

Significant Decreased Dielectric Constant and Loss of Polystyrene–Clay Nanocomposite Materials by Using Long-Chain Intercalation Agent

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ABSTRACT: Polystyrene–clay nanocomposite (PsCN) materials have been prepared by a free radical polymerization process. Montmorillonite (MMT), modified by two different organics, was investigated: one contains a short chain and three benzyl groups on the ammonium ion (DAETPB), while the other contains a long chain (HTAC). The organic modification determines the extent of exfoliation or intercalation of the materials. Exfoliation is more likely to occur using HTAC, as then the gallery of clay has been opened more due to the long chain structure. Exfoliation of MMT in polystyrene (PS) matrix was revealed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were employed to confirm the increased

thermal stability of these PsCN materials. Dielectric properties of polystyrene–clay nanocomposites, in the form of film with clay loading from 1.0 to 5.0 wt %, were measured under frequencies of 100 Hz~1 MHz at 25~70°C. Decreased dielectric constant and low dielectric loss were observed for PsCN materials. Especially, the decrease of dielectric constant was found to be related to the extent of exfoliation of clay. It is recognized that the confinement effect of clay results in the suppression of the dielectric response of the nanocomposite materials at low frequency. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2402–2410, 2004

Key words: polystyrene; clay; nanocomposite; dielectric properties

INTRODUCTION

Nanocomposites composed of clay and polymer have been studied extensively for some time and it has been shown that most of the properties are enhanced by the presence of a small amount of clay. Compared to pristine polymers, the polymer–clay nanocomposites possess many desirable properties, such as enhanced gas barrier; fire-retardant, corrosion resistance, and ionic conductivities; increased thermal stability and mechanical strength; and decreased absorption in organic liquids.^{1–6} The naturally low dielectric constant of polymer attracts applications for use as electronic insulating materials. However, the dielectric responses of polymer–clay nanocomposites have seldom been studied.

Several attempts to prepare polystyrene–clay nanocomposites have been reported.^{7–13} A common technique involves impregnating clay with styrene monomer followed by polymerization. Kato et al.⁷ reported that the intercalation of polystyrene in stearyltrimethyl-ammonium cation exchanged montmorillonite

(MMT) by an *in situ* polymerization. Akelah and Moet^{8,9} prepared polystyrene nanocomposites using acetonitrile as a solvent. Recently, Doh and Cho¹⁰ reported the synthesis of intercalated polystyrene–MMT nanocomposites by *in situ* polymerization of styrene containing dispersed organophilic MMT.^{11–13} Although the data of dielectric response of polymer are available,^{14–20} studies of the dielectric properties of polymer–clay nanocomposites are rare.¹⁴ We recently reported²¹ that dielectric constant at low frequencies of polystyrene has been completely suppressed due to the intercalation of clay. However, more needs to be explored before the low dielectric constant of polymer–clay nanocomposites can be manipulated.

In the present investigation, cation-exchanged montmorillonites using two different intercalating agents were prepared and their influences on exfoliation and dielectric responses were compared. The decreased dielectric constants of these nanocomposites were found to be related to the extent of exfoliation of clay.

EXPERIMENTAL

Materials

The MMT, with a cation exchange capacity (CEC) of 98 mEq/100 g, was supplied by Pai Kong company, Tai-

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wan. [2-(Dimethylamino)ethyl] triphenylphosphonium bromide (Aldrich, 97.0%, DAETPB) and hexadecyltrimethylammonium chloride (Fluka, 98.0%, HTAC) were used as intercalating agents. Styrene was purchased from Fluka Chemical (99.0%). Benzoyl peroxide (Fluka, 97.0%) was used as a free radical initiator. Tetrahydrofuran (Mallinckrodt, 99.0%), methanol (Mallinckrodt, 99.8%), hydrochloric acid (37%), *N*-methyl-2-pyrrolidinone (Mallinckrodt, 99.0%), and polystyrene ($M_w = 350,000$, Aldrich) were used as received.

Preparation of organophilic clay^{2,3}

The organophilic clay was prepared by a cation exchange method, by a reaction between the sodium cations of MMT clay and 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 containing 2.4 g of intercalating agent in another 30 mL of distilled water (beaker B) was magnetically stirred, followed by the addition of 1.0M 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 at a rate of approximately 10 mL/min with vigorous stirring to the MMT suspension (beaker A).²² The mixture was stirred overnight at room temperature. The organophilic clay was recovered by ultracentrifuging (9,000 rpm, 30 min) and filtering the solution in a Buchner funnel. Purification of products was performed by washing and filtering samples repeatedly at least four times, to remove any excess of ammonium ions. The organophilic clay was thus obtained.

Preparation of polystyrene–clay nanocomposites

An appropriate amount of organophilic clay (0.1 g) was introduced into 100 mL of tetrahydrofuran while magnetically stirring overnight at room temperature. Styrene monomer (9.9 g) was subsequently added to the solution, which was stirred for another 24 h. Upon addition of benzoyl peroxide (0.115 g), the solution was stirred for 24 h at 85°C under nitrogen atmosphere. The as-synthesized lamellar nanocomposite precipitates were then obtained by precipitating from an excess amount of methanol (500 mL) and subsequent drying under dynamic vacuum at room temperature for 48 h. The precipitated PsCN powders were used for X-ray diffraction (XRD), thermogravimetric analysis/differential scanning calorimetry (TGA/DSC), and transmission electron microscopy (TEM) characterizations.

Preparation of free-standing films of PsCN

The molecular weight of the synthesized PS materials was 44,700, as determined by GPC. As the intercalation of clay content increased to 5 wt %, the M_w of PsCN decreased to 23,900. For the dielectric measurement on a free-standing disc type film (around 70–90 μm), it is necessary to make it strong and flat enough for good characterization. To enhance the mechanical strength of the films for dielectric characterization, a commercial polystyrene with high molecular weight ($M_w = 350,000$) was blended into the casting solution for film formation. Typically, 0.25g of as-synthesized PS or PsCN materials blended with 0.25 g of commercialized PS was dissolved in 10 mL of NMP under magnetic stirring at room temperature for 24 h. The solution was cast onto a microscope glass slide 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 in distilled water for 1 h to give the free-standing film of PS and PsCN materials. The influences of the blending process is discussed under Results and Discussion.

Characterization of nanocomposites

The normal characterization of the structure of a nanocomposites requires XRD measurements, to show changes in the d spacing of the clay, and TEM, to image the individual clay layers, and thus show the exact nature of the polymer–clay interaction. Wide-angle XRD study of the samples was performed on a Rigaku D/MAX-3C OD-2988N X-ray diffractometer with a copper target and Ni filter at a scanning rate of 2°/min. The samples for TEM study were taken from a microtomed section of polystyrene–clay nanocomposites of 60–90 nm thickness mounted in resin. A TEM (JEOL-200FX), with an acceleration voltage of 120 kV, was employed for the observation. Fourier transform infrared (FTIR) spectra were obtained at a resolution of 4.0 cm^{-1} with a FTIR (BIO-RAD FTS-7) at room temperature ranging from 4,000 to 400 cm^{-1} . The FTIR spectra provide further evidence that both materials (PS and clay) were intercalated.

TGA and DSC were employed to determine the thermal stability of specimens. TGA scans were performed on a Mettler-Toledo TGA/SDTA851 thermal analysis system in air atmosphere. The scan rate was 20°C/min and the temperature range was from 40 to 800°C. DSC was performed on a Perkin–Elmer DSC-7 differential scanning calorimeter at a heating or cooling rate of 10°C/min in nitrogen atmosphere. The temperature range was from 25 to 150°C. The glass transition temperatures (T_g) of PS and PsCN materials were recorded based on the second scanning.

Dielectric parameters, such as capacitance and dissipation factor ($\tan\delta$), were measured by a Zentech

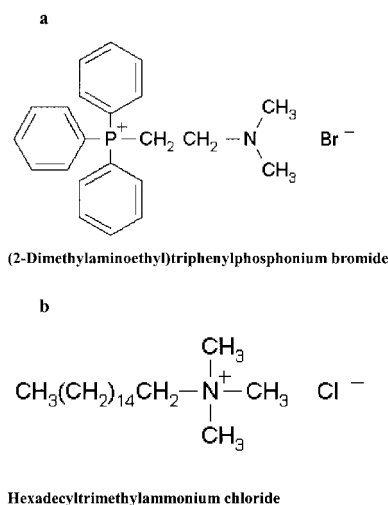


Figure 1 (a) Chemical structure of organophilic clay DAETPB. (b) Chemical structure of organophilic clay HTAC.

3305 automatic component analyzer at various frequencies (100 Hz to 1 MHz) at temperatures of 25 to 70°C. Above 70°C, PsCN film specimens softened and measurement could not be well characterized. The softening of film specimens may be due to the formation process by which the blending materials for films were dried on glass substrate at 60~70°C under a hood for 2 h. During the dielectric measurement above 70°C, residual solvent may evaporate and destroy the flatness of the films. A vacuum evaporated gold electrode was deposited on both side of the nanocomposite film (area 1.5 cm diam.). Thickness of samples was 70~90 μm .²³ Dielectric constants (ϵ_r) of specimens were calculated by the equation: $C = \epsilon_r \epsilon_0 \frac{A}{d}$. ϵ_0 is

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

RESULTS AND DISCUSSION

This study focused on two organically modified clays, one of which is labeled as DAETPB, in which the ammonium salt contains a short chain, two methyl groups, and three benzyl groups, and the other is labeled HTAC, in which the ammonium cation contains one long chain and three methyl groups. The structures of the ammonium salts used to prepare the clays are shown in Figure 1. It will be shown shortly that the two intercalating agents give a different extent of exfoliated structure of clay materials upon free radical polymerization with styrene.

X-ray diffraction

Figure 2. shows the wide-angle powder XRD patterns for organophilic clay with different intercalating agents and those for PsCN materials with 3 and 5% of these two modified clays. The d_{001} spacing was calculated from peak positions using Bragg's law: $n\lambda = 2d\sin\theta$; where λ is the X-ray wavelength (1.5418 Å). For organophilic clay and PsCN materials, the diffraction peaks in the $2\theta = 2\text{--}10^\circ$ region were recorded. The d_{001} spacing of vacuum-dried pristine MMT clay was 1.21 nm ($2\theta = 7.3^\circ$). After the cation exchange, the d_{001} space increased to 2.05 nm ($2\theta = 4.3^\circ$, for the case of HTAC) and 1.88 nm ($2\theta = 4.7^\circ$, for the case of DAETPB), respectively. Figure 2 also shows a lack of any diffraction peaks for the PS-Clay3%(HTAC), indi-

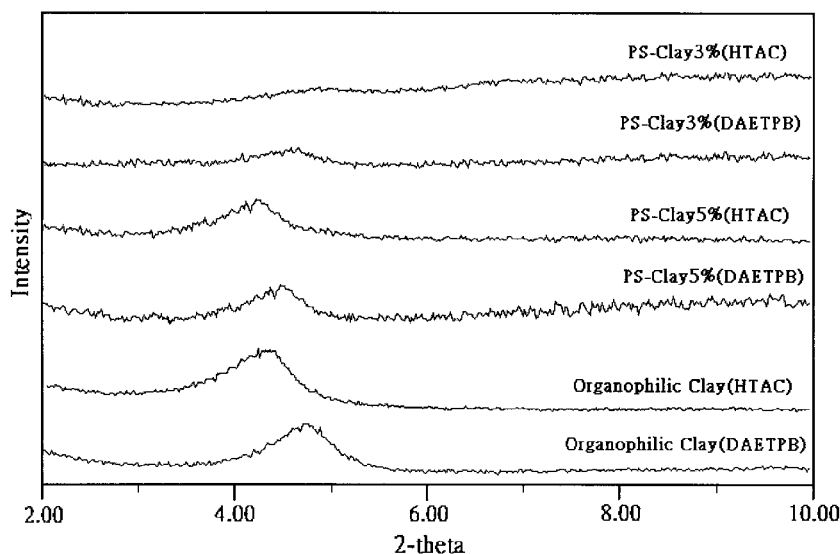


Figure 2 Wide-angle powder X-ray diffraction patterns of organophilic clay and PsCN materials with clay 3% and 5%.

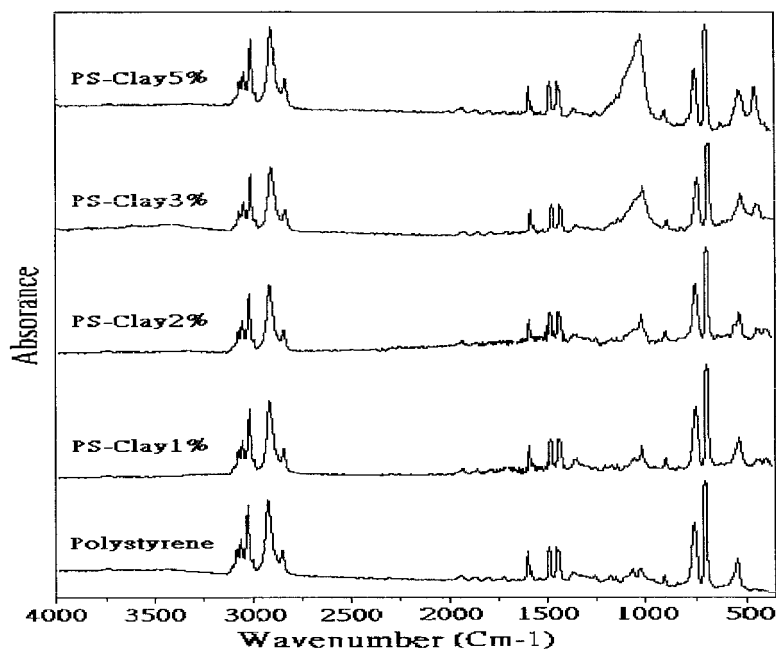


Figure 3 FTIR spectra of PS and a series of PsCN materials produced by using HTAC.

cating a possible exfoliation situation. The PS-Clay3%(DAETPB) has a small peak appearing at $2\theta = 4.5^\circ$. When the amount of organoclay increased to 5.0 wt %, small peaks appeared at $2\theta = 4.1^\circ$ (HTAC) and 4.5° (DAETPB), respectively, corresponding to d spacings of 2.16 and 1.96 nm. This implies that there is a small amount of organoclay that cannot be exfoliated in the PS and exists in the form of an intercalated layer structure. Further examination by TEM observation is necessary to reveal details of microstructures to assist the interpretation of XRD results. However, it is clear that HTAC is more effective than DAETPB in producing an exfoliated structure of PS-clay nanocomposites.

FTIR

Figure 3 shows the FTIR spectra of PS and a series of PsCN materials produced by using HTAC. Table 1 illustrates the infrared band assignments of PS and MMT clay. The characteristic vibration bands of PS are at 1,450, 1,500, 1,600, (aromatic C=C), 700, 750 (Monosubst. Benzene), and 2900~3200 cm^{-1} (aromatic C-H), and those of MMT clay are shown at 1,100 (Si-O), 500+ (Al-O), and 400+ cm^{-1} (Mg-O).²⁴ As the loading of MMT clay is increased, the intensities of MMT clay bands become stronger in the FTIR spectra of PsCN materials. The result for DAETPB is similar and has already been reported in a previous study.²¹

TEM

Direct evidence of nanometer-scale dispersion of intercalated MMT can be found in the TEM. Two cases

of PS that contained 3 wt % modified MMT, but with different intercalation agents (DAETPB and HTAC), were chosen for comparison. Their TEM micrographs are shown in Figure 4(a)–(d). In these figures, the light regions represent PS, and the dark lines correspond to the silicate layers. Figure 4(a) ($\times 10,000$) and Figure 4(b) ($\times 50,000$) show a mixed intercalated-exfoliated structure for DAETPB-modified PsCN materials. A majority of intercalation stacks in the polymer matrix were observed. Figure 4(c) ($\times 10,000$) and Figure 4(d) ($\times 50,000$) also show a mixed intercalated-exfoliated structure for HTAC-modified PsCN materials. However, a more exfoliated microstructure and many small flakes of clays in the polymer matrix could be identified [Fig. 4(c)]. More exfoliation of clay materials by HTAC than by DAETPB within the PS matrix are demonstrated.

TABLE I
FTIR Band Assignments of PS and PsCN Materials

Frequency (cm^{-1})	Source	Assignment
3,600+	MMT Clay	Free H ₂ O
2,900~3,200	Polystyrene	Aromatic C—H
1,600	Polystyrene	Aromatic C=C
1,500	Polystyrene	Aromatic C=C
1,450	Polystyrene	Aromatic C=C
1,100	MMT Clay	Si—O (stretching)
700	Polystyrene	Monosubstituted benzene
750	Polystyrene	Monosubstituted benzene
500+	MMT Clay	Al—O (stretching)
400+	MMT Clay	Mg—O

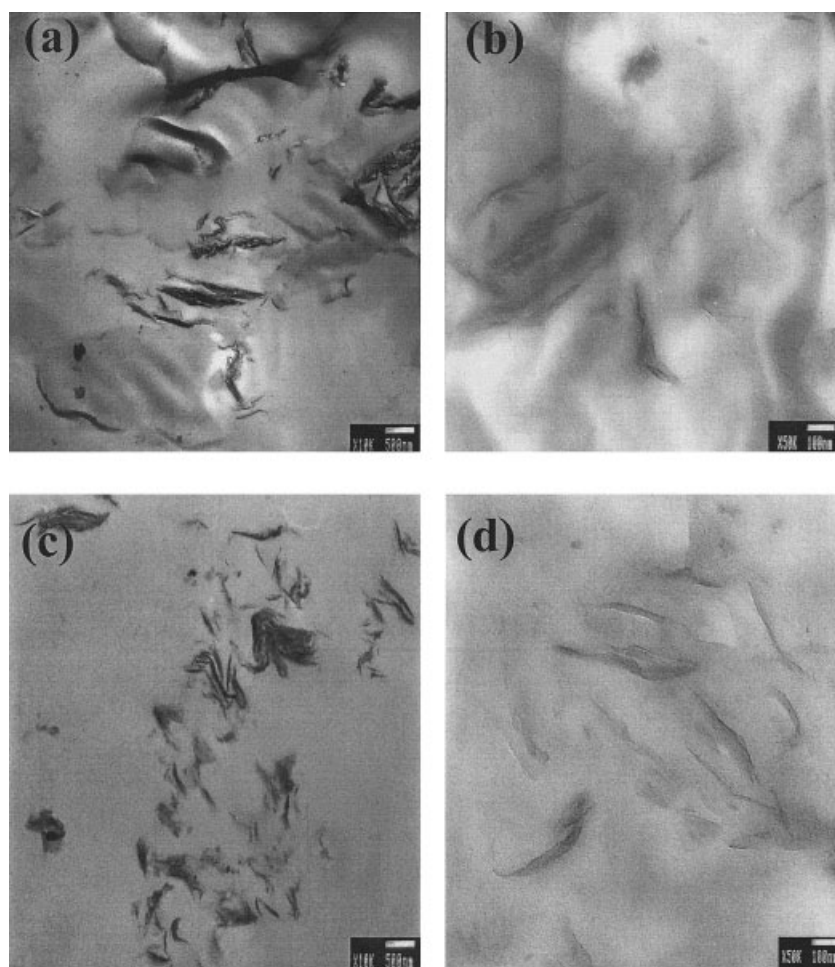


Figure 4 TEM micrographs for (a) PS-Clay3% (DAETPB) ($\times 10,000$); (b) PS-Clay3% (DAETPB) ($\times 50,000$); (c) PS-Clay3% (HTAC) ($\times 10,000$); and (d) PS-Clay3% (HTAC) ($\times 50,000$).

Thermal properties

Figure 5 shows typical TGA curves for PS and a series of HTAC-modified PsCN materials. As the amount of intercalating clay increases, the thermal degradation temperature (T_d) and the residual weight after complete volatilization both increase. DSC also indicates that the glass transition temperatures (T_g) are increased by the intercalation of clay, as shown in Figure 6. It is clear that the PsCN materials have improved thermal stabilities due to the intercalated and exfoliated clay: the retarding effect of clay platelets on the decomposition of polymer is obvious.

The thermal properties of pure PS and PsCN materials with different intercalating agents are summarized and presented in Table II,^{25,26} which shows that the T_d and the T_g of the PsCN materials are higher than those of pure PS and shift toward higher temperatures as the amount of clay increases. In Table II, the T_g of PsCN materials generally increased slightly with increasing amounts of clay. This is tentatively attributed to the confinement of the intercalated polymer

chains within the clay galleries that prevents the segmental motions of the polymer chains. In both cases (T_g and T_d), HTAC results in a higher thermal stability than DAETPB. From the micrographs of TEM, the exfoliation of the PsCN-HTAC series is better than that of PsCN-DAETPB. It is believed that the thermal degradation temperature and the glass transition temperature are also related to the extent of exfoliation, which is why PsCN-HTAC is thermally more stable than PsCN-DAETPB.

Dielectric properties

The clay concentration in the film specimens was only half of that discussed in the powder counterpart so far. Therefore, the clay contents are shown in their actual percentages in the films in Figures 7-10. As shown in Figure 7, the dielectric constants of synthesized PS and commercial PS are around 10 to 11 at 10 kHz. As the amount of DAETPB-modified clay intercalated with PS increases, the dielectric constant of composite ma-

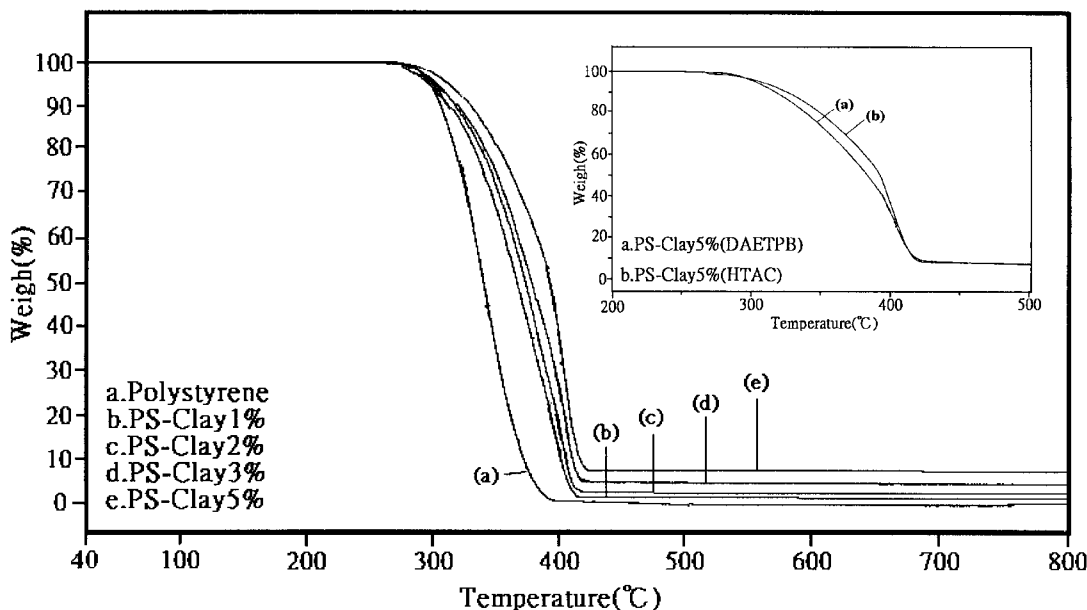


Figure 5 Thermogravimetric curves of PS and a series of PsCN materials (HTAC). (Inset) The superimposed curves of HTAC and DAETPB.²¹

materials decreases.²¹ Composites produced with HTAC show an even lower dielectric constant, as shown in Figure 8. The dielectric constant is less than 6.5 and there is a significant decrease of dielectric loss to less than 0.04 when 2.5 wt % HTAC-modified clay is added. Comparing the results of DAETPB and HTAC, it is clear that dielectric constant and loss decreased much less by using HTAC than DAETPB.

The magnitude of the decrease of dielectric constant is much larger at low frequencies, as shown in Figure

9 for DAETPB.²¹ In the case of HTAC, as shown in Figure 10, the trend is similar to the case of DAETPB, only the value is lower. At a frequency of 120 Hz, the dielectric constant of PS is 25 and is decreased to 9 by the intercalation of 2.5 wt % HTAC-modified clay.

From the above results, it is believed that the polarization of dipole orientation is largely reduced due to the randomly exfoliated and intercalated layer structures. The nanoscopic-confinement effects from layered-silicate inorganic hosts are also reported by Anastasiadis et al.¹⁴ In their investigation, XRD showed that polymer is confined within 1.5–2.0 nm. This confinement effect is directly reflected in the local

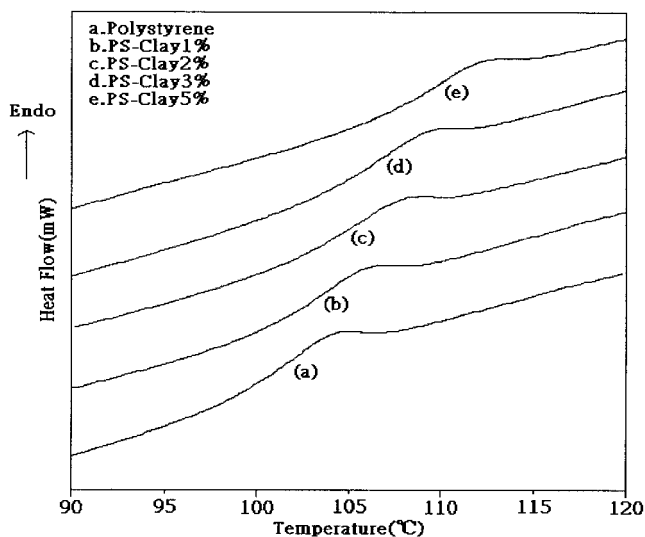


Figure 6 DSC thermograms of PS and a series of PsCN materials (HTAC). Thermograms data for DAETPB are listed in Table II.²¹

TABLE II
Thermal Degradation Temperature (T_d) and Glass Transition Temperature (T_g) of Pure PS and PS-Clay Nanocomposites

Sample	T_d (°C)	T_g (°C)
Polystyrene	306.73 ± 1.44	100.95 ± 0.33
PS-Clay1% (DAETPB) ^a	315.34 ± 1.45	103.31 ± 0.34
PS-Clay2% (DAETPB)	322.03 ± 1.23	104.54 ± 0.28
PS-Clay3% (DAETPB)	330.59 ± 1.50	105.42 ± 0.27
PS-Clay5% (DAETPB)	357.75 ± 1.38	107.07 ± 0.38
PS-Clay1% (HTAC) ^b	329.32 ± 1.16	103.95 ± 0.20
PS-Clay2% (HTAC)	341.45 ± 1.11	105.57 ± 0.22
PS-Clay3% (HTAC)	354.22 ± 1.43	107.27 ± 0.38
PS-Clay5% (HTAC)	368.30 ± 1.45	110.25 ± 0.30

^a PsCN materials by intercalating agent DAETPB. Figures of the TGA and DSC curves were reported in previous study.²¹

^b PsCN materials by intercalating agent HTAC.

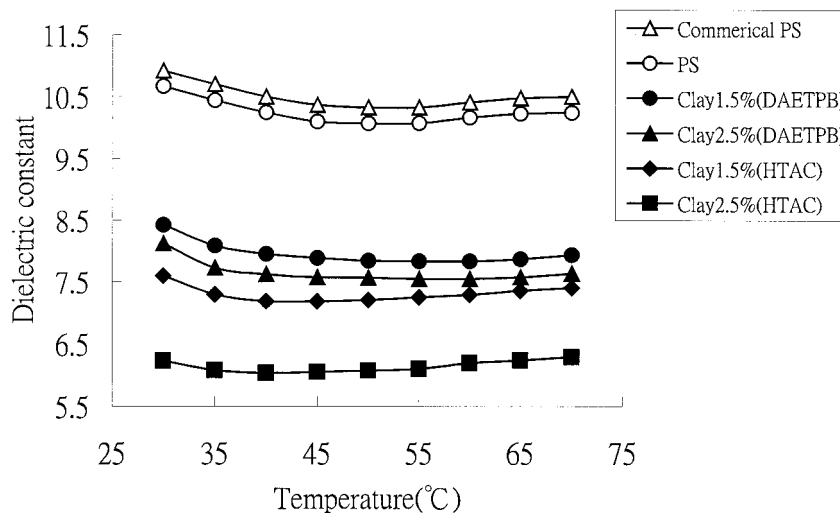


Figure 7 The dielectric constant of polystyrene—clay nanocomposites at 10 kHz.

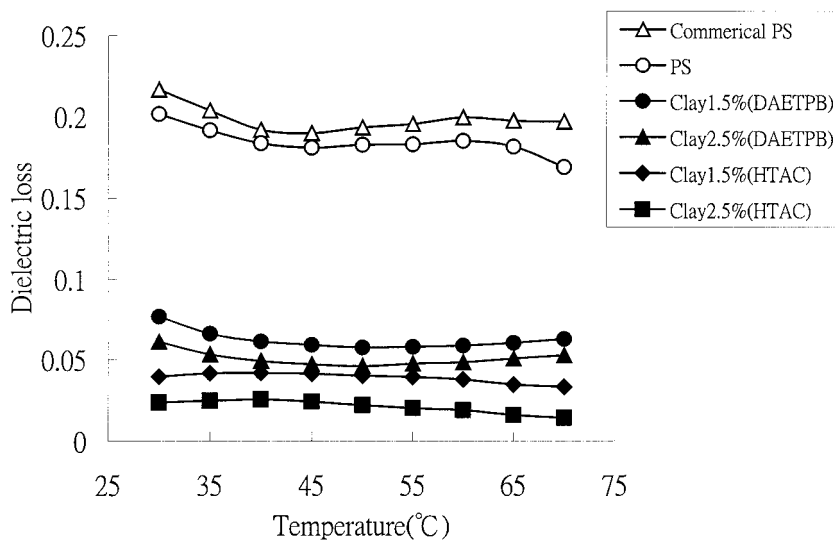


Figure 8 The dielectric loss of polystyrene—clay nanocomposites at 10 kHz.

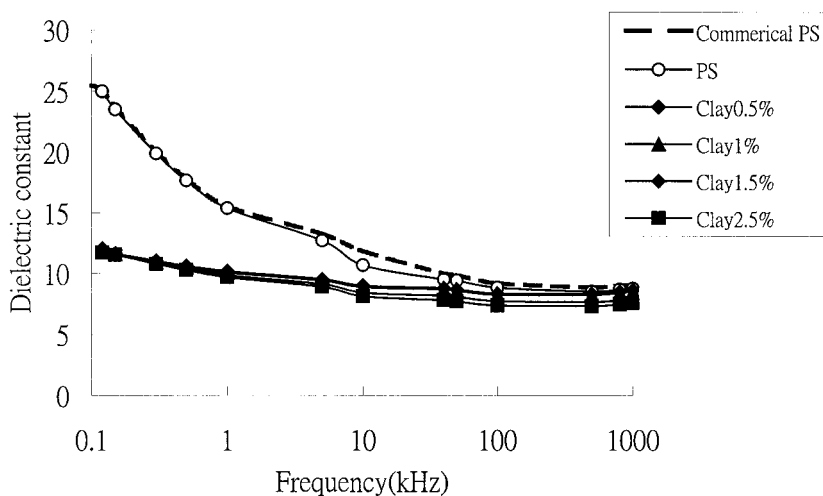


Figure 9 The dielectric constant of polystyrene—clay nanocomposites (DAETPB) at various frequencies under 30°C.

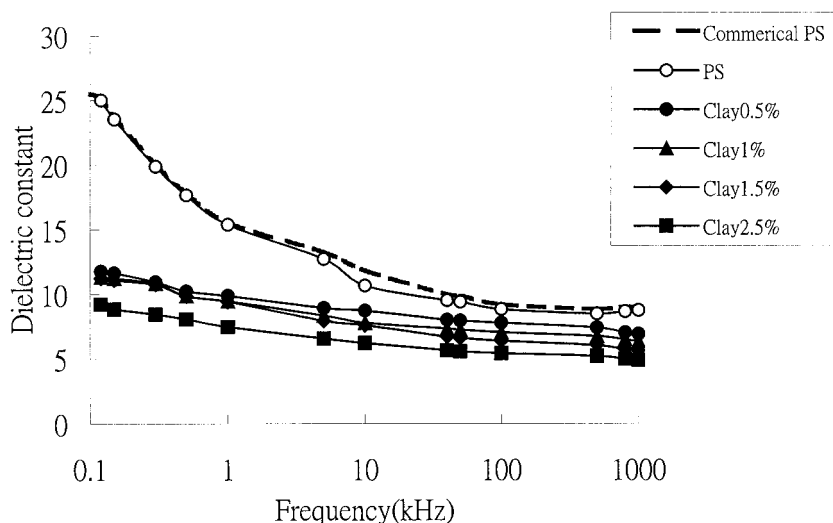


Figure 10 The dielectric constant of polystyrene—clay nanocomposites (HTAC) at various frequencies under 30°C.

reorientational dynamics. It might be understood²¹ that the decrease of dielectric constant at low frequencies of PsCN materials is due to this confinement effect. The dipole orientation from the benzene side of PS is constrained and not easily changed due to the confinement of clay at the nanoscale. This effect becomes more significant when HTAC is employed as an intercalating agent. The long chains (HTAC) open the gallery of clay structure wider and result in a more exfoliated structure than with the benzyl groups (DAETPB). As shown in XRD patterns (Fig. 2) and TEM micrographs [Fig. 4(a)–(d)], it is confirmed that HTAC does result in a more exfoliated structure than that of DAETPB. The suppression of the dielectric response of polymer is thus enhanced.

The blending of PsCN with commercial PS would not ruin the intercalation, since huge molecules of commercial PS could hardly enter the gallery of clay. The significant decreases of dielectric constants and losses come from the intercalation and exfoliation of clay, since the conventional mixing of < 2.5 wt % nonorganophilic clay and commercial PS does not show such a decrease. The reduced dielectric constant and loss by intercalation and exfoliation of clay remains an interesting topic of research.

CONCLUSION

A series of polystyrene–clay nanocomposite (PsCN) materials have been prepared by a free radical polymerization process. With organic treatment, using a long chain intercalation agent (HTAC in the present study), possibilities to obtain more exfoliated nanocomposites are increased. The as-synthesized PsCN materials were characterized by FTIR, XRD, TG/DSC,

TEM, and dielectric spectroscopy. Compared to pure PS, the PsCN materials modified by HTAC showed a higher T_g and a higher thermal degradation temperature than those modified by DAETPB. More significant decreases of dielectric constant and dielectric loss was observed for HTAC-modified PsCN materials than for DAETPB-modified ones. It is thought that the confinement effect of intercalating clay has significantly suppressed the polarization of dipole orientation of the polymer at low frequency and that the exfoliation would enhance this effect.

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