

Preparation and Properties of Layered Silicate/Polyimide Hybrid Films

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ABSTRACT: Layered silicate/polyimide (PI) hybrid films were prepared from 4,4'-oxydianiline, 3,3',4,4'-oxydiphthalic anhydride, and chemically modified montmorillonite via an *in situ* intercalation polymerization pathway. The X-ray diffraction and transmission electron microscopy results indicated that the silicates were homogeneously dispersed as exfoliated layers in the PI hybrid film with 2% silicate. The mechanical properties and thermal stabilities of the PI hybrid films changed with the content of the layered silicates. The coefficient of thermal expansion and water uptake of the PI hybrid films decreased with increasing

silicate contents because of the barrier effect of platelike silicate layers, which prevented the diffusion and penetration of water. The dielectric strength and electrical aging performance of the PI hybrid films could also be improved as the silicate layer highly dispersed in the films. For the hybrid PI film with 5% layered silicate, the time to failure during electrical aging exceeded 280 h, which was 2.5 times as long as that of pure PI film. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1176–1183, 2005

Key words: dielectric properties; films; polyimides

INTRODUCTION

Polyimide (PI) films have been extensively employed in the aerospace and aviation industries and in the microelectronic and electric fields as advanced packaging and insulating materials because of their outstanding combined mechanical properties, thermal stability, and electrical insulating properties. With the rapid development of advanced industry, PI films with unique functions are usually required. Therefore, much research has been done on PIs with special features, such as photosensitivity and optoelectric properties.^{1,2}

In recent years, layered silicate/PI nanocomposites have attracted a great deal of research interest. Layered silicate/PI nanocomposites are usually prepared through pathways such as solution mixing, melt blending, or *in situ* polymerization.^{3–7} PIs incorporated with layered silicates have improved mechanical and thermal properties.^{8–16} Moreover, some work on clay/PI nanocomposites has demonstrated that the silicate layers also provide excellent gas-barrier properties.^{3,4} However, few reports deal with the dielectric properties of layered silicate/PI nanocomposites.

In this study, a layered silicate/poly(amic acid) resin derived from 4,4'-oxydianiline (ODA), 3,3',4,4'-oxydiphthalic anhydride (ODPA), and chemically

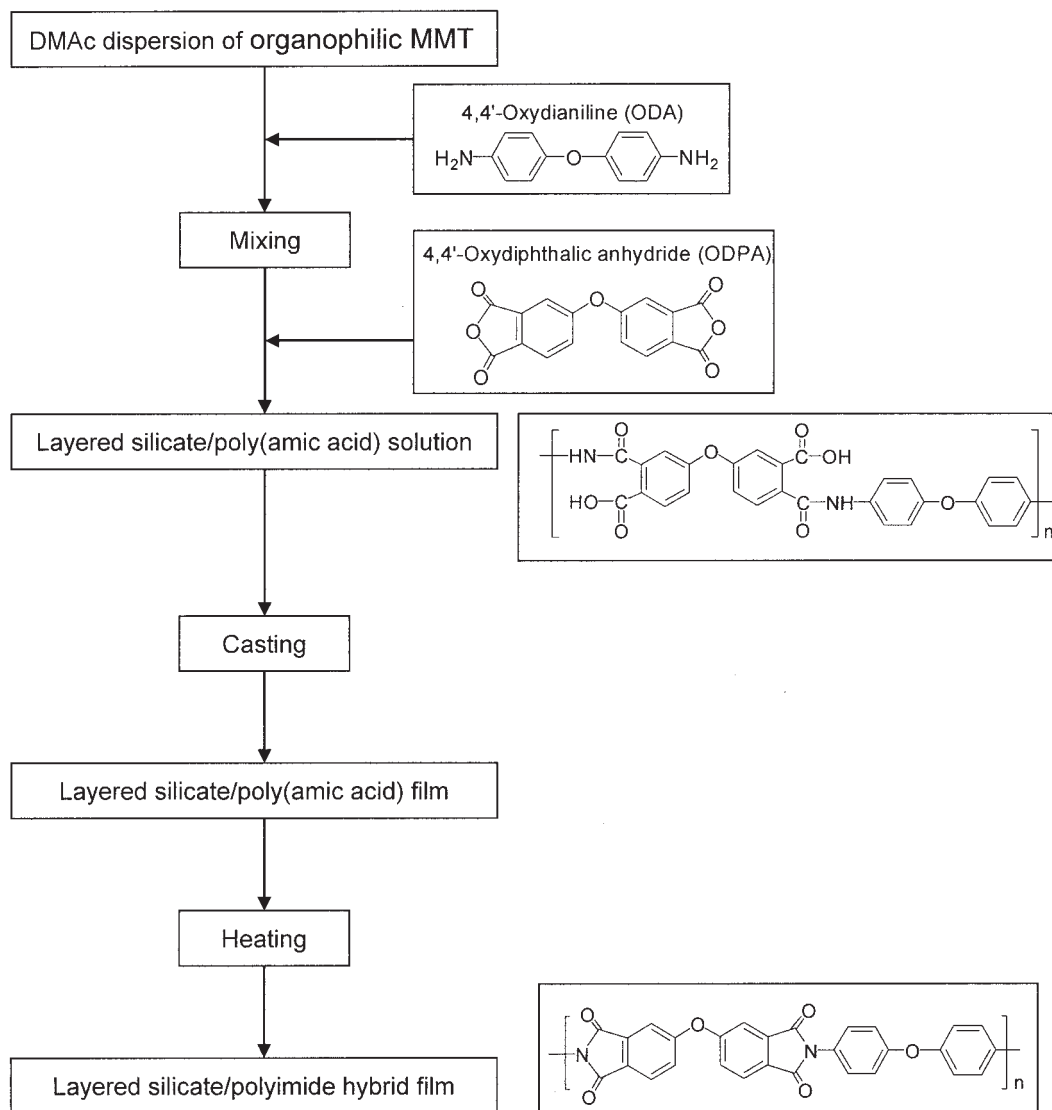
modified montmorillonite (MMT) was synthesized with an *in situ* polymerization pathway and was then thermally imidized to yield layered silicate/PI hybrid films. The ODPA-based PI was chosen because it has been reported to have good mechanical, thermal, and electrical properties, which make it a candidate for many potential applications.^{1,17} The preparation of the layered silicate/PI hybrid films was investigated. The mechanical and thermal properties and dielectric properties of PI hybrid films with different silicate contents were characterized and examined along with their microstructure.

EXPERIMENTAL

Materials

Sodium montmorillonite (Na⁺-MMT) with a cation-exchange capacity of 100 mequiv/100 g was supplied by the Institute of Process Engineering of the Chinese Academy of Sciences (Beijing, China). Hexadecyltrimethyl ammonium bromide [HTAB; C₁₆H₃₃(CH₃)₃N⁺Br⁻; analytical-reagent-grade] was purchased from Beijing Beihua Fine Chemicals Co. (Beijing, China) and was used as received. ODPA was purchased from the Shanghai Research Institute of Synthetic Resins (Shanghai, China) and was recrystallized from acetic anhydride before use. ODA was purchased from Beijing Beihua Fine Chemicals and was purified by sublimation. *N,N*-Dimethylacetamide (DMAc) was purchased from Beijing

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Scheme 1 Preparation of layered silicate/PI hybrid films.

Beihua Fine Chemical and was dried over molecular sieves before use.

Preparation of the layered silicate/PI hybrid films

The surface of Na^+ -MMT was chemically treated by the dispersion of Na^+ -MMT (60 g) in 2000 mL of deionized water, followed by the addition of HTAB (52 g) in 400 mL of deionized water with vigorous stirring at 80°C for 3 h. The white precipitate was isolated by filtration and washed repeatedly with hot water until no Br^- was detected in the filtrate. The product was vacuum-dried at 80°C for 24 h.

The *in situ* polymerization method was applied to prepare the layered silicate/poly(amic acid) with the procedure shown in Scheme 1. In a typical experiment, 2.40 g of the treated layered silicate was added to 160 mL of DMac and dispersed by an

ultrasonic device to yield a suspension. Then, 18.80 g of ODA (93.89 mmol) was added to the suspension under a nitrogen atmosphere. After the ODA completely dissolved (ca. 0.5 h), 29.11 g of ODPA (93.89 mmol) and an additional 69.6 mL of DMac were added. The mixture was stirred at room temperature for 6 h under nitrogen to give a homogeneous and viscous layered silicate/poly(amic acid) solution.

The layered silicate/poly(amic acid) solution was cast onto a glass substrate, and this was followed by successive heating at 80, 120, 180, 250, and 300°C (each for 1 h). The PI hybrid film was then peeled from the glass substrate.

A series of layered silicate/PI films, 45 ± 5 μm thick, with layered silicate contents of 0, 2, 5, 10, and 20 wt % were prepared with a similar procedure.

Characterization

The wide-angle X-ray diffraction (XRD) measurements were conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu $K\alpha$ radiation, which was operated at 40 kV and 200 mA. Transmission electron microscopy (TEM) photographs were obtained with a JEM 2010 electron microscope. The samples for TEM observations were prepared by the placement of a small strip of the sample film in an epoxy resin and by the curing of the resin overnight at 80°C. The samples were then cut with a Leica Ultracut R and deposited onto a 200-mesh copper net. Scanning electron microscopy (SEM) micrographs were taken with a Hitachi S-4300 scanning electron microscope with film samples coated with platinum. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) were recorded on a PerkinElmer 7 series thermal analysis system at a heating rate of 20°C/min. The measurements of the in-plane coefficients of thermal expansion (CTEs) of the samples were carried out on a PerkinElmer 7 series thermal analysis system at a heating rate of 10°C/min. The CTE of each sample was determined by the calculation of the result in a temperature range of 50–150°C. The water uptake was determined by the weighing of the changes in the polymer film ($5.0 \times 5.0 \times 0.045$ cm) before and after immersion in distilled water at 50°C for 24 h. The mechanical properties were measured on a Instron 1122 tensile apparatus with 120×10 mm specimens in accordance with GB1040-79 at a drawing rate of 50 mm/min. The dielectric strength and electrical aging were tested on an electric assembly consisting of a cylinder electrode and a plane electrode in accordance with the IEC-343 standard. In the electrical aging test, the voltage applied to the sample was 750 V.

RESULTS AND DISCUSSION

Intercalation of MMT with HTAB

Na^+ -MMT was intercalated by the organic surfactant, HTAB, to form the organically modified layered silicate. In this procedure, HTAB was reacted with Na^+ -MMT by an ion-exchange reaction to form $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$ -MMT salt. The XRD curves of Na^+ -MMT and organically modified MMT are shown in Figure 1. Na^+ -MMT shows a diffraction peak at $2\theta = 7.0^\circ$, which corresponds to the (001) crystal surface of layered silicates with an interlayer spacing of 12.6 Å. However, the chemically treated MMT shows two separated peaks at 2θ values of 2.2 and 4.5° with corresponding interlayer spacing of 39.9 and 19.7 Å, respectively. It is suggested that the layered silicate was exchanged and swelled by HTAB to yield intercalated silicates with an interlayer distance larger than that of the original Na^+ -MMT. The thermal stability of

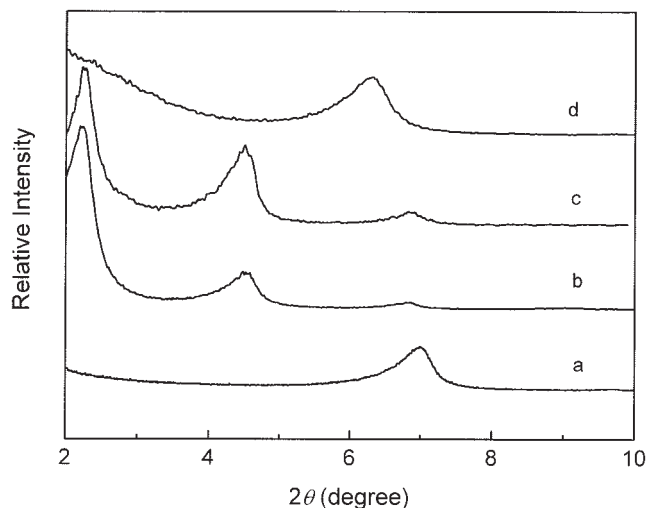


Figure 1 XRD patterns of (a) Na^+ -MMT, (b) organically modified MMT, (c) organically modified MMT treated at 180°C for 1 h, and (d) organically modified MMT treated at 250°C for 1 h.

chemically modified MMT was also studied. Figure 1(c,d) shows that as the chemically modified MMT was treated at 180°C, besides the peaks at 2θ values of 2.2 and 4.5° , a weak peak at $2\theta = 6.8^\circ$ was detected. Moreover, as the treatment temperature increased to 250°C, only the peak at $2\theta = 6.3^\circ$ was observed. This could be interpreted by the thermal decomposition of the chemically modified sites in the layered silicate.

Preparation of the layered silicate/PI hybrid films

The layered silicate/PI hybrid films were prepared by an *in situ* polymerization intercalation pathway; that is, silicate powder was dispersed in the solvent by an ultrasonic device, in which aromatic diamine was also dissolved. Then, the aromatic dianhydride was added stepwise to polycondense with the aromatic diamine to produce a homogeneous and viscous layered silicate/poly(amic acid) resin. The silicate particles were well dispersed in the solution, and no particle clustering or aggregation was observed. The absolute viscosity of the layered silicate/poly(amic acid) solution could be controlled in the range of 100–120 P at 25°C by the adjustment of the molar ratio of diamine to dianhydride. The layered silicate/PI hybrid films were prepared by the casting of the resin solution onto a glass plate. After thermal imidization, a series of PI hybrid films with different silicate contents were obtained.

The XRD patterns of the PI hybrid films are shown in Figure 2. The PI hybrid films with a silicate content of 2% did not show any peak in the range of $2\theta = 4$ – 20° , and this indicated that the silicate layers were highly dispersed in the matrix resin as exfoliated

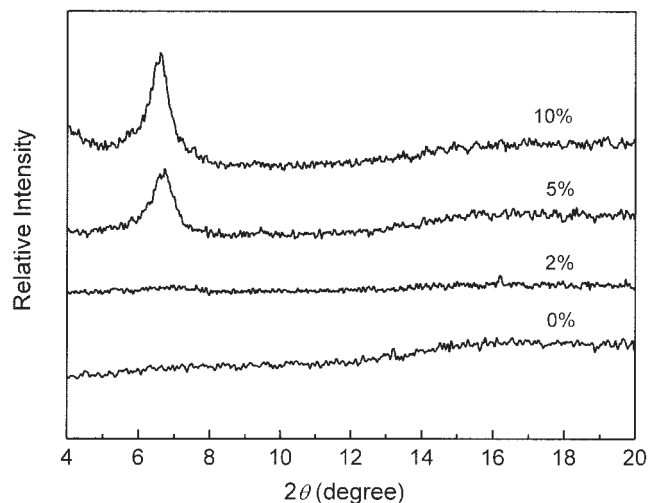


Figure 2 XRD patterns of layered silicate/PI hybrid films with different silicate contents.

layers. However, as the silicate content increased to 5%, the diffraction peak at $2\theta = 6.7^\circ$, corresponding to an interlayer spacing of 13.1 \AA , was observed. This revealed that silicate particle aggregation occurred. Moreover, as the silicate content increased to 10%, the diffraction peak became stronger and sharper because of the further aggregation of silicate particles.

Figure 3 compares the XRD of layered silicate/PI hybrid films, with a silicate content of 5%, thermally cured at different final treatment temperatures. The 5% layered silicate/PI hybrid film did not show any diffraction peak after curing at 80°C , and this indicated that the layered silicate particles were well dispersed in the matrix resin as exfoliated layers. However, as the treatment temperature was raised to 180°C , a broad and weak diffraction peak at $2\theta = 6.7^\circ$

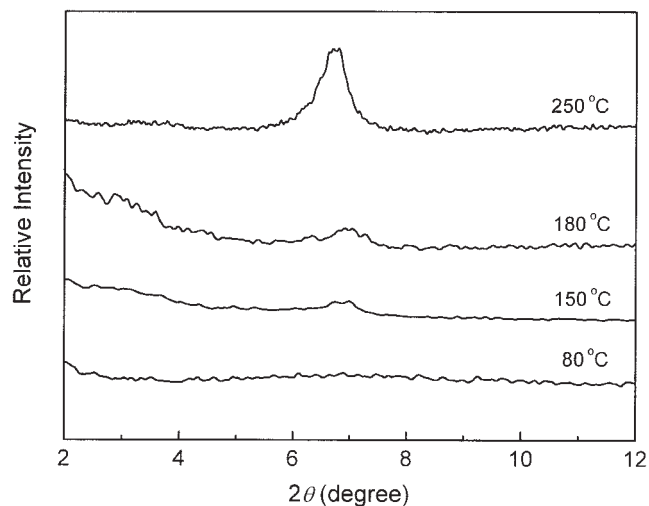


Figure 3 XRD patterns of 5% layered silicate/PI hybrid films treated at different temperatures.

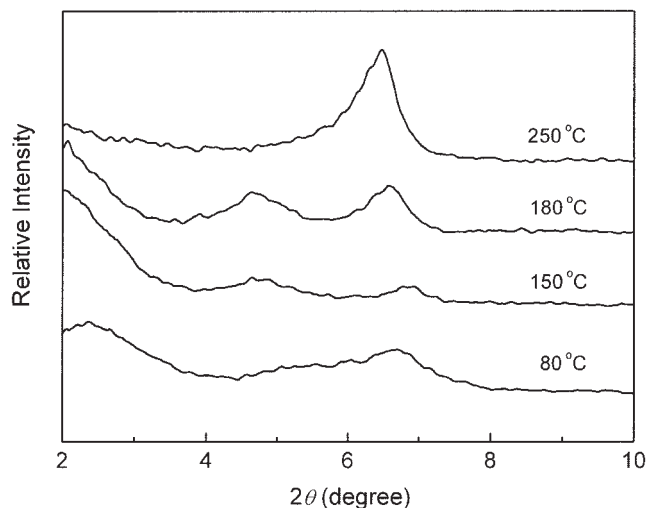


Figure 4 XRD patterns of 10% layered silicate/PI hybrid films treated at different temperatures.

was observed. This implied that some of the silicate layers could not be exfoliated and aggregated in the imidized film. Moreover, as the final curing temperature increased to 250°C , the diffraction peak became sharper and stronger. This suggests the further aggregation of silicate layers with the extent of thermal imidization.

The layered silicate/PI hybrid film with a silicate content of 10% showed a similar tendency in the thermal treatment procedure (Fig. 4). The XRD patterns of the film treated at 80°C show two broad peaks at 2θ values of 2.3 and 6.6° , indicating that some of the silicates were hard to disperse as exfoliated layers and aggregated in the matrix resin. As the thermally cured temperature increased to 180°C , three wide diffraction peaks at 2θ values of 2.2 , 4.7 , and 6.6° were detected. However, two of them disappeared as the curing temperature further increased to 250°C ; only the peak at $2\theta = 6.6^\circ$ remained. The same phenomenon was also observed for chemically modified MMT, as shown in Figure 1. The reduction of interlayer spacing can be explained by the collapse of the silicate layers because of the thermal decomposition of the chemically modified sites, as mentioned before.

TEM micrographs provided additional evidence of the dispersion state of the intercalated silicate layers in the PI hybrid films. In Figure 5(a), the layered silicates (2%) are dispersed homogeneously in the hybrid film and intercalated completely to give thin silicate layers. When the silicate content in the hybrid film increased to 10%, some of the layered silicates were not swollen and layer-separated, as in their original state, as shown in Figure 5(b).

Mechanical and thermal properties

The mechanical properties of the layered silicate/PI hybrid films slightly changed with the silicate content

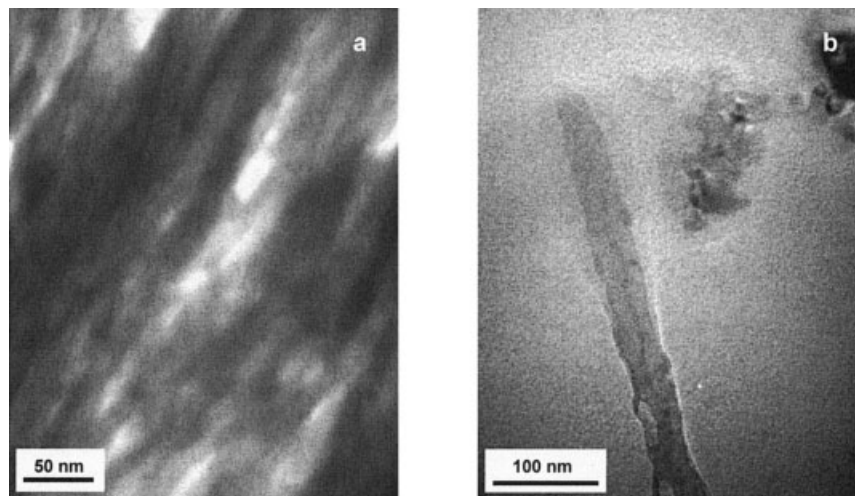


Figure 5 TEM photographs of layered silicate/PI hybrid films with (a) 2% and (b) 10% silicate.

(Table I). The Young's moduli increased gradually as the silicate content increased. The film with 5% layered silicate had a Young's modulus of 3.9 GPa, which was 39% higher than that of the pure PI film (2.8 GPa). This was mainly attributed to the reinforcing effect of the silicate particles on the film. The tensile strength increased slightly with the addition of the silicate particles in comparison with that of the pure film. For the hybrid film with 10% layered silicate, the tensile strength was 141.9 MPa, 15% higher than that of the pure film (123.1 MPa). However, the elongation at break decreased constantly with an increase in the silicate content. For the hybrid film with 10% layered silicate, the elongation at break was 8.9%, which was 40% lower than that of the pure film (14.9%). Obviously, the layered silicates could improve the stiffness of PI but degraded the flexibility of the polymer chain.

Figure 6 presents the DMA curves of the PI hybrid films with different silicate contents. Although the onset decline temperatures of the storage modulus curves, located at 230–250°C, did not apparently change, the storage modulus values increased distinctly in the range of 50–230°C with the silicate content increasing.

TABLE I
Mechanical Properties of Layered Silicate/PI Hybrid Films with Different Silicate Contents

Silicate content (wt %)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation (%)
0	2.8	123.1	14.9
2	3.4	133.7	13.7
5	3.9	136.1	10.1
10	4.0	141.9	8.9
20	4.4	124.8	3.7

Table II summarizes the thermal properties of PI hybrid films with different silicate contents. The PI hybrid films showed better thermal stability than pure PI. The thermal decomposition temperatures for the hybrid films were higher than 580°C (Fig. 7). The temperature at 5% weight loss was 588°C for the hybrid film with 5% layered silicate, 19°C higher than that of the pure PI film.

The glass-transition temperatures (T_g 's) of the hybrid films with different silicate contents, measured by DSC, slightly decreased. This might be explained by the weak interaction between the MMT and matrix resin, which led to the increase in the free volume and the cooperative motions of the main-chain segment.^{7,18}

The in-plane CTE of the PI hybrid films decreased gradually with increasing silicate content. The hybrid

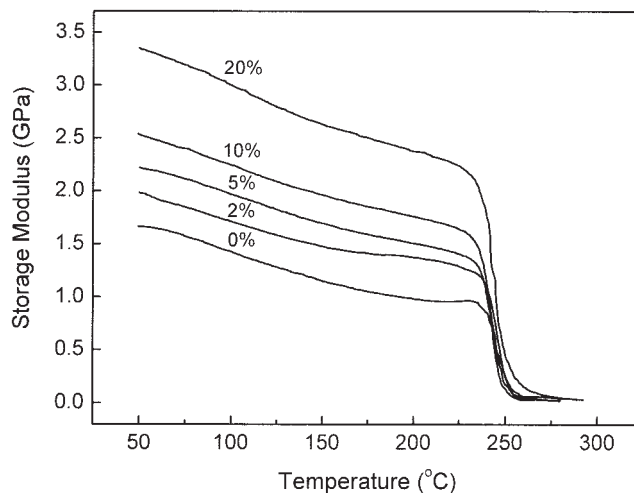


Figure 6 Storage modulus curves of layered silicate/PI hybrid films with different silicate contents.

TABLE II
Thermal Properties of Layered Silicate/PI Hybrids with Different Silicate Contents

Silicate content (wt %)	Decomposition temperature (°C)		T_g (°C) ^a	CTE (ppm/°C)
	T_d	T_5		
0	564	569	267	38.4
2	582	591	264	34.1
5	580	588	264	32.2
10	580	585	264	28.1
20	580	585	262	21.8

T_d = onset decomposition temperature; T_5 = decomposition temperature at 5% weight loss.

^a Determined by DSC.

film with 10% layered silicate had a CTE of 28.1 ppm/°C, 27% lower than that of the pure PI film. As the silicate content increased to 20%, the film CTE further decreased to 21.8 ppm/°C.

Dielectric and electrical properties

The dielectric strength and electrical aging properties are two important parameters for PI films applied as electrical insulation materials, especially for high-electric-field and high-temperature applications. A phenomenon generally known as corona, which can cause ionization in an insulating layer, has been recognized as the major reason for the electric breakdown of an insulation material or system when the voltage stress reaches a critical level. It has been reported that PI films with the addition of some ultrafine inorganic additives show great corona-resistance properties.^{19,20}

Figure 8 shows the dielectric strength of PI hybrid films with different silicate contents. The dielectric

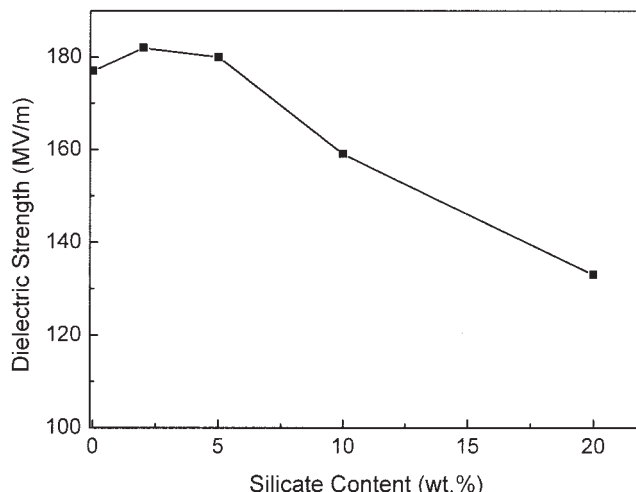


Figure 8 Effect of the silicate content on the dielectric strength of layered silicate/PI hybrid films.

strength slightly increased as the silicate content increased and then dramatically decreased. The hybrid film with 5% layered silicate had a dielectric strength (180 MV/m) 11 and 26% higher than those of the films with 10 and 20% layered silicate, respectively. Similar results were also reported by Magaraphan et al.²¹ It is suspected that the silicate aggregates in PI films, found at high silicate contents, might act as impurities that cause some defects and thus diminish the dielectric strength.

Figure 9 shows the electrical aging of PI hybrid films determined by the detection of the time to failure for the films as a voltage of a constant electric field was applied. The PI hybrid films showed improved electrical aging performance in comparison with the pure PI film. The hybrid PI film with 5% layered silicate especially exhibited significant enhanced perfor-

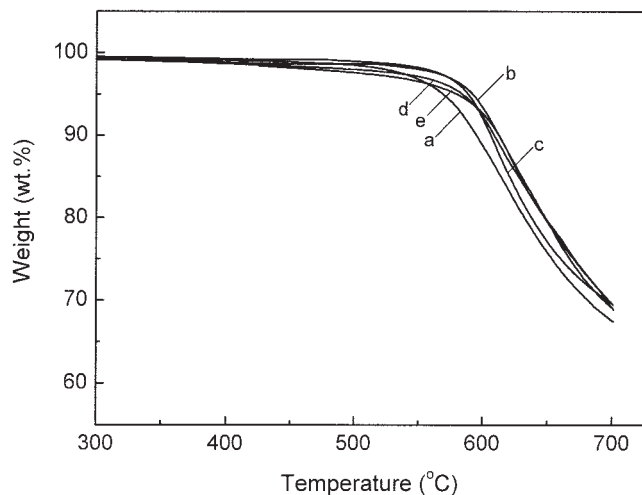


Figure 7 TGA curves of layered silicate/PI hybrid films with (a) 0, (b) 2, (c) 5, (d) 10, and (e) 20% silicate.

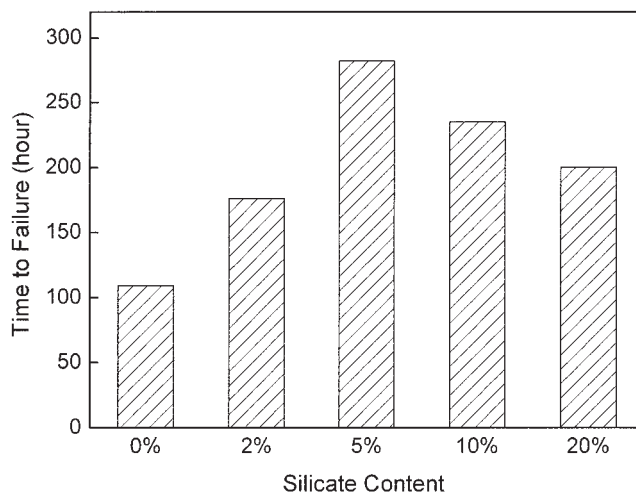


Figure 9 Time to failure of layered silicate/PI hybrid films in electrical aging.

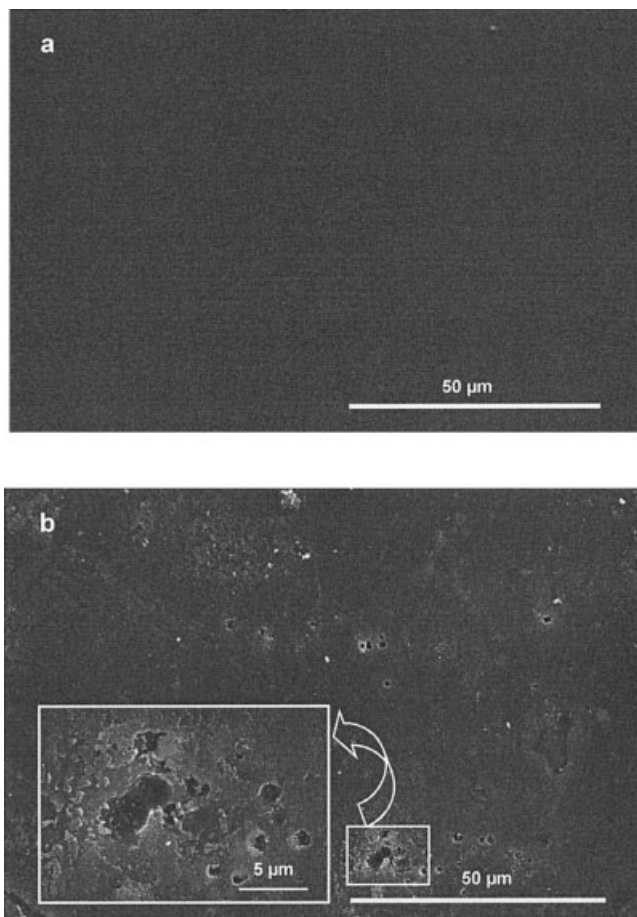


Figure 10 SEM micrographs of pure PI (ODPA-ODA) films (a) before and (b) after electrical aging.

mance: the time to failure of the film with 5% layered silicate in electrical aging at 750 V (280 h) was 2.5 times as long as that of the pure PI film (109 h). The improved dielectric properties of the PI hybrid film with 5% layered silicate were attributed to the high dispersion and adequate addition of silicate particles in the matrix resin, which exhibited an excellent barrier effect to obstruct or delay the corona damage.

The surface morphology of the pure PI film and PI hybrid film with 5% silicate before and after electrical aging was investigated with SEM micrographs, as shown in Figures 10 and 11. Both the pure PI film and hybrid film showed a smooth surface before electrical aging. However, the films showed interesting surface changes after electrical aging. A craterlike structure was observed on the surface of the pure PI film where the electric breakdown occurred. On the other hand, a fine grainlike or flakelike structure was detected on the surface of the hybrid film. We suppose that the craterlike structure on the surface of the pure PI film after electrical aging was derived from the local discharge at the defective point of the PI film, leading to melting followed by decomposition and final damage of the film. In contrast, the fine grainlike or flakelike

structure, which was detected on the surface of the PI hybrid film after electrical aging, might be related to the homogeneous distribution of the electric field in electrical aging caused by highly dispersed silicate layers in the hybrid film. We suspect that the silicate layers in the hybrid film effectively limited the local discharge, and this caused the matrix resin to melt and decompose at a relatively slow rate under the action of a homogeneous electric field. Further detailed work is under investigation.

Water uptake

The water uptake of the PI hybrid films was determined by the weighing of the films before and after immersion in distilled water at 50°C for 24 h (Fig. 12). The results indicated that the PI hybrid films had lower water absorption than the pure PI films. The hybrid film with 5% layered silicate had 0.87% water uptake versus 1.36% for the pure PI film. Similar results were also found by Yano and Jiang et al.^{3,9,10} It is thought that the decrease in the water uptake was due to the platelike silicate in the hybrid film forming

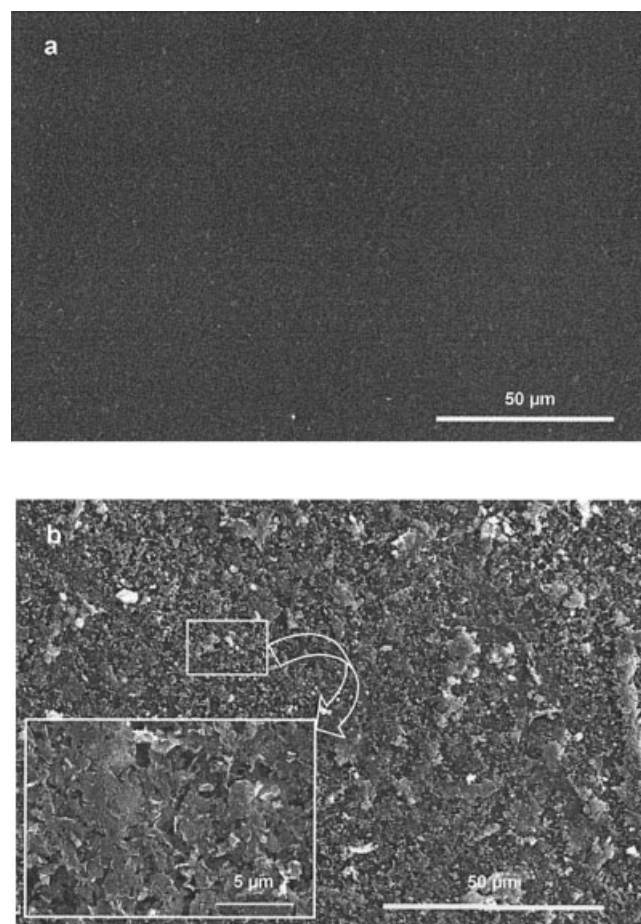


Figure 11 SEM micrographs of layered silicate/PI hybrid films with 5% silicate (a) before and (b) after electrical aging.

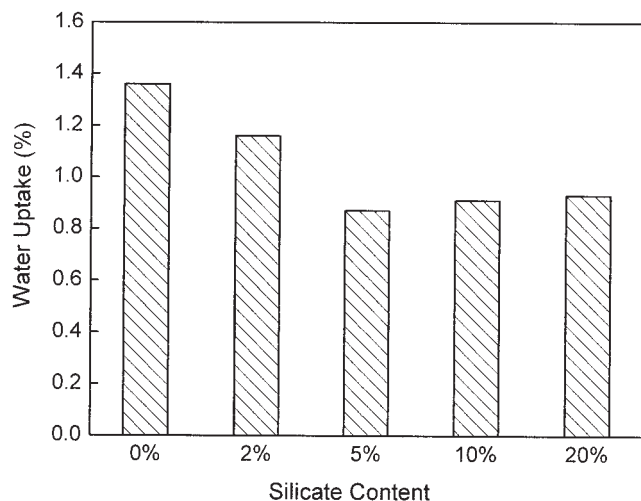


Figure 12 Water uptake of layered silicate/PI hybrid films with different silicate contents.

barrier layers to water molecule diffusion and penetration. However, the water uptake did not decrease monotonically with increasing silicate content. This could be explained by the fact that the number of water molecules bound to the layered silicate surfaces increased as the silicate content increased.¹⁰ Additionally, as the silicate content increased, the aggregation of silicates occurred, and this reduced the intercalation of the matrix resin.

CONCLUSIONS

Layered silicate/PI hybrid films, derived from ODPA, ODA, and chemically modified MMT, were prepared successfully via an *in situ* intercalation polymerization pathway. The mechanical properties and thermal stabilities of the PI film were improved as the layered silicates homogeneously dispersed in the matrix resin. The PI hybrid films also showed decreased CTEs in

comparison with that of the pure PI film. The water absorption of the PI hybrid films was lower than that of the pure PI film because of the platelike silicate in the hybrid film forming barrier layers to water molecule diffusion and penetration. The PI hybrid film with a silicate content of 5% exhibited enhanced dielectric strength and electrical aging performance.

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