

POLYMER-CLAY NANOCOMPOSITES: CHEMICAL GRAFTING OF POLYSTYRENE ONTO CLOISITE 20A *

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Abstract An account of the experiments on preparing polystyrene (PS) nanocomposites through grafting the polymer onto organophilic montmorillonite is reported. Cloisite 20A was reacted with vinyltrichlorosilane to replace the edge hydroxyl groups of the clay with a vinyl moiety. Because the reaction may liberate HCl, it was performed in the presence of sodium hydrogencarbonate to prevent the exchange of quaternary alkylammonium cations with H⁺ ions. Only the silanol groups on the edge of the clay react with vinyltrichlorosilane. The radical polymerization of the product with styrene as a vinyl monomer leads to chemical grafting of PS onto the montmorillonite surface. The homopolymer formed during polymerization was separated from the grafted organoclay by Soxhlet extraction. Chemical grafting of the polymer onto Cloisite 20A was confirmed by infrared spectroscopy. The prepared nanocomposite materials and the grafted nano-particles were studied by XRD. Exfoliated nanocomposites may be obtained for 0.5 wt%–1 wt% clay content. The nanocomposites were studied by thermogravimetric analysis (TGA) dynamic thermal analysis (DTA) and dynamic mechanical analysis (DMTA).

Keywords: Grafting; Polystyrene; Nanocomposites; Cloisite 20A; Organophilic clay.

INTRODUCTION

The field of polymer nanocomposites has attracted considerable attention recently. Among various nanocomposites, much attention has been paid to polymer/montmorillonite (MMT) nanocomposites, because its lamellar elements display high in-plane strength, stiffness, high aspect ratio, high thermal stability and better barrier properties even with small amount of silicate^[1–4]. Natural clays are generally hydrophilic and it is necessary that they are modified so that miscibility between the clay and the polymer is enhanced. A cation exchange process achieves the organic modification of the clay. The inorganic cation, usually sodium, is replaced by an organic cation, typically ammonium and phosphonium^[5].

PS is an inexpensive, hard thermoplastic and one of the most widely used commercial polymers because of its favorable mechanical, electric insulation, thermal insulation and good solvent resistance properties.

PS-clay nanocomposites have been prepared by several researchers. Doh and Cho reported the synthesis of intercalated PS-MMT nanocomposites by *in situ* polymerization of styrene containing dispersed organophilic MMT. The hybrid materials exhibited higher thermal stability compared with the virgin PS or PS/pristine-MMT microcomposites^[6]. Yang *et al.* prepared the exfoliated PS/MMT nanocomposite by emulsion polymerization in the presence of MMT modified with zwitterion aminoundecanoic acid. The exfoliated PS/MMT nanocomposite showed greatly improved thermal and mechanical properties compared to the neat polystyrene^[7]. Wilkie *et al.* used ammonium salts containing quinolone and pyridine units to modify the clay. The quinolinium modified

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clay has a higher thermal stability than the pyridinium modified clay. Intercalated PS-nanocomposites were then prepared by both in situ bulk polymerization and melt blending processes^[8].

The preparation and use of vinyl monomer-montmorillonite intercalates, by a cation exchange process of montmorillonite and vinylbenzyltrimethylammonium chloride, have been reported by several researchers. Free-radical polymerizations of the penetrated styrene between the interlayers have resulted in grafted polystyrene-montmorillonite materials. Akelah and Moet demonstrated the formation of intercalated nanocomposites by solution polymerization in acetonitrile^[9, 10]. However, exfoliated and partially exfoliated nanocomposites were achieved in bulk^[11] and emulsion polymerizations^[12], respectively. Wilkie and coworkers compared bulk, solution, suspension and emulsion polymerization as well as melt blending. They showed that exfoliation is more likely to occur if the ammonium ion contains a double bond. They also demonstrated solution polymerization always produces intercalated systems^[13]. Fang *et al.* prepared PS/clay nanocomposites by the γ -ray irradiation technique. Exfoliated nanocomposites were obtained by using organophilic clay containing reactive methacrylate groups, while intercalated structures were achieved using non-reactive organoclay. The enhancement of the thermal properties of PS/nanocomposites made by using the reactive organophilic clay was much higher than that of the thermal properties of PS/nanocomposites incorporating non-reactive clay^[14]. Similar results were also obtained by Sanderson *et al.* using clay modified with acrylate-containing surfimers and non-polymerizable surfactant^[15]. The preparation and characterization of exfoliated PS-clay nanocomposites using a cationic radical initiator-intercalated montmorillonite hybrid have been reported by Lee *et al.* The thermal and mechanical properties of nanocomposites were improved drastically with lower clay loading of up to 3 wt%^[16]. Wilkie *et al.* reported the synthesis of oligomerically-modified clay containing maleic anhydride. They used the organically modified clay to prepare PS-clay nanocomposites by melt blending. The results showed a mixed immiscible/intercalated/delaminated morphology. The maleic anhydride modified clay improved the compatibility between the clay and the PS^[17]. The use of quaternary ammonium salts of sulfonated polystyrene as compatibilizer for melt intercalation of PS and pristine Na-MMT has been reported by Weiss *et al.* The nanocomposites containing ionomers exhibited higher storage moduli compared to nanocomposites without the compatibilizer^[18].

Nevertheless, the clay remains hydrophilic after these modifications. This hydrophilic nature can be attributed to the polar silanol groups located at the edges of layered silicates. To make the organoclay more compatible with polymers, the edge silanol groups can be replaced with polymer chains that make the organoclay more compatible with the polymer to be used later^[19, 20]. Baoli *et al.* reported a different strategy to immobilize carbon-carbon double bonds at the surface of silica particles. The silica surfaces were treated with excess 2,4-toluene diisocyanate, after which the residual isocyanate groups were converted into polymerizable vinyl groups by reaction with hydroxypropylacrylate. PS/silica nanocomposites were prepared by conventional radical copolymerization of styrene with silica macro-monomer. The results revealed that the silica nanoparticles acted as cross-linking points in the PS/silica nanocomposites^[21]. Perez *et al.* reported the synthesis and characterization of random copolymers based on poly(styrene-co-triethoxyvinylsilane) and their application as macro-silanes for grafting silica particles with PS chains in a single step reaction. It was found that the grafting density depends on the molecular weight of the copolymers^[22].

We recently reported the grafting of polyacrylamide^[23], poly(methyl methacrylate)^[24] and polyvinyl acetate^[25] onto Cloisite 20A. In the present study, we wish to report the grafting of PS onto Cloisite 20A nanoparticles. Organophilic clay was vinyl-modified by silylation reaction with vinyltrichlorosilane and then free radically co-polymerized with styrene in the presence of benzoylperoxide (BPO) as an initiator. In this method, the polymer chain was grafted to the edges of the layered silicate via a strong Si-C linkage that was quite stable in acidic and weak alkaline aqueous media^[26]. The grafted polymer acts as a compatibilizer between the polymer and the clay phases because it has the same polarity as the polymer. Chemical grafting of the polymer onto the surface of Cloisite 20A was clearly confirmed by FT-IR spectroscopy after Soxhlet extraction and separation of homopolymer. The prepared nanocomposites and grafted nano-particles were studied by XRD. The properties of the nanocomposites were investigated by conventional TGA and DMTA techniques.

EXPERIMENTAL

Materials

The commercial nanoclay Cloisite 20A was purchased from Southern Clay Products (Gonzales, TX) and dried under vacuum at 60°C for 24 h before silylation. Vinyltrichlorosilane and styrene were obtained from Fluka Co. and Merck Co., respectively. BPO was obtained from Merck Co. and re-crystallized from ether prior to use. All the other chemicals were of the reagent grade and were used without further purification.

Measurements

The FTIR (KBr) spectra were recorded on a Perkin Elmer RXI spectrophotometer (2 wt% in KBr, resolution 4 cm⁻¹, number of scans was 6). TGA and DMTA curves were obtained on Linseis STA PT 1000 and Triton Tritec 2000 DMN instruments, respectively. Wide angle X-ray diffraction (XRD) measurements were performed at room temperature on a Simence D500 X-ray diffractometer (Germany), using Ni-filtered Co-K α radiation. The scanning rate was 1 (°)/min over a 2 θ range of 2°–10°.

Preparation of Vinyl-modified Clay

The preparation of vinyl-modified clay was performed according to the method described earlier^[23–25]. A 10.000 g portion of Cloisite 20A and NaHCO₃ (42.000 g, 0.5 mol) were placed in a 500 mL three-neck round bottom flask charged with 300 mL of anhydrous acetone. The system was vigorously stirred under nitrogen for 15 min. Then a 50 mL portion of vinyltrichlorosilane was added drop wise to the suspension over 3 h. The mixture was gently refluxed for 8 h, and the product was filtered, successively washed with acetone, acetone/H₂O (50/50), filtered, dried under vacuum at 40°C, and stored for the subsequent experiment. FTIR (KBr): 3636 (m, OH), 3064 (w, vinylic CH), 3026 (w, vinylic CH), 2927 (m, surfactant), 2854 (m, surfactant), 1469 (m, CH₂), 1045 cm⁻¹ (s, Si–O).

Polymer Grafting

In a three-necked round bottomed flask equipped with a magnetic stirrer and a reflux condenser, silylated Cloisite 20A (5.000 g), styrene (2.916 g, 28 mmol) and BPO (0.130 g, 0.54 mmol) were placed in 15 mL of toluene. The flask was purged by dry, oxygen-free argon for 20 min. The mixture was heated while magnetically stirred at 90–95°C for 24 h. Then the reaction mixture was transferred into a Soxhlet apparatus and extracted with toluene for 72 h. The grafted powder was then dried at 40°C for 24 h in a vacuum oven. FTIR (KBr): 3636 (m, OH), 2927 (m, surfactant), 2854 (m, surfactant), 1469 (m, CH₂), 1045 cm⁻¹ (s, Si–O), 699 (w, arom. C–H).

Blank Experiment

The blank experiment was performed under the same conditions using unmodified Cloisite 20A.

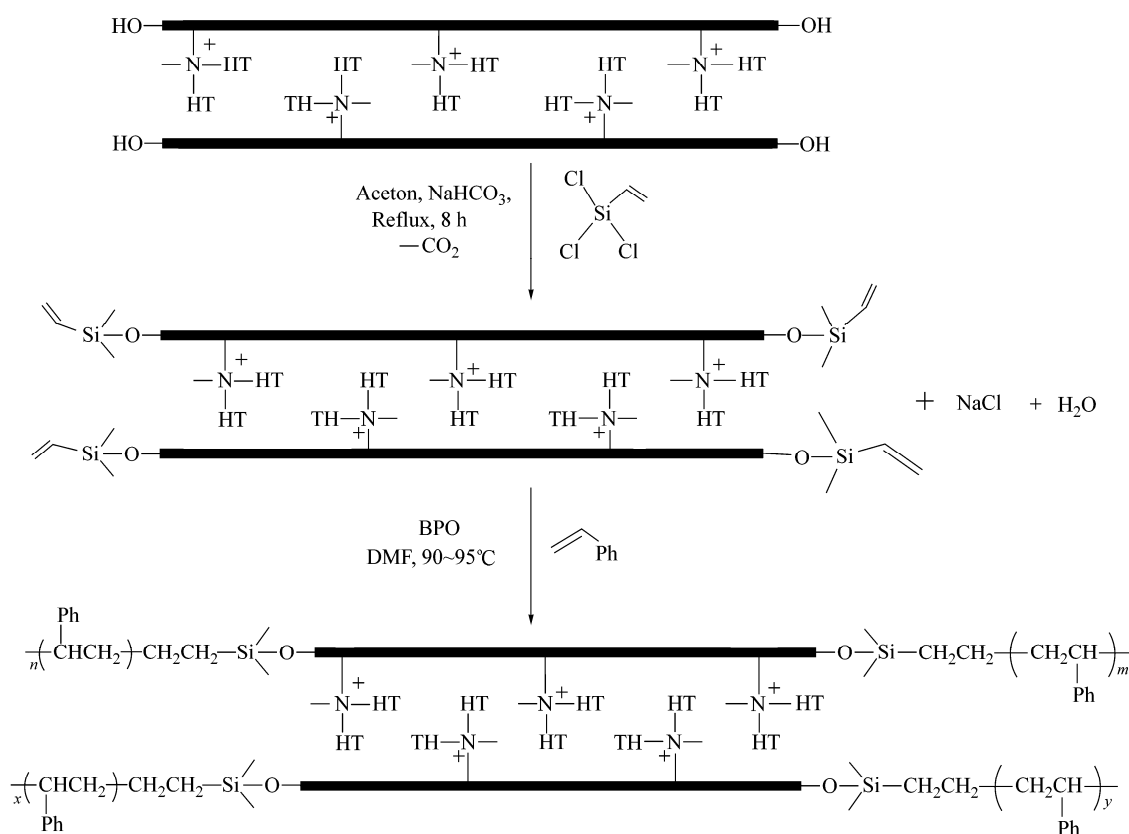
Typical Procedure for Preparing the PS Clay Nanocomposite (1 wt%)

In a three-necked round bottomed flask equipped with a magnetic stirrer and a reflux condenser, silylated Cloisite 20A (0.040 g) was dispersed in 15 mL of toluene. The suspension was stirred at room temperature for 24 h under argon. Styrene (4.000 g, 38.46 mmol) and BPO (0.19 g, 0.78 mmol) were added, and the mixture was stirred at room temperature for an additional 24 h under argon. The reaction mixture was heated at 90–95°C for 24 h. The viscous suspension was trickled slowly into 100 mL of MeOH while vigorous stirring, filtered, thoroughly washed with MeOH and then dried at 60°C for 24 h in a vacuum oven.

RESULTS AND DISCUSSION

Organophilic clay Cloisite 20A was silylated with vinyltrichlorosilane. Because the reaction liberates HCl, it is very important that the quaternary alkylammonium cations are not exchanged with H⁺ ions. If the protons are not removed, the silylation reaction can occur on both external and internal surfaces, decreasing the basal spacing. The internal surface silylation is eliminated by capturing the protons with a base such as sodium hydrogencarbonate so that the basal spacing almost was not changed^[27]. In the FTIR spectrum of the silylated

Cloisite 20A (Fig. 1b), absorption bands appeared at 3064 and 3026 cm^{-1} that can be attributed to the stretching of the vinylic C—H bonds. In the next step, vinyl-modified Cloisite 20A was copolymerized with styrene by free-radical polymerization reaction in the presence of BPO as an initiator (Scheme 1).



Scheme 1 Chemical grafting of polystyrene onto Cloisite 20A

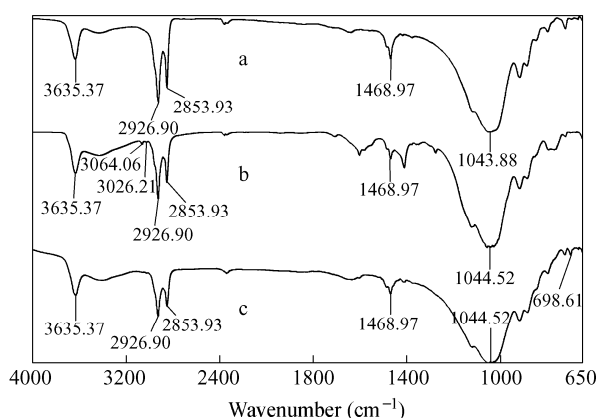


Fig. 1 FT-IR spectrum (KBr) of (a) Cloisite 20A, (b) silylated Cloisite 20A and (c) PS-grafted Cloisite 20A

To confirm the grafting reaction by conventional analytical methods, the homopolymer must be separated from the grafted organoclay particles. For this reason, after completion of the polymerization, the product was

extracted by using Soxhlet apparatus with toluene to remove the homopolymer. The complete removal of the homopolymer was confirmed by doing a blank polymerization experiment with the unmodified Cloisite 20A. After 72 h of Soxhlet extraction of the blank experiment product with toluene, the FTIR spectrum observed was the same as that for Cloisite 20A, and the absorption bands related to PS were not observed. In the FTIR spectrum of the separated Cloisite 20A grafted with PS, the absorption band observed at 699 cm^{-1} is related to out of plane bending vibration of aromatic C—H bonds. The strong, broad band in the region of $1000\text{--}1160\text{ cm}^{-1}$ is likely due to siloxane (Si—O—Si) bond (Fig. 1, curves a–c).

The radical polymerization of styrene with different amounts of the vinyl-modified organoclay in the presence of BPO in toluene leads to the formation of PS-clay nanocomposite materials (PCNs) in which some PS chains are grafted onto the montmorillonite surface. A schematic representation for grafted clay particle is shown in Fig. 2. Therefore, a wide range of grafted organoclay materials with desired polarities can be prepared by utilizing this approach with vinyl monomers of different polarities.

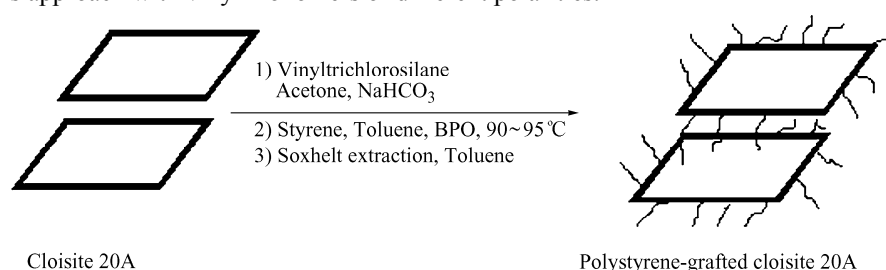


Fig. 2 Schematic representation for a PS-grafted Cloisite 20A

The amount of grafted polymer can be estimated by TGA measurement^[25–28]. After prolonged Soxhlet extraction of the PS-grafted Cloisite 20A it was found to give a weight loss after heating at 375°C . The difference between weight losses of silylated Cloisite 20A and PS-grafted Cloisite 20A after heating at 375°C ($\Delta m = 0.13\%$) can be attributed to the weight of the grafted polymer. Therefore, the amount of grafted polymer (1.3 mg/g of clay) can be calculated from Eq. (1).

$$\text{Grafted amount (mg/g)} = \frac{\Delta m}{100} \times 1000 \quad (1)$$

Wide-angle powder X-ray diffraction patterns of Cloisite 20A, silylated Cloisite 20A and PS-grafted Cloisite 20A are shown in Fig. 3, curves a–c. A strong peak is observed at $2\theta = 3.42^{\circ}$, corresponding to the (001) plane for Cloisite 20A, indicating that the interlayer d -spacing of the organoclay is approximately 2.6 nm. This value is comparable to the value (2.4 nm) reported by the supplier (Southern Clay Products, Inc.). The interlayer d -spacing is decreased to 2.4 nm ($2\theta = 3.70^{\circ}$) after the silylation that is in agreement with results obtained by Zhang^[27]. The interlayer d -spacing reaches 2.1 nm ($2\theta = 4.28^{\circ}$) after grafting and complete drying. The diffraction peaks and the calculated basal spacing of the products are summarized in Table 1.

Table 1. Diffraction peaks and basal spacing of Cloisite 20A, silylated Cloisite 20A, PS-grafted Cloisite 20A and nanocomposites

Product	Diffraction peak and basal spacing	
	Typical diffraction peak ($^{\circ}$)	Basal spacing (nm)
Cloisite 20A	3.42	2.6
Silylated Cloisite 20A	3.70	2.4
PS-grafted Cloisite 20A	4.28	2.1
PCN 0.5% ^a	—	—
PCN 1%	—	—
PCN 3%	3.00	2.9
PCN 5%	3.28	2.7

^a Polymer-clay nanocomposites

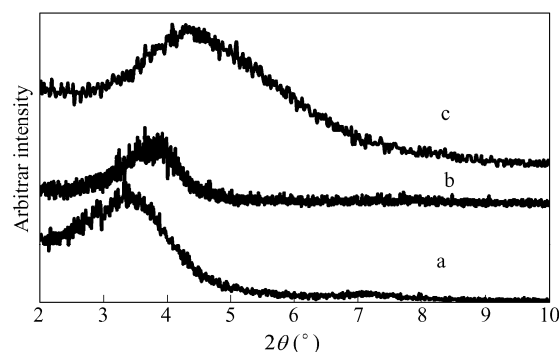


Fig. 3 Wide-angle powder X-ray diffraction patterns of (a) Cloisite 20A, (b) silylated Cloisite 20A and (c) PS-grafted Cloisite 20A

The wide-angle powder X-ray diffraction patterns of Cloisite 20A and a series of PS-clay nanocomposite materials are shown in Fig. 4 and summarized in Table 1. No peak is observed at clay loadings of 0.5 wt%–1 wt% (PCN 0.5% and PCN 1%) at $2\theta = 2^\circ$ – 10° , as opposed to the peak at $2\theta = 3.42^\circ$ (d -spacing = 2.6 nm) for Cloisite 20A. This observation indicates less agglomeration and potentially exfoliated nanocomposites at clay loadings of 0.5 wt%–1 wt%. At loading levels of 3 wt%–5 wt% (PCN 3% and PCN 5%), the diffraction peaks appear near each other at $2\theta = 3.00^\circ$ (d -spacing = 2.9 nm) and 3.28° (d -spacing = 2.7 nm). The intensities of the peaks increase with increasing organoclay concentration. This observation implies that the grafted organophilic clay is not exfoliated in the PS matrix and exists in intercalated layers at clay loadings higher than 1 wt%.

The results of thermal and mechanical analyses by TGA, DTA, and DMTA are summarized in Table 2. The glass transition temperatures (T_g) measured by DTA and DMTA methods show a same trend. The T_g value is not detected by DMTA for PCN 1%, but it is higher than those for virgin polymer and PCN 0.5%, measured by DTA. This observation is tentatively attributed to the interaction of polymer chains with the clay galleries that prevents the segmental motions of the polymer chains^[29]. Further addition of organoclay up to 5 wt% leads to a decrease in T_g . This may be attributed to the dispersed degree of the clay layers in addition to the interaction of the sheets with the chains of the PS. Additionally, a large amount of intercalating reagents in the organophilic clay may act as a plasticizer or as a lubricants, the glass transition temperature is lower than that with a low amount of clay^[30]. DTA and DMTA curves of the PS and nanocomposites with 0.5 wt%–5 wt% clay loadings are shown in Figs. 5 and 6, respectively.

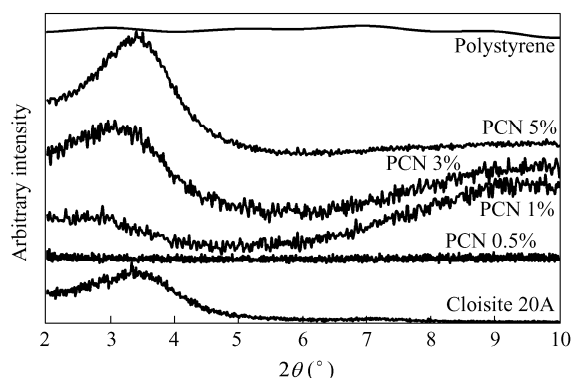


Fig. 4 Wide-angle powder X-ray diffraction patterns of polystyrene, Cloisite 20A, and PS-clay nanocomposites

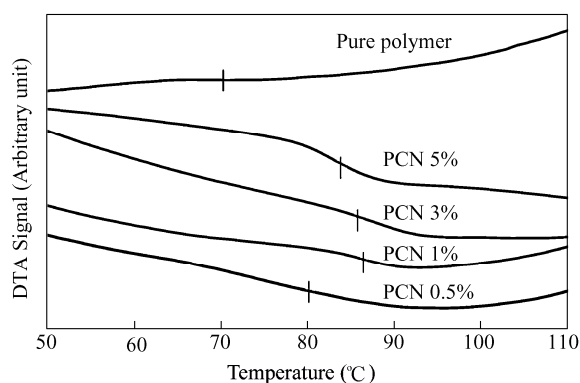


Fig. 5 DTA curves of polystyrene and PS-clay nanocomposite materials (PCNs) (N_2 atmosphere, scan rate of 10 K/min)

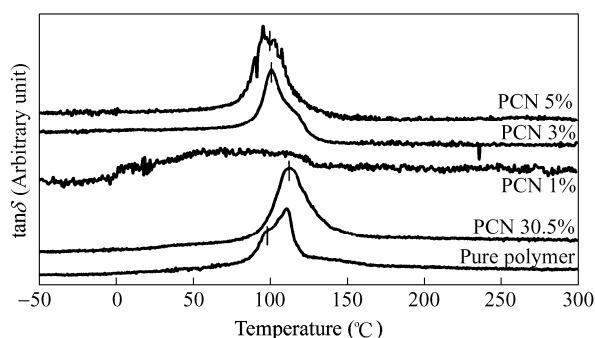


Fig. 6 DMTA curves of polystyrene and PS-clay nanocomposite materials (PCNs) (N_2 atmosphere, scan rate of 10 K/min)

Table 2. Thermal and mechanical analysis (DMTA and TGA) results

Polymer	T_g (°C) ^a	T_g (°C) ^b	T_D (°C) ^c	10% weight loss (°C) ^d	Char yield ^e (%)
PS	94.0	70.7	331.4	349.2	1.06
PCN 0.5%	109.3	80.1	376.6	392.0	8.04
PCN 1%	N.D. ^f	87.0	350.9	365.1	3.45
PCN 3%	99.4	86.4	335.6	362.7	4.59
PCN 5%	96.6	84.2	337.5	355.6	3.34

^a Obtained from DMTA measurements based on $\tan \delta$ versus temperature curves;

^b Obtained from DTA measurements;

^c Initiation temperature of first stage decomposition;

^d Obtained from TGA measurements;

^e At 500°C;

^f Not detected

Variation of storage modulus with temperature for polystyrene and its nanocomposites has been shown in Fig. 7. An increase in storage modulus is observed for PCN 0.5% with respect to virgin polymer especially below glass transition temperature. At low clay content (PCN 0.5%), due to better dispersion and formation of exfoliated structure, strong interactions between PS-grafted Cloisite 20A and PS matrix exist. PCNs 1%–5% have lower storage moduli than pure PS.

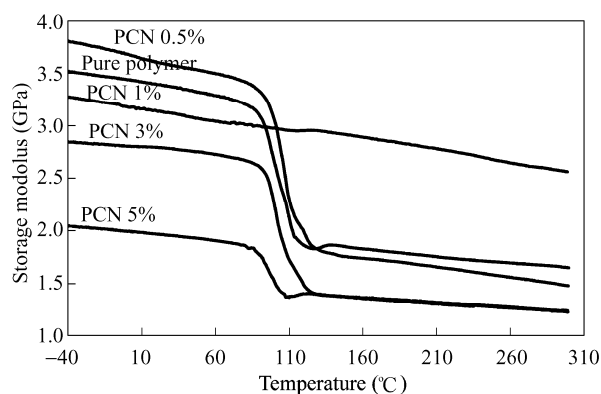


Fig. 7 Temperature dependence of storage modulus of polystyrene and polymer-clay nanocomposite materials (PCNs) (N_2 atmosphere, scan rate of 10 K/min)

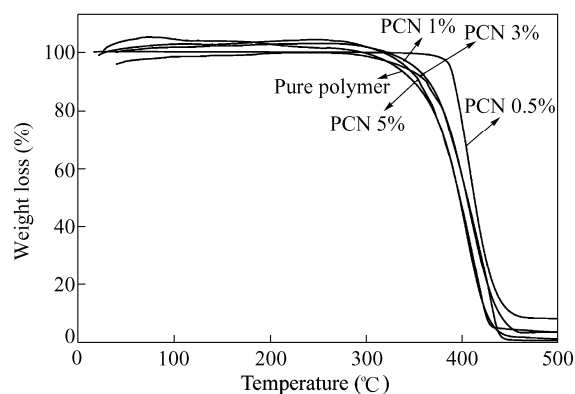


Fig. 8 TGA thermograms of polystyrene and PS-clay nanocomposite materials (N_2 atmosphere, scan rate of 10 K/min)

TGA curves of the PS and nanocomposites with 0.5 wt%–5 wt% clay loadings are shown in Fig. 8. Evidently the decomposition onset temperatures (T_D), 10% weight loss, and char yields of PS/clay nanocomposites (particularly in the case of PCN 0.5%) are improved compared to the pure PS. A possible reason

for the enhancement of thermal stability is that clay is an inorganic material with high thermal stability and great barrier properties, which can prevent heat from transmitting quickly and thus limit the continuous decomposition of the nanocomposites. T_D , 10% weight loss, and char yield of the PCN 0.5% are 376.6°C, 392.0°C, and 8.04%, respectively. These values are much higher than those of pure polymer and also other PS/clay nanocomposites. This observation may be due to much better dispersion at low clay loadings and formation of exfoliated nanostructure. At higher clay loadings, coagulation may occur^[14].

CONCLUSIONS

Polystyrene was chemically grafted onto Cloisite 20A after silylation of the edge silanol groups of the clay by vinyltrichlorosilane. To demonstrate successful grafting, the homopolymer formed during polymerization was separated from grafted Cloisite 20A by Soxhlet extraction. Chemical grafting of the polymer onto the Cloisite 20A surface was confirmed by FTIR spectroscopy. The interlayer d -spacing of grafted organophilic clay was investigated by XRD. Only a small change (approximately 0.5 nm) was observed in the interlayer d -spacing of the grafted clay with respect to Cloisite 20A. Polymer-clay nanocomposites with different clay contents were prepared by free radical copolymerization of vinyl-silylated Cloisite 20A and styrene monomer in toluene. The interlayer d -spacing and surface changes in the prepared nanocomposite materials were studied by XRD. Exfoliated nanocomposites were obtained for clay contents of 0.5 wt%–1 wt%, and intercalated nanocomposites formed at 3 wt%–5 wt% clay loading. The thermal and mechanical properties of the nanocomposites were also studied by TGA, DTA, and DMTA. The glass transition temperature increased from 70.7°C for pure PS to 87.0°C for PCN 1%, indicating an effective interaction between the polymer matrix and the PS-grafted clay particles. DMTA studies reveal the improvement of thermal and mechanical properties of exfoliated PCN 0.5%. Based on TGA measurements, it is observed that the thermal stability of the nanocomposites, particularly in the case of PCN 0.5%, is improved with respect to virgin PS.

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