrystalline polyimides. These different chemical structures of polyimide are shown in Figure 1.

## EXPERIMENTAL

### Materials

Source clay Swy-2 (Wyoming Na<sup>+</sup>-montmorillonite) was obtained from the Clay Minerals Depository at the University of Missouri (Columbia, MO). *p*-Phenylenediamine (PPD) was obtained from Janssen in Geel, Belgium. 4,4'-Oxydianiline

(ODA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) were purchased from TCI in Tokyo, Japan. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) and pyromellitic dianhydride (PMDA) were obtained from Chriskev (Leawood). *N,N*-Dimethylacetamide (DMAc) was purchased from Tedia (OH).

### Synthesis of PAA and montmorillonite/PAA Nanocomposites

The powders of montmorillonite modified by PPD or ODA were termed PPD-Mont or ODA-Mont, respectively. Detailed preparation of swelling-agent-modified montmorillonite (Mont) has been published elsewhere.<sup>22,23</sup> Poly(amic acid) (PAA) was synthesized by placing 0.015 mol of ODA into a three-neck flask containing 29.64 g DMAc under nitrogen purge at 25°C. After ODA was completely dissolved in DMAc, 0.0151 mol of BPDA dividing into three batches was added batch-by-batch to the flask, with a time interval of 30 min. When BPDA was dissolved in DMAc, the mixtures in the flask were stirred for 1 h, and a viscous PAA solution was obtained; 1, 3, and 5 wt % of PPD-Mont in DMAc were prepared by putting 0.074, 0.222, and 0.371 g of PPD-Mont in 19.95 g DMAc, respectively, and by mixing each of them for 12 h. These PPD-Mont suspensions were then mixed with the PAA to obtain PPD-Mont/PAA in DMAc. The final solid content of PPD-Mont/PAA in DMAc is 13%. BPDA-ODA nanocomposite films were prepared by applying PPD-Mont/PAA on glass slides with a doctor blade. These glass slides containing PPD-Mont/PAA were placed in a vacuum oven at 30°C for 48 h before the imidization step. Imidization of PPD-Mont/PAA was carried out by putting the samples in an air-circulation oven at 100, 150, 200, and 300°C for 1 h, respectively, and then at 400°C for 5 min to ensure complete imidization. Furthermore, the synthesis and preparation procedures of PPD-Mont/PMDA-ODA and ODA-Mont/BTDA-ODA have been reported elsewhere.<sup>22,23</sup>

### Characterization

An X-ray diffraction (XRD) study of the samples was carried out with Mac Science M18 X-ray diffractometer (50 kV, 250 mA) with a copper target and Ni-filter at a scanning rate of 4°/min. The samples for transmission electron microscopy (TEM) observation was prepared by putting Mont/polyimide films into epoxy capsules and

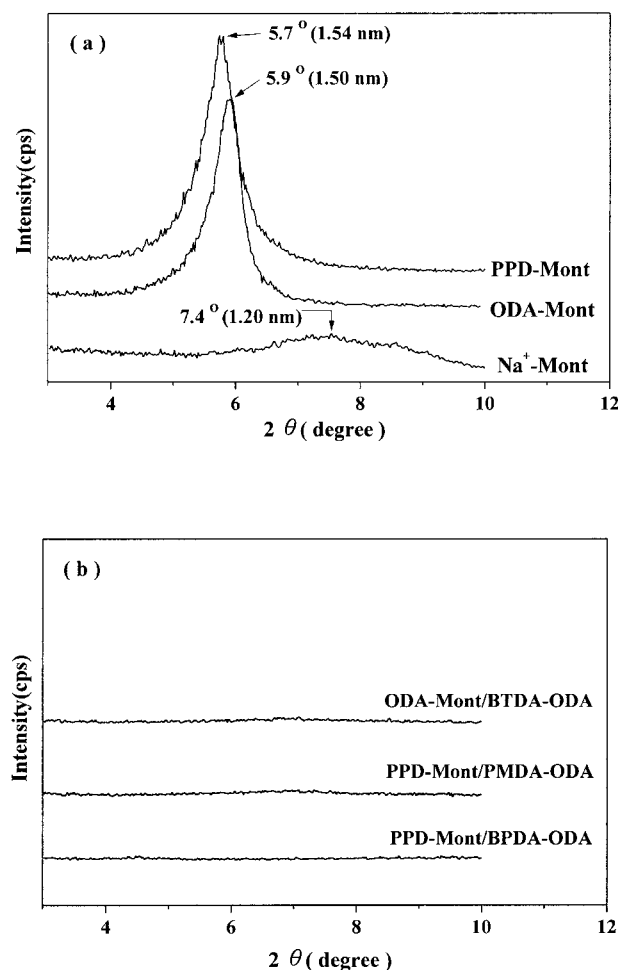
then by curing the epoxy at 70°C for 24 h in a vacuum oven. Subsequently, the cured epoxies containing Mont/polyimide were microtomed with Leica Ultracut Uct into 90-nm-thick slices in a direction normal to the plane of the films. A layer of carbon  $\sim 1$  nm thick was deposited on these slices, on mesh 200 copper nets for TEM observation. The type of TEM used is JEOL-2000 FX, and its accelerated voltage was 200 kV. The thermal-gravimetric and the thermal transitions analyses of Mont/polyimide films were carried out with a Du Pont TGA 2950 and with a Du Pont DSC 2910 differential scanning calorimeter (DSC), respectively, at a heating rate of 20°C/min. In the DSC measurements, the samples were first heated to 400°C for 1 min and were then quenched in liquid nitrogen to wipe out the thermal history. The DSC data of the samples were obtained at the second heating. The in-plane CTE of the Mont/polyimide nanocomposite films were measured with macro tension probe at a heating rate of 5°C/min. The average in-plane CTE within a temperature range of 50–250°C was recorded after an initial conditioning step (heat 250°C, hold 5 min, cool). Moisture absorption measurements of thin polyimide nanocomposite films  $\sim 15$   $\mu\text{m}$  were carried out in a humidity chamber at 30°C for 72 h under 85% relative humidity condition. The percentage of moisture absorption was calculated based on equation (1):

$$\text{Moisture absorption (\%)} = [(W_1 - W_0)/W_0] \times 100\% \quad (1)$$

where  $W_1$  and  $W_0$  represent the moisture-absorption weight and the dried weight of Mont/polyimide, respectively.

## RESULTS AND DISCUSSION

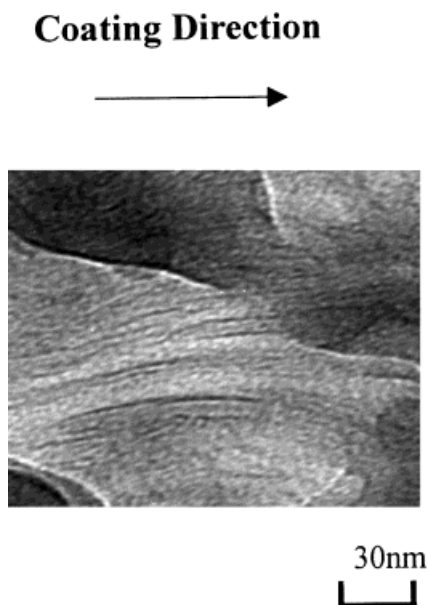
The wide-angle X-ray diffraction (WAXD) curves of swelling-agent-modified montmorillonite (Mont) are presented in Figure 2(a). Figure 2(a) shows broad diffraction peaks at  $2\theta = 7.4^\circ$  (d-spacing = 1.20 nm) for pure montmorillonite. For PPD-Mont and ODA-Mont, strong diffraction peaks were displayed at  $2\theta = 5.7^\circ$  (1.54 nm) and  $2\theta = 5.9^\circ$  (1.50 nm), respectively, indicating that layered silicates were intercalated by PPD or ODA molecules. The WAXD patterns of Mont/polyimide of different chemical structures are shown in Figure 2(b). In Figure 2(b), the disappearance of the XRD peak at



**Figure 2** X-ray diffraction curves of (a)  $\text{Na}^+$ -montmorillonite and swelling-agent-modified montmorillonite, and (b) 3/97 Mont/polyimide films.

$2\theta = 310^\circ$  in all three types of polyimide containing 3 wt % swelling-agent-modified montmorillonite implied that the spacing between the layered silicates have been either intercalated to a distance of  $>3$  nm or exfoliated in polyimide. Further evidence of this nanometer-scale dispersion of intercalated silicate layers in BPDA-ODA can be supported by their TEM, as shown in Figure 3. In Figure 3, the thickness of the silicate layers (dark lines) was  $\sim 1.0$  nm, and some domains appear to contain parallel silicate layers with basal spacing of about 4–8 nm in the case of 3/97 PPD-Mont/BPDA-ODA, which is similar to that in the case of PPD-Mont/PMDA-ODA<sup>22</sup> or ODA-Mont/BTDA-ODA.<sup>23</sup>

The thermal properties of Mont/polyimide nanocomposites at different compositions are presented in Table I, which shows that the thermal degradation temperatures of high-degree-crystal-



**Figure 3** Transmission electron micrographs of cross-sectional view of 3/97 PPD-Mont/BPDA-ODA nanocomposite films.

linity BPDA-ODA, semicrystalline PMDA-ODA, and amorphous BTDA-ODA increased with the amount of swelling-agent-modified montmorillonite. The maximum increase of 27°C occurred in the case of 5/95 Mont/polyimide as compared with that of pure polyimide. The DSC results of Mont/polyimide at different compositions are also given in Table I. In the Table I, the glass transition temperature ( $T_g$ ) increased slightly with the amount of swelling-agent-modified montmorillonite. This phenomenon can be explained by the fact that the layered silicates, which were modified with PPD or ODA molecules, contained available

-NH<sub>2</sub> functional group that reacted with dianhydride end groups of PAA molecules. Therefore, the main-chain motion of polyimide molecules was retarded by these silicate layers near their original glass transition temperatures because the space between some portions of these layered silicates was close to 4 nm, as illustrated in the TEM. The melting points of pure BPDA-ODA and PMDA-ODA are 466 and 532°C, respectively, and the melting points of PPD-Mont/BPDA-ODA and PPD-Mont/PMDA-ODA nanocomposites are not dependent on the amount of layered silicates. Furthermore, the normalized heat of fusion ( $\Delta H_m$ ) (based on the actual polyimide weight in the nanocomposites) of PPD-Mont/BPDA-ODA and PPD-Mont/PMDA-ODA decreased with the increasing amount of layered silicates as presented in Table I, indicating that the presence of the dispersed layered silicates retarded the crystallization of polyimide.

The in-plane CTE of Mont/polyimide at various compositions is displayed in Figure 4. In Figure 4, the in-plane CTE of pure BPDA-ODA (26.2 ppm/°C) was lower than that of pure PMDA-ODA (32.9 ppm/°C) and pure BTDA-ODA (43.9 ppm/°C), owing to the fact that molecular chain of BPDA-ODA was more rigid than that of PMDA-ODA or BTDA-ODA. For all three types of Mont/polyimide, the in-plane CTE decreased with the increasing amount of layered silicates in polyimide, but at different extent. For the case of amorphous BTDA-ODA, the in-plane CTE of 5/95 ODA-Mont/BTDA-ODA was 31.0 ppm/°C, 30% lower than that of pure BTDA-ODA. For the high-degree-crystallinity BPDA-ODA, the in-plane CTE of 5/95 PPD-Mont/BPDA-ODA was reduced to 21.1 ppm, a decrease of 20% as compared with that of

**Table I** Thermal Degradation Temperature, Glass Transition Temperature, Melting Point and Heat of Fusion of Mont/polyimide Nanocomposites for Different Compositions

	PPD-Mont/BPDA-ODA				PPD-Mont/PMDA-ODA				ODA-Mont/BTDA-ODA			
	0	1	3	5	0	1	3	5	0	1	3	5
Contents of mont (wt %)	0	1	3	5	0	1	3	5	0	1	3	5
Degradation temperature <sup>a</sup> (°C)	629	636	646	652	618	626	637	643	583	595	607	610
$T_g$ (°C)	341	342	344	344	370 <sup>b</sup>	372 <sup>b</sup>	375 <sup>b</sup>	376 <sup>b</sup>	276	277	279	279
$T_m$ (°C)	466	465	465	465	532	533	534	534	NE	NE	NE	NE
$\Delta H_m^c$ (J/g)	18.7	12.6	7.9	6.9	4.5	4.0	3.1	2.3	NE	NE	NE	NE

NE, nonexistence.

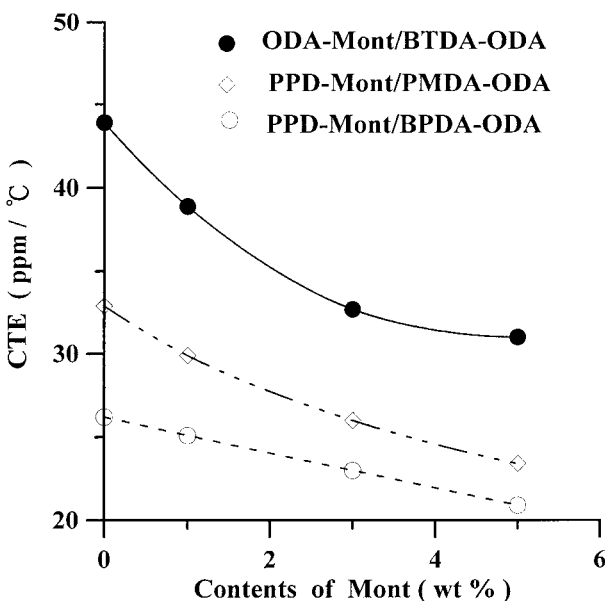
<sup>a</sup> Temperature at 5% weight loss.

<sup>b</sup> Determined by DMA.

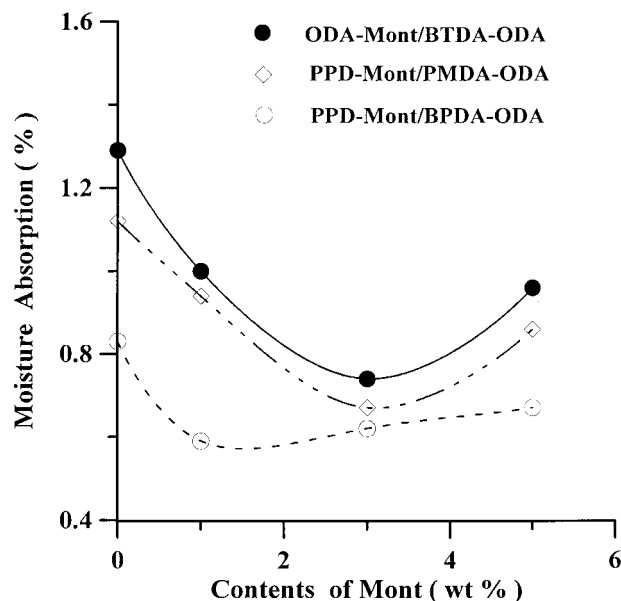
<sup>c</sup> Normalized against polyamide.

pure BPDA-ODA (26.2 ppm/°C). This can be explained by the fact that the dispersed layered silicates can reduce the thermal expansion of BPDA-ODA and also retard the crystallization of BPDA-ODA. The crystallinity in BPDA-ODA held its CTE down in such a way that the CTE was lower than that in the amorphous BTDA-ODA.

The moisture absorption of Mont/polyimide nanocomposites at different compositions was shown in Figure 5. The moisture absorption of the pure BPDA-ODA was 0.83%, which was lower than that of pure PMDA-ODA (1.12%) and pure BTDA-ODA (1.29%) because of the crystallinity factor. In Figure 5, the moisture absorption of ODA-Mont/BTDA-ODA nanocomposite films reached a minimum value at 3 wt % ODA-Mont content. This phenomenon can be explained by the mechanism of moisture absorption of Mont/polyimide being controlled by two competing factors. The first factor is that the mean free path of water vapor molecules, in diffusing through the Mont/polyimide film, was much larger than that of pure polyimide because of the presence of impermeable layered silicates. The second factor is that the silicate layer is still partially hydrophilic after modification, and therefore the moisture adsorbed on silicates increased with the amount of silicates. These two competing effects resulted in a maximum reduction of 43% in moisture adsorption for the case of 3/97 ODA-Mont/BTDA-ODA as compared with that of pure BTDA-



**Figure 4** In-plane coefficients of thermal expansion, averaged 50–250°C, of Mont/polyimide nanocomposite films at different compositions.



**Figure 5** Moisture absorption of different compositions of Mont/polyimide nanocomposite films.

ODA. For the high-degree-crystallinity BPDA-ODA, the largest decrease in the moisture absorption of PPD-Mont/BPDA-ODA nanocomposites was 30% in the case of 1/99 PPD-Mont/BPDA-ODA as compared with that in pure BPDA-ODA.

## CONCLUSIONS

The thermal expansion and the moisture absorption of montmorillonite/polyimide nanocomposites having different chemical structures were found to be affected by the presence of dispersed layered silicates from montmorillonite. These silicates produced two opposing effects. One effect was an inhibition of thermal expansion and moisture absorption of BTDA-ODA, PMDA-ODA and BPDA-ODA, due to the rigid and impermeable layered silicates at low concentration. The other effect was a retardation of crystallization in semicrystalline BPDA-ODA and PMDA-ODA by silicates at higher concentration, which resulted in a lowering of thermal expansion and moisture absorption.

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