Synthesis and Dielectric Properties of Poly(methyl methacrylate)–Clay Nanocomposite Materials

Hong-Wen Wang, Chain-Fang Shieh, Kung-Chin Chang, Hsuan-Chih Chu

Department of Chemistry and Center for Nanotechnology, Chung-Yuan Christian University, ChungLi 320, Taiwan, Republic of China

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ABSTRACT: Poly(methyl methacrylate) (PMMA)–clay nanocomposite (PCN) materials were synthesized through *in situ* intercalative polymerization. A cationic surfactant, [2(dimethylamino)ethyl]triphenylphosphonium bromide, was used as an intercalating agent with pristine Na^+-montmorillonite (MMT). The synthesized PCN materials were subsequently investigated by a series of characterization techniques, including wide-angle powder X-ray diffraction, Fourier transform IR spectroscopy, transmission electron microscopy, thermogravimetric analysis, and differential scanning calorimetry. Compared to pure PMMA, the PCN materials exhibit higher thermal degradation temperatures and glass-transition temperatures. The dielectric properties of PCN blending with a commercial PMMA material in film form with clay loading from 0.5 to 5.0 wt % were measured under frequencies of 100 Hz–1 MHz at 35–100°C. Significantly depressed dielectric constants and losses were observed for these PCN-blending materials. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2175–2181, 2005

Key words: poly(methyl methacrylate); clay; nanocomposite; dielectric properties

INTRODUCTION

The advantages of hybrid polymer–clay nanocomposites were first demonstrated by Toyota Research Center in Japan for nylon nanocomposites.[1,2] There has been substantial interest in research and applications since then because of their excellent properties.[3] Enhanced thermal stability,[4–9] fire retardancy,[10–12] mechanical strength,[7–9] storage modulus, gas barrier corrosion resistance,[13] ionic conductivities,[14] and decreased absorption in organic liquids[15] have been reported for various polymer–clay nanocomposite materials. The nature of the low dielectric constant of polymers also attracts applications in electronic insulating materials. The dielectric responses of poly(methyl methacrylate) (PMMA) have been reported.[16,17] However, for increasing applications of the polymer–clay nanocomposites, the dielectric performance of PMMA–clay nanocomposites (PCNs) has not been well studied and deserves more exploration.

Clay is one type of layered silicate, and the most commonly used clay in the preparation of polymer–clay nanocomposites is montmorillonite (MMT). MMT is composed of silicate sheets of about 1-nm thickness and 100–1000 nm length. It contains negatively charged layered silicates ionically bonded with metal cations such Na^+, Ca^{2+}, K^+, or Mg^{2+}. Before the preparation of polymer–clay nanocomposites, modification is generally required through a cation exchange reaction between organic cations and inorganic cations to render hydrophilic MMT more organophilic and to increase its interlayer d_{001} spacing. Then, the monomer of organic compounds may easily enter the galleries of the interlayer and the polymerization process then results in two idealized polymer-layered silicate structures, which are intercalation and exfoliation. It has been reported that organic compounds such as poly(amic acid),[6–8] styrene,[18,19] aniline,[20,21] vinyl alcohol,[22,23] styrene–acrylonitrile copolymer,[24,25] and MMA[9,11–13,26–38] may enter the silicate interlayer galleries and undergo various polymerization processes. In general, the greatest property enhancements have usually been observed in nanocomposites with an exfoliated structure.

In this report, we present PCNs by an *in situ* intercalative polymerization. The structure of PCNs was characterized by wide-angle powder X-ray diffraction (WAXRD), Fourier transform IR spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). The dielectric behaviors of these nanocomposites were also investigated.

EXPERIMENTAL

Materials

MMT, with a cation exchange capacity (CEC) of 98 meq/100 g, was supplied by Pai Kong Company (Taiwan).

Correspondence to: H.-W. Wang (hongwen@cycu.edu.tw).
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[2-(Dimethylamino)ethyl]triphenylphosphonium bromide (97.0%, Aldrich) was used as an intercalating agent, which possesses a relatively longer chain structure than other surfactants and exhibits an excellent swelling effect for our clay materials. MMA was purchased from Fluka Chemical (99.0%), Benzoyl peroxide (BPO, 97.0%, Fluka) was used as a free radical initiator. Toluene (Mallinckrodt, 99.0 %), hexane (98.5%, Mallinckrodt), hydrochloric acid (Riedel-de Haen), *N*-methyl-2-pyrrolidinone (NMP, 99.0%, Mallinckrodt), and commercial PMMA [weight-average molecular weight (M_w) = 350,000, Acros] were used as received.

Preparation of organophilic clay

The organophilic clay was prepared by a cation exchange method, which is a reaction between the sodium cations of the MMT clay and the alkyl ammonium ions of the intercalation agent. Typically, 5 g of MMT clay with a CEC value of 98 meq/100 g was stirred in 600 mL of distilled water (beaker A) at room temperature overnight. A separate solution was prepared containing 2.4 g of intercalating agent in another 30 mL of distilled water (beaker B) under magnetic stirring, followed by adding 1.0*M* HCl aqueous solution to adjust the pH value to 3–4. After stirring for 3 h, the protonated amino acid solution (beaker B) was added to the MMT suspension (beaker A) at a rate of approximately 10 mL/min with vigorous stirring. The mixture was stirred overnight at room temperature. The organophilic clay was recovered by ultracentrifuging (9000 rpm, 30 min) and filtering the solution in a Buchner funnel. Purification of products was performed by washing and filtering samples repeatedly (at least 4 times) to remove any excess ammonium ions. The organophilic clay was thus obtained.

Synthesis of PMMA

A typical procedure to prepare PMMA involved placing 10 g of MMA, 0.121 g of BPO, and 100 mL of dry toluene into a 250-mL three-necked round-bottomed flask connected to a condenser, a thermometer, and a nitrogen gas inlet/outlet. Nitrogen gas was bubbled into the flask throughout the reaction. Under magnetic stirring, the solution was heated to 85°C and maintained for 24 h. The reaction mixture solution was then poured into about 600 mL of hexane to precipitate the polymer. After filtration, the polymer was dried under a vacuum at room temperature for 48 h. The PMMA material was thus obtained.

Preparation of PCNs

An appropriate amount of organophilic clay (0.1 g) was introduced into 100 mL of toluene under magnetic stirring overnight at room temperature. Then, 9.9 g of MMA monomer was subsequently added to the solution, which was stirred for another 24 h. Upon the addition of BPO (0.120 g), the solution was stirred for 24 h at 85°C under a nitrogen atmosphere. The as-synthesized lamellar nanocomposite precipitates were then obtained by precipitating from an excess of hexane (500 mL) and subsequent drying under a dynamic vacuum at room temperature for 48 h. The PCN materials were thus obtained.

Preparation of free-standing films of PCN materials

The M_w value of the synthesized PMMA materials is 39,400, as determined by gel permeation chromatography analysis by Yeh's group at our university.[13] As the intercalation of clay content increased to 5 wt %, the M_w of PCN materials decreased to 23,200. These values were much lower than those in the literature,[33] which is probably attributable to the different polymerization conditions and chemicals used. The decrease in the molecular weights of PMMA due to the intercalation of clay might be explained by the fact that some molecular chains end tethered on silicate layers encounter second radicals and terminate by coupling, and no further polymerization will proceed inside the silicate layers.[33] For the dielectric measurement on a free-standing disk-type film (~60–80 μm), it is necessary to make it strong and flat enough for a good characterization. To enhance the mechanical strength of the films for dielectric characterization, a commercial PMMA with high molecular weight (M_w = 350,000) was blended into the casting solution for film formation. Typically, 0.25 g of as-synthesized PMMA or PCN materials blended with 0.25 g of commercial PMMA were dissolved in 10 mL of NMP solvent under magnetic stirring at room temperature for 24 h. The synthesized PMMA or PCN materials were expected to be uniformly mixed with the commercial PMMA. The solution was cast onto a slide of microscope glass substrate. The solvent was allowed to evaporate at 60–70°C under a hood for 2 h. The sample-coated glass substrate was then immersed into the distilled water for 1 h to give the free-standing film of PMMA and PCN materials. For a logical comparison between specimens, the content of intercalated clay is the only variable in these blending systems, which we refer to as PMMA blending (synthesized PMMA + commercial PMMA, which contained no clay) and PCN blending (synthesized PCN + commercial PMMA, which contained 1–5 wt % clay) in this report.

Characterization of nanocomposites

The characterization of the structures of nanocomposites requires WAXRD to show the changes in the *d*

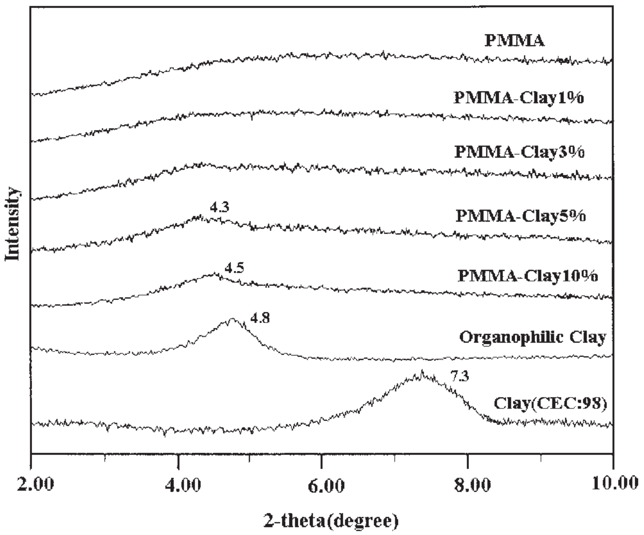

Figure 1 Wide-angle powder X-ray diffraction patterns of pristine MMT clay, organophilic clay, and a series of PCN materials.

spacing of the clay and TEM to image the individual clay layers and thus show the exact nature of the polymer–clay interaction. The WAXRD study of the samples was performed on a Rigaku D/MAX-3C OD-2988N X-ray diffractometer with a Cu target and Ni filter at a scanning rate of 2°/min. The sample for the TEM study was prepared by putting PCN-blending materials (containing PMMA–clay3%) into an epoxy resin capsule followed by curing the epoxy resin at 80°C for 24 h in a vacuum oven. Then, the cured epoxy resin containing PCN-blending materials was microtomed into 60–90 nm slices with a Reichert–Jung Ultracut-E. Subsequently, one layer of carbon about 10 nm thick was deposited on these slices on mesh 300 copper nets for TEM observations on a Jeol-200FX with an acceleration voltage of 120 kV. FTIR spectra were obtained at a resolution of 4.0 cm^{-1} using a Bio-Rad FTS-7 at room temperature and with a range of 4000–400 cm^{-1}.

TGA and DSC were employed to record the thermal stability of specimens. TGA scans were performed on a Mettler–Toledo TGA/SDTA851 thermal analysis system in an air atmosphere. The scan rate was 20°C/min, and the temperature range was 40–800°C. DSC was performed on a DuPont TA Q10 differential scanning calorimeter at a heating or cooling rate of 10°C/min in a nitrogen atmosphere. The temperature range was 35–150°C. The glass-transition temperatures (T_g) of PMMA and PCN materials were recorded based on the second scanning.

Dielectric parameters such as the capacitance and dissipation factor (tan δ) were measured by a Agilent 4284 LCR precision meter at various frequencies (1 kHz–1 MHz) under temperatures from 35 to 100°C. Above 100°C, the PCN film specimens softened and measurements could not be well characterized. A vacuum evaporated gold electrode was deposited on both sides of the nanocomposite films (area 1.6 cm in diameter) after drying at 80°C overnight before the dielectric characterization. The thickness of the samples was 60–80 μm. The dielectric constants (ε_r) of the specimens were calculated by the equation

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d} \tag{1}$$

where ε_0 is the vacuum permittivity, which equals 8.85×10^{-12} F/m; A is the electrode area; and d is the thickness of the specimen.

RESULTS AND DISCUSSION

XRD study

Figure 1 displays a series of WAXRD patterns obtained from the pristine MMT clay, organophilic clay, and a series of PCN materials. The diffraction intensities in $2\theta = 2$–$10°$ were recorded. The diffraction curves revealed for the PCN materials are essentially the same as that of the MMT, except for the peak positions of d_{001} spacing and their intensities. The d_{001} spacing of vacuum dried pristine MMT clay was 1.21 nm ($2\theta = 7.3°$). After the cation exchange, the d_{001} spacing increased to 1.84 nm ($2\theta = 4.8°$), as shown in the organophilic clay of Figure 1. Figure 1 also shows

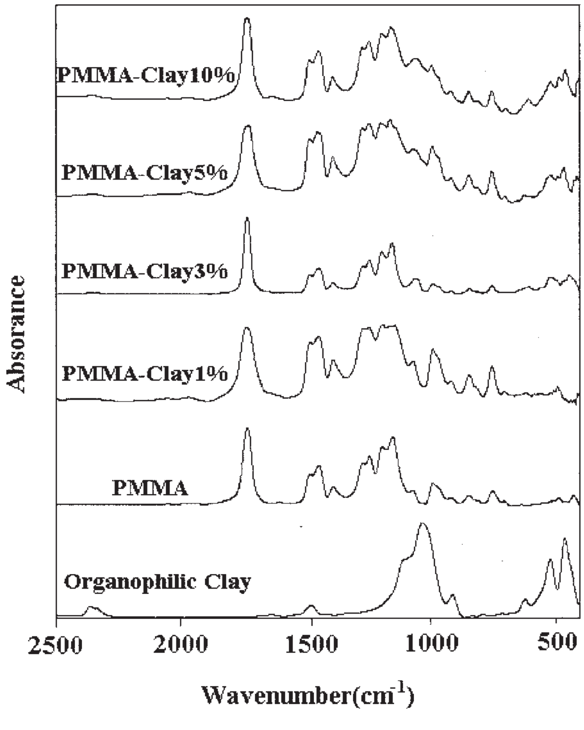

Figure 2 FTIR spectra of organophilic clay, PMMA, and a series of PCN materials.

TABLE I
FTIR Band Assignments of PMMA and PCN Materials

Frequency (cm^{-1})	Source	Assignment
1730	PMMA	C═O
1450	PMMA	C—O
1100	MMT clay	Si—O (stretching)
500+	MMT clay	Al—O (stretching)
400+	MMT clay	Mg—O

a lack of any obvious diffraction peaks for PMMA–clay1% and PMMA–clay3%. The lack of diffraction peaks could mean that the d_{001} spacing between the layered silicates have been either intercalated to a distance of more than 4.42 nm ($2\theta < 2°$) or exfoliated completely in PMMA. However, because the quantities of clay in these PCNs were low (for the case of 1–3 wt %), the intensities may be just too weak to show their characteristics. To further assess intercalation or exfoliation in these materials, TEM observations were required. When the amount of organoclay increases to 5.0 wt %, there is a small peak appearing at $2\theta = 4.3°$ (clay5%) and 4.5° (clay10%), corresponding to d_{001} spacings of 2.05 and 1.96 nm, respectively. This implies that there is a small amount of organoclay that cannot be exfoliated in the PMMA and it exists in the form of an intercalated layer structure.

FTIR study

The representative FTIR spectra of the organophilic clay, PMMA, and a series of PCN materials are shown in Figure 2. Table I illustrates the assignments of the IR bands for PMMA and MMT clay. The characteristic vibration bands of PMMA are at 1450 (C—O) and 1730 cm^{-1} (C═O), and those of MMT clay are at 1100 (Si—O), 500 (Al—O), and 400+ cm^{-1} (Mg—O). As the loading of MMT clay is increased, the intensities of MMT clay bands become stronger in the FTIR spectra of PCN materials.

TEM study

Figure 3(a,b) shows the images of the PCN-blending materials (containing PMMA-3 wt % clay), and the nanocomposite displays a mixed nanomorphology. The clay sheet is about 200–500 nm in length, which is also reported by Theng.[39] In Figure 3(a,b), the black lines represent the intersection of the clay layers and the white areas represent the PMMA matrix. The individual silicate layers, along with two and three layer stacks, were exfoliated in the PMMA matrix. In addition, some larger intercalated layers can also be identified [Fig. 3(a)]. Although intercalation as well as exfoliation structures coexist in the PMMA matrix, direct evidence that the silicate layers uniformly dispersed and intercalated in the polymer matrix was demonstrated.

Thermal properties

Figure 4 shows the DSC traces of the synthesized virgin PMMA and a series of PCN materials (not blended). All samples were annealed at 150°C for a few minutes and then examined in the DSC apparatus. The pure PMMA has an endotherm at 80.5°C, corresponding to the T_g of PMMA. In contrast, the PCN

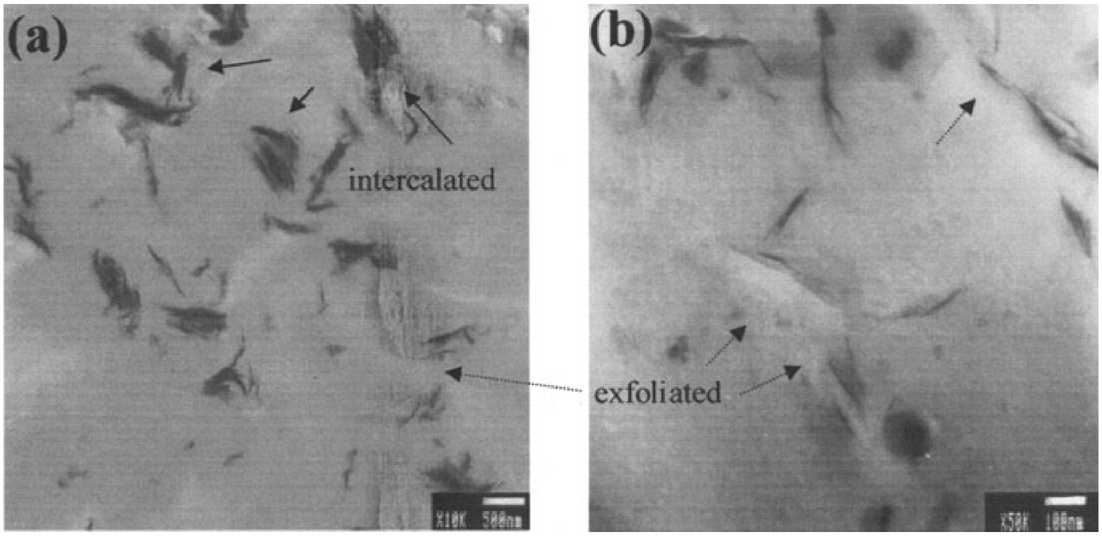

Figure 3 TEM micrographs for PCN-blending materials (contain synthesized PMMA–clay3%) at (a) lower or (b) higher magnification for (dotted arrows) and exfoliated structure (solid arrows) and an intercalated structure that were observed in this specimen.

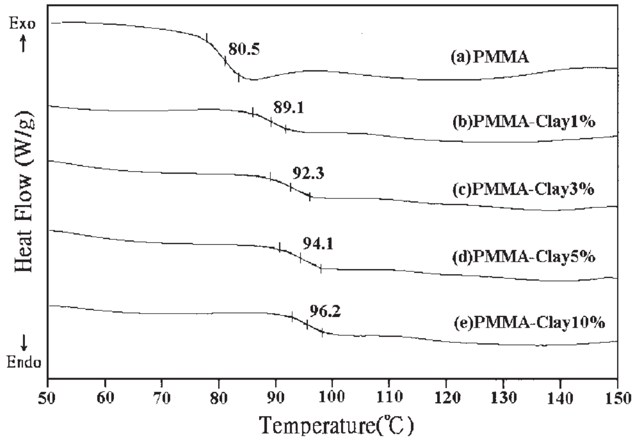

Figure 4 DSC thermograms of PMMA (curve a), PMMA–clay1% (curve b), PMMA–clay3% (curve c), PMMA–clay5% (curve d), and PMMA–clay10% (curve e).

materials exhibit an increasing endothermic trend at around 89–96°C with the increasing amount of MMT clay added. The T_g values of PCN materials are slightly higher than pure PMMA. This could be attributed to the fact that the confined polymer chains in the gallery on the MMT were not free from chain motion. The low T_g values obtained in this study were ascribed to the low molecular weight (M_w = 39,400) of the synthesized PMMA materials. Similar values were also reported by Jiang.[37]

The TGA thermogram of weight loss as a function of temperature for PMMA blending and a series of PCN-blending materials are shown in Figure 5. The thermal stability of the PCN-blending materials was increased with increased clay content. The onset thermal degradation temperature accessed by TGA increased from 321.9°C for PMMA-blending materials to 339.0°C for PCN-blending materials (containing PMMA–10 wt % clay). Enhancement of the thermal stability of the nanocomposites was observed. These results were slightly lower than those of Kumar's report[9] but higher than Blumstein's.[38] The thermal behaviors of the PCN materials demonstrated that the decomposition of PMMA was retarded because of the insertion of polymer into the interlayer of the inorganic host. After ~500°C, the curves all became flat and mainly the inorganic residues (i.e., SiO_2, Al_2O_3, MgO) remained. It is clear that the PCN materials exhibit improved thermal stabilities because of the intercalated and exfoliated clay. The retarding effect of clay platelets on the decomposition of the polymer is obvious.

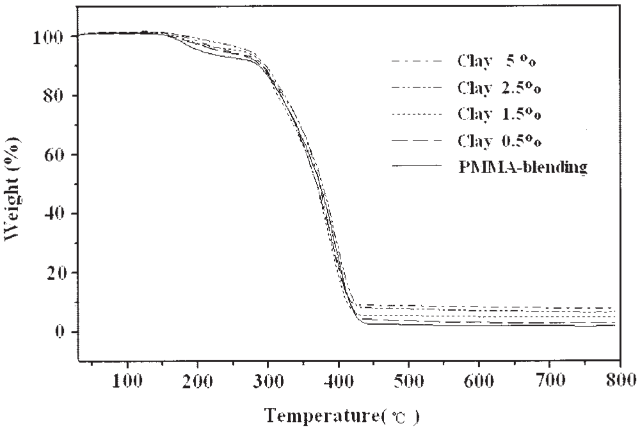

Figure 5 TGA thermogram of the weight loss as a function of temperature for PMMA-blending and a series of PCN-blending materials. The clay contents are shown for their percentage after blending with commercial PMMA.

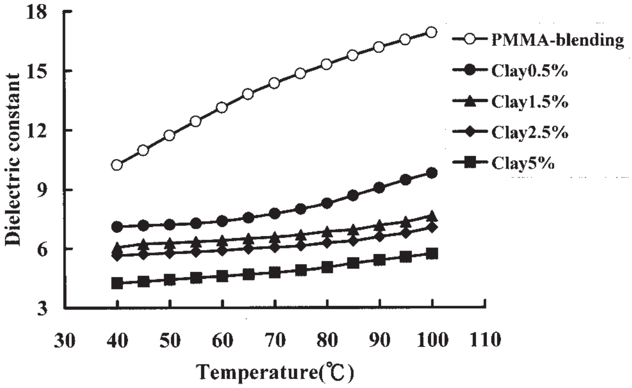

Figure 6 The dielectric constant of PCN-blending nanocomposites at 1 kHz.

Dielectric properties

Although the PCN blendings used for dielectric characterization were made from blending as-synthesized PCN with a commercial PMMA, their dielectric properties were significantly modified by the incorporation of nanoclay. The clay concentration in the PCN-blending film specimens was only half of that discussed in its powder counterpart so far. Therefore, the clay contents are shown as their actual percentages in the blended films in Figures 6–9. In Figure 6, the dielectric constant of PMMA blending was about 10 at 40°C and increased to 18 at 100°C. It is known that dielectric constants are independent of temperature for nonpolar polymers whereas they increase with increasing temperature[32] for polar polymers. As the amount of clay intercalated with PMMA increases, the composite materials show decreased dielectric constants (Fig. 6) and losses (Fig. 7). Figure 7 shows the dielectric loss decreases from over 0.25 to below 0.1 at 100°C as the amount of intercalated clays increase from 0 to 5%. The dielectric constant increase with temperature for PMMA is thought to be due to the weakly polar nature. The depressive dielectric constants and reduced dielectric losses were obviously related to the amount of intercalated clay.

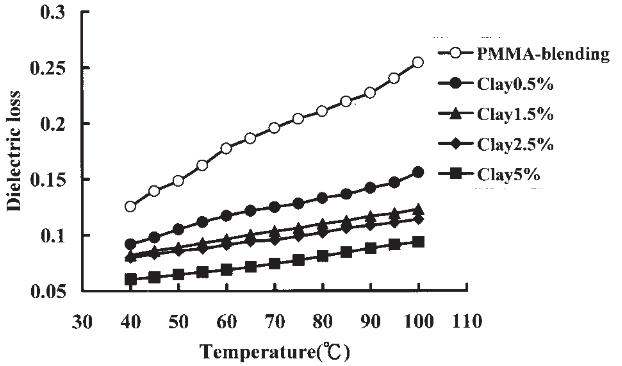

Figure 7 The dielectric loss of PCN-blending nanocomposites at 1 kHz.

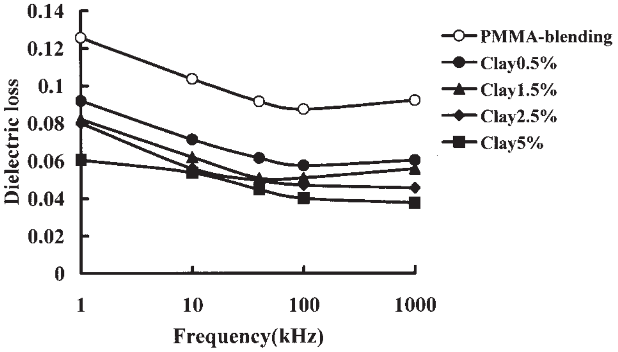

Figure 9 The dielectric loss of PCN-blending nanocomposites at various frequencies under 40°C.

The decreases of the dielectric constants and losses were observed for all studied frequencies up to 1 MHz, (Figs. 8, 9). Figure 8 and Figure 9 show the respective dielectric constants and losses of PCN-blending materials at various frequencies and 40°C. At a frequency of 1 kHz, the dielectric constant of PMMA blending decreased from 10 to 4 and loss decreased from 0.125 to 0.060 with the addition of 5% clay. The dielectric constants and losses of PMMA decrease significantly according to the increasing amount of clay. It is thought that the decrease of the dielectric constant and loss of PCN-blending materials was related to the dispersion of clay within the polymer matrix. The synthesized PCNs with intercalated/exfoliated clay were thoroughly mixed with the commercial PMMA. The dipole orientation from the polar side of PMMA was constrained and was not easily moved because of the confinement and interference of clay. The dielectric constants and losses were thus largely suppressed.

CONCLUSIONS

A series of PCN materials was prepared by effectively dispersing the inorganic nanolayers of MMT clay in an organic PMMA matrix via *in situ* intercalative polymerization. The as-synthesized PCN materials were characterized by WAXRD, FTIR, and TEM. The TEM studies clearly showed that the MMT clay was intercalated and randomly dispersed in the PCN-blending materials. Compared to the pure PMMA, the PCN materials with 10 wt % clay loading exhibited higher thermal degradation temperatures up to 339°C and glass-transition temperatures up to 96.2°C. The improvement of the thermal properties could be attributed to the fact that the confined polymer chains in the gallery of MMT were not free from chain motion. A significant decrease of the dielectric constant and loss was observed for the PCN-blending materials because the dispersive clay largely interfered with the polarization of dipole orientation.

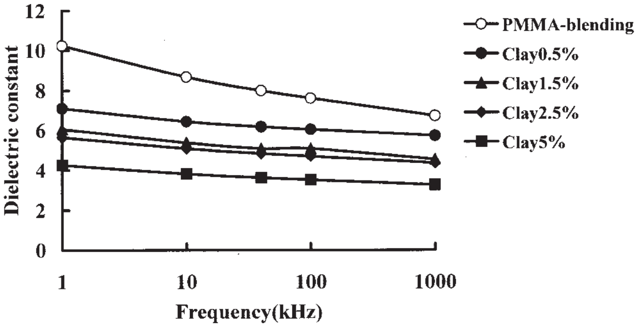

Figure 8 The dielectric constant of PCN-blending nanocomposites at various frequencies under 40°C.

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