

Synthesis and Characteristics of Polystyrene–Clay Nanocomposites via *In Situ* Intercalative Polymerization in a Direct Current Electric Field

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ABSTRACT: Polystyrene (PS)/montmorillonite nanocomposites were prepared by the free-radical polymerization of styrene-containing dispersed clay in a direct current electric field. The intercalation spacing in the nanocomposites, the dispersion, and the orientation of these composites were investigated. The nanocomposites had

higher T_g and better thermal stability when compared with the virgin PS. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2723–2727, 2010

Key words: polystyrene; montmorillonite; nanocomposites; electric field

INTRODUCTION

Inorganic particles are widely used as reinforcement additives for polymers. At present, polymers reinforced by low weight percentages (1–10 wt %) of nanoscopically dispersed and organically modified layered silicates are attracting the attention of academic and industrial researchers because they provide numerous commercial opportunities.¹ The lower loadings facilitate processing and reduce components. In addition, because of the nanometer-sized particles obtained by dispersion, these nanocomposites exhibit markedly improved mechanical, thermal, optical, physicochemical, electrical, and flammable properties.^{2–6} However, few approaches are developed to control the spatial and oriented morphology of nanomaterials when compared with the conventional ways with fiber and weaving as additives. For example, with tuning effects of electric field, epoxy-layered silicate nanocomposite,^{7–10} styrene-acrylonitrile copolymer/clay nanocomposite,¹¹ and polypropylene/layered silicate nanocomposites¹² have been recently prepared under an applied electric field.

Melt intercalation and polymerized intercalation are the two main ways to prepare the polystyrene (PS)–clay composites.^{13–20} A general way involves

impregnating clay in styrene monomers followed by polymerization. However, the hydrophilic nature of untreated clay impedes its homogeneous dispersion in polymer matrix, and the modification of clay is necessary.^{13,14} For example, Akelah and Moet¹⁶ prepared the PS–clay intercalated composites through the solution method with the (vinylbenzyl) trimethyl ammonium chloride-modified Na-montmorillonite (MMT) and Ca-MMT; Doh and Cho¹⁸ obtained the PS–clay intercalated nanocomposites with a higher decomposition temperature; Fu and Qutubuddin¹⁹ prepared the PS–clay exfoliated nanocomposites with a higher dynamic modulus. In our previous work,²¹ we also prepared PS–MMT nanocomposites by free-radical polymerization of styrene-containing dispersed clay in static state. We found the twin-benzyltrimethyldecylammonium bromine montmorillonite (TBDO-MMT) particles were easily dispersed and swollen in styrene monomer. Although MMT is organically modified, it still contains electric charges more or less, and TBDO-MMT will probably be easily intercalated by PS if a direct current (DC) electric field is applied because of the dielectrophoretic effects. Therefore, in this article, a new method is developed to prepare PS–MMT nanocomposites by the free-radical polymerization of styrene-containing dispersed clay in a DC electric field.

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EXPERIMENT

Materials

The TBDO-MMT were supplied by Huate Company (Hangzhou, Zhejiang, China). Styrene (Shanghai

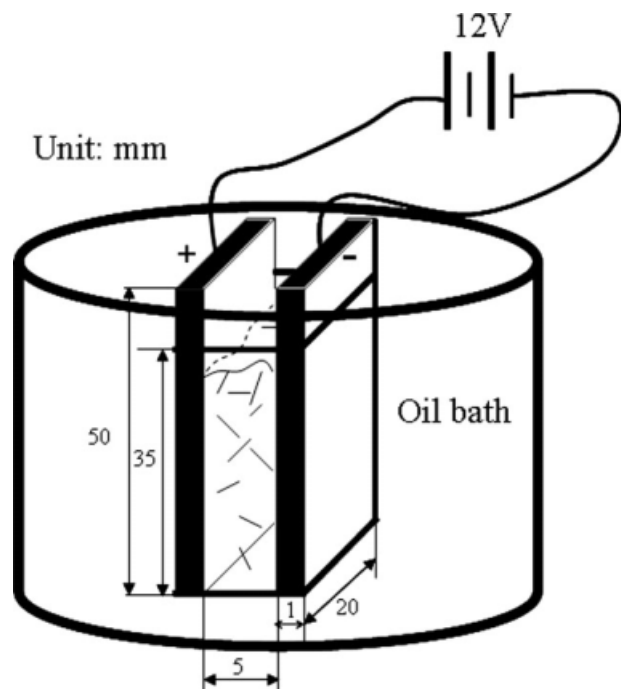


Figure 1 The preparing apparatus in DC electric field.

Chemical Solvent) was purified by distillation under a reduced pressure at 30°C. Benzoyl peroxide (BPO) (Shanghai Lingfeng Chemical Solvent Factory) was purified by crystallization using chloroform as the solvent at room temperature.

Synthesis of polystyrene–clay nanocomposites

Certain amount of TBDO-MMT and BPO were dispersed and swollen in styrene monomers. The mixture was stirred for 10 min and ultrasonically treated for another 30 min to obtain a homogenous system, and then degassed and continuously polymerized at 120°C for 72 h. All the polymerization reactions were carried out in a self-made apparatus in the open atmosphere (as shown in Fig. 1). The copper electrodes (35 mm × 20 mm × 1 mm) are 5 mm apart connecting with a DC electric field at the voltage of 12 V. No leakage current was detected, and no deposition was observed in the polymerizing

process. The as-polymerized PS/TBDO-MMT sample was dried in vacuum at 60°C for 24 h. By comparison, virgin PS was also prepared according to the aforementioned conditions with or without electric field. The detailed reaction conditions are given in Table I.

Characterization of polystyrene–clay nanocomposites

X-ray diffraction (XRD) patterns were obtained using a Philips PW1710 X-ray diffractometer equipped with a Ni-filtered Cu K α source. The voltage and the current of the X-ray tubes were 40 kV and 100 mA, respectively. The basal spacing of the MMT was estimated from the position of (001) peak in the XRD pattern.

The microstructure of nanocomposites was observed using a JEM-1200EX transmission electron microscope (TEM), and the ultrathin film was cut under cryogenic conditions using a Reichert-Jung Ultracut E microtome.

Properties of polystyrene–clay nanocomposites

The glass transition temperature (T_g) of the as-prepared samples was measured using a Perkin-Elmer PYRIS-1 differential scanning calorimeter (DSC). Transition temperatures were calibrated using indium and zinc standards. All DSC measurements were performed under an inert (N₂) atmosphere at a heating rate of 10°C/min. The sample weight was about 3–5 mg.

The thermal stability analysis was performed using a Perkin-Elmer TGA7 thermogravimetric analyzer (TGA) at a heating rate of 20°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

In our previous work, TBDO-MMT particles were easily dispersed and swollen in styrene monomer. Through the free-radical polymerization of styrene-containing dispersed clay, PS–MMT nanocomposites were successfully prepared.²¹ On the other hand,

TABLE I
The Dosage and Reaction Conditions

	Styrene (g)	MMT (mg)	BPO (mg)	Temp (°C)	Time (h)
Before electric field application	2.5	0 (0%)			
	2.425	75 (3%)			
	2.375	125 (5%)			
	2.25	250 (10)			
After electric field application	2.5	0 (0%)	12.5	120	72
	2.425	75 (3%)			
	2.375	125 (5%)			
	2.25	250 (10)			

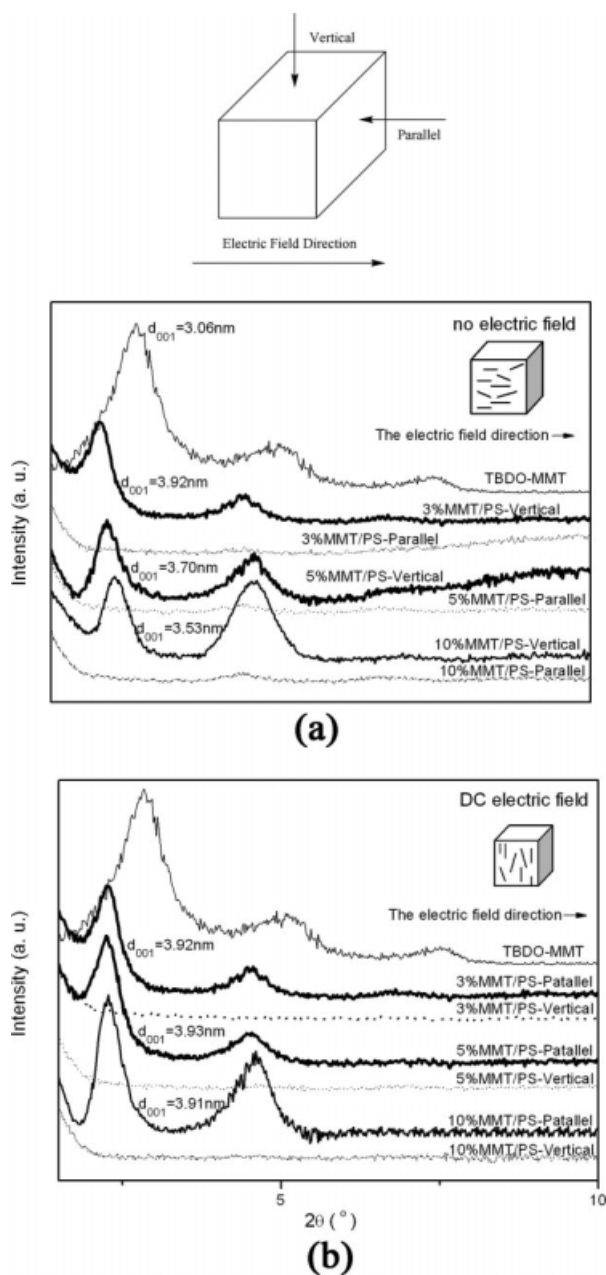


Figure 2 Small-angle X-ray diffraction curves of the samples: (a) no electric field and (b) DC electric fields.

most inorganic-organic nanocomposites may be broadly described as polarized particles (inorganic) suspended in a dielectric medium (polymer). In these systems, an electric field, either AC or DC, will induce a dipole on the particle in accord with the Clausius-Mossotti relation.²² Coupled to the field or field gradient, the induced dipole will result in a rotational or translational force, respectively, on the particles, and further leads their orientation. In this system, though MMT is organically modified, it still contains electric charges more or less, and TBDO-MMT will probably be easily intercalated by PS if a DC electric field is applied because of dielectro-

phoretic effects. Figure 2 lists the XRD patterns of composites obtained with different TBDO-MMT contents, directions, and electric fields. As with the 3.06-nm interlayer spacing of the (001) plane (d_{001}) for TBDO-MMT (Card No. 2-37), the nanocomposites containing 10, 5, and 3% TBDO-MMT are about 3.53, 3.70, and 3.92 nm without the electric field [as shown in Fig. 2(a)], respectively. When DC electric field was applied [as shown in Fig. 2(b)], the d_{001} of TBDO-MMT, the nanocomposites containing 10, 5, and 3% TBDO-MMT is about 3.06, 3.91, 3.93, and 3.92 nm, respectively. Compared with the initial interlayer spacing of the organic TBDO-MMT, the gallery expansion existing in the nanocomposites indicates the intercalation of TBDO-MMT layers by PS. However, the d_{001} of the samples decreases with the increase of TBDO-MMT content without electric field, implying that the dispersion of TBDO-MMT would become worse with the increase of TBDO-MMT content due to the aggregation of TBDO-MMT, and on the other hand, the d_{001} of the samples under DC electric field hardly changes with the increase of TBDO-MMT content. These results mean that DC electric field is beneficial for the intercalation reaction of PS into the TBDO-MMT because of the dielectrophoretic effects even with higher TBDO-MMT content. Although the XRD patterns of the obtained composites without electric field does not seem to be different, closed observation reveals that diffraction intensity (vertical to the electric field) was enhanced because of the TBDO-MMT layers preferentially orienting parallel to the electrodes in PS matrix [as shown in Fig. 2(a)], which is possible owing to the layer structure of MMT so that the MMT slices prefer to lie in the polymer before applying DC electric field; while the reorientation of intercalated MMT would be perpendicular to the electrodes occurs upon the application of DC field and lead to the increase of intensity parallel to the electrodes [as shown in Fig. 2(b)], which may be assigned to dielectrophoretic effects of MMT, similar to the polarized particles (inorganic) suspending in a dielectric medium (polymer).

In general, TEM is combined with XRD to testify the microstructure of the obtained nanocomposites, and it can directly observe the dispersion of TBDO-MMT in the polymer matrix. Figure 3 shows the TEM images of PS-MMT (5%) nanocomposites with or without DC electric field, in which the dark regions are the layers of MMT. TEM images reveal that all the initial particles are intercalated. As seen from Figure 3(a,b), the MMT layers are tightly stacked and randomly dispersed in the composite if no electric field was applied. However, under DC electric field [Fig. 3(c,d)], some stacks or tactoids of silicate layers are clearly observed as thick dark lines perpendicular to the electric field direction, which

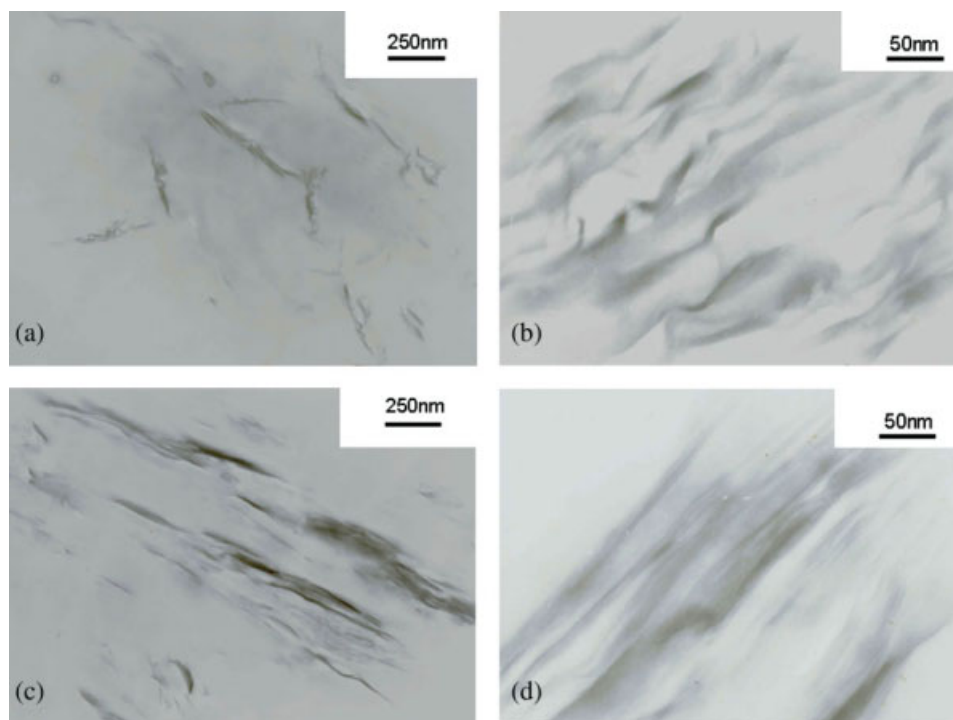


Figure 3 TEM images of PS/clay nanocomposite: (a and b) no electric field and (c and d) DC electric fields.

indicates that the reorientation of layer-stacking occurs throughout PS matrix. The results are consistent with those of the aforementioned XRD patterns.

Figure 4 shows the DSC curves of PS and PS/TBDO-MMT nanocomposites with or without electric field. From which we can see that the glass transition temperature (T_g) of PS/TBDO-MMT nanocomposites decreases with increasing MMT loading without electric field. In this situation, the TBDO-MMT could be perfectly intercalated by PS when TBDO-MMT content is low. While, excessive TBDO-MMT could be worse dispersed in PS, and the high viscosity of organophilic MMT dispersed in styrene monomer affects the diffusion of initiator molecules and MMT platelets block chain propagation during polymerization if TBDO-MMT content is high, which would further led to the decrease in T_g of PS. Furthermore, more TBDO-MMT content could serve as a plasticizer for PS and drop the T_g of the PS. The results are consistent with the previous works.^{19,23} However, if DC electric field is applied, the T_g of the obtained PS/TBDO-MMT nanocomposites is about 38°C higher than that of the composites obtained without DC electric field. As to the T_g increasing of nanocomposite obtained under DC electric field, we believe the movement of polymer segments was greatly restricted by the oriented clay layers, and it would result in the improvement of T_g . On the other hand, TBDO-MMT is more perfectly and uniformly dispersed in PS matrix, which is consistent with that of the TEM images, and it also leads to the chain

movement difficulty. Furthermore, the dielectrophoretic effects could make the diffusion of initiator molecules and MMT platelets help chain propagation during polymerization under DC electric field, and this result is also beneficial to enhance their T_g . Similar results were also observed by other works.^{24–26}

To further study the effects of DC electric field on the properties of the obtained nanocomposite, the TGA curves of PS–MMT (5% MMT) nanocomposites

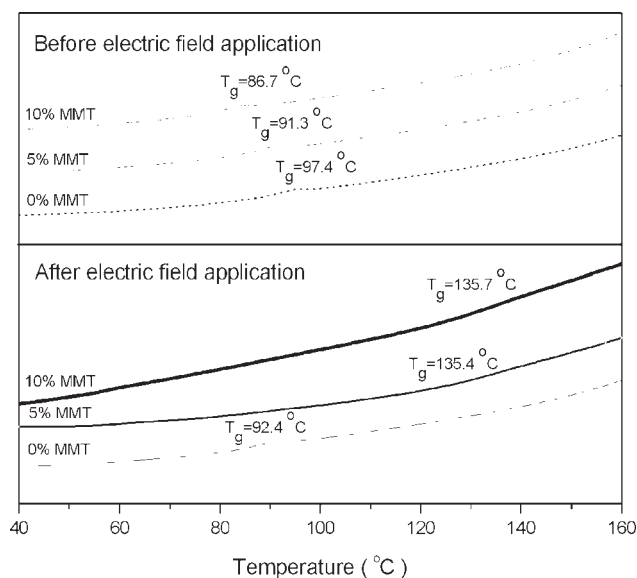


Figure 4 DSC curves of PS/clay nanocomposites.

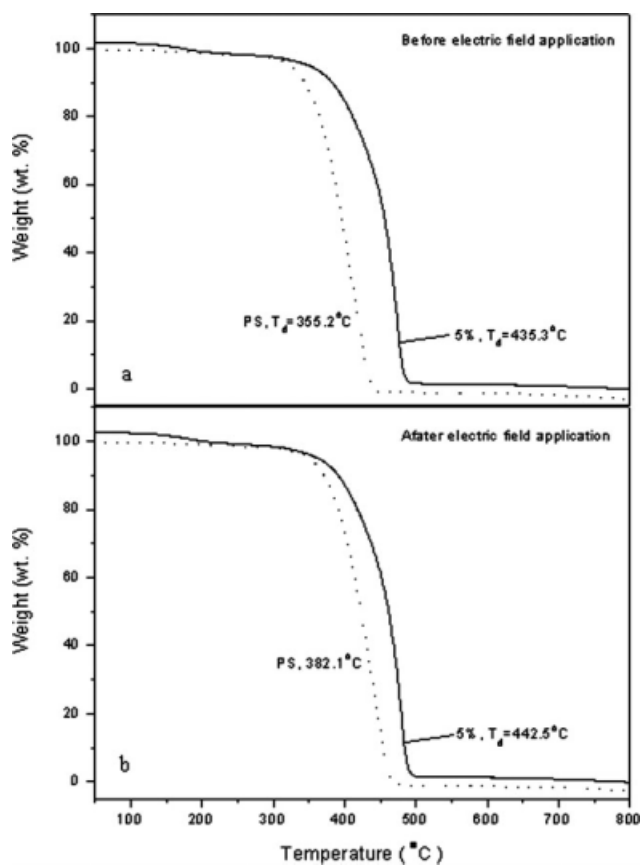


Figure 5 TGA curves of PS/clay nanocomposites.

with or without electric field are shown in Figure 5. In this study, the temperature at which 20 wt % loss of the polymer takes place is taken as the onset degradation temperature (T_d). It can be found from Figure 5 that the T_d of PS increase with the addition of TBDO-MMT in PS matrix. The better thermal stability of nanocomposites may be because the clay layers are most likely to hinder the out diffusion of the volatile decomposition products, as a result of the confinement of PS polymer chains between MMT layers as well as the MMT surface-polymer interactions in the nanostructured hybrid of PS and TBDO-MMT. Therefore, the improvement in the thermal stability will lead to the better service performance of the hybrid composite at elevated temperature. Similar results were also observed by Gilman and Muelhaupt and coworkers.^{27,28} In addition, the T_d of the nanocomposite obtained with the electric field is higher than those of the samples obtained without electric field, illustrating that the more dominantly oriented and more perfectly dispersed clay layers should have more effective hin-

drance for the out diffusion of the volatile decomposition products.

CONCLUSION

PS-MMT nanocomposites were successfully prepared by free-radical polymerization of styrene-containing dispersed clay in a DC electric field, and the DC electric field is beneficial for the orientation and the intercalation of the MMT in the nanocomposite. Further results reveal that the application of DC electric field can improve the T_g and the thermal stability of nanocomposites.

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