

Synthesis of polystyrene-clay nanocomposites via emulsion polymerization using a reactive surfactant

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Summary

Polystyrene-clay nanocomposites were synthesized via emulsion polymerization of styrene in the presence of montmorillonite particles and a reactive cationic surfactant as the emulsifier. The reactive surfactant, vinylbenzyl dodecyldimethylammonium chloride (VDAC), was synthesized by the quaternization reaction of vinylbenzyl chloride with dimethyldodecylamine. Partially exfoliated nanocomposites were achieved as revealed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Polystyrene-clay nanocomposites prepared by emulsion polymerization have higher glass transition temperature and dynamic modulus than pure polystyrene.

Keywords: clay, emulsion polymerization, montmorillonite, polymerizable surfactant, polystyrene, nanocomposites

Introduction

In recent years, polymer nanocomposites have attracted great interest because of dramatically improved properties compared with conventional composites [1]. Polymer-clay nanocomposites consist of clay nanolayers dispersed in a polymeric matrix [2, 3]. Polymer-clay nanocomposites exhibit enhanced thermal and mechanical properties [4-7], improved barrier properties [8, 9] and reduced flammability [10]. Intercalated polystyrene (PS)-clay nanocomposites have been prepared via in situ polymerization of styrene in the presence of organophilic clay [11, 12]. Akelah et al. [13] synthesized intercalated PS-clay nanocomposites using a short chain reactive surfactant and solvents to facilitate intercalation. Qutubuddin and coworkers [14,15] synthesized exfoliated PS-clay nanocomposites via in situ polymerization of styrene and a reactive organoclay. Weimer et al. [16] prepared exfoliated PS-clay nanocomposites by anchoring a living free radical initiator inside the clay galleries. The synthesis of intercalated PS-clay nanocomposites was also achieved via polymer melt intercalation [17,18]. Hasegawa et al. [19] synthesized PS nanocomposites via melt intercalation using an organoclay prepared by ion exchange with protonated

amine-terminated PS. Exfoliated PS-clay nanocomposites were also prepared by melt blending of styrene-vinylloxazoline copolymer with an organophilic clay [20].

Emulsion polymerization is a relatively new approach to synthesize polymer-clay nanocomposites. PS-clay and poly(methyl-methacrylate) (PMMA)-clay nanocomposites were synthesized via emulsion polymerization using an anionic surfactant (sodium lauryl sulfate) as emulsifier [21, 22]. PS-reactive organoclay intercalated nanocomposites were prepared by emulsion polymerization [23]. The reactive organoclay was synthesized by exchanging the inorganic cations (Na^+) with aminomethylstyrene. Since the alkyl chain of aminomethylstyrene is short, it is not very effective in expanding the clay interlayer [23]. Most recently, PMMA-clay nanocomposites were synthesized by emulsion polymerization with decyltrimethylammonium chloride and [2-methacryloyloxy)ethyl]-trimethylammonium chloride to modify the surface of dispersed clay [24].

The synthesis of PS-clay nanocomposites via emulsion polymerization using a reactive surfactant is reported in this communication. The advantage of the present approach over other procedures of emulsion polymerization [21-23] is that it combines cationic exchange of clay and emulsion polymerization in one step by using a reactive cationic surfactant, vinylbenzyltrimethyl-dodecylammonium chloride (VDAC). This method is called one-step emulsion polymerization. Exfoliation of clay nanolayers in the nanocomposites was achieved as revealed by X-ray diffraction and TEM.

Experimental

Materials

Sodium montmorillonite (Na-MMT) (Trade name Mineral Colloid BP) which contains exchangeable primarily Na^+ cations was supplied by Southern Clay Products Incorporation. It is a fine powder with an average particle size of 75 μm in the dry state, and a cation exchange capacity (CEC) of 90 mEq/100g. Styrene was purchased from Aldrich Chemical Company and purified by distillation under reduced pressure at 30 $^{\circ}\text{C}$. The free radical initiator, potassium persulfate (KPS), was purified by recrystallization twice from methanol. VDAC was synthesized by the quaternization reaction of vinylbenzyl chloride with dimethyldodecylamine (one half stoichiometric excess) under the protection of inhibitors in diethyl ether, and purified by recrystallization from ethyl acetate, as described in a previous paper [15].

Synthesis of Polystyrene-Clay Nanocomposites by Emulsion Polymerization

PS-clay nanocomposites were prepared using the following procedure. VDAC was added to an aqueous clay suspension and stirred for several hours. The molar amount of added VDAC was one half of the added clay times the CEC/100. Next styrene was added to form an emulsion. Finally, KPS was added to initiate polymerization at 70 $^{\circ}\text{C}$ in an oil bath. The prepared PS-clay nanocomposites were precipitated in methanol, filtered and washed with hot water and acetone, then dried in a vacuum oven. The vacuum dried PS-clay powder was compression molded to obtain samples for TEM and Dynamic Mechanical Analysis (DMA).

Characterization of Nanocomposites

X-ray diffraction (XRD) patterns were obtained by using a Phillips XRG 3100 X-ray generator equipped with a Ni-filtered Cu-K α (1.5418 Å) source that was connected to a Phillips APD 3520 type PW 1710 diffractometer controller. All samples were dried in a vacuum oven for at least 24 hours before XRD measurements. The morphology of the prepared emulsion latex was imaged using a JEOL 200 EX scanning electron microscopy (SEM). The microstructure of molded nanocomposites was imaged using a JEOL 1200 EX transmission electron microscopy (TEM). Samples for TEM were cut to 60 nm thick sections with a diamond knife.

The thermal properties of PS-MMT nanocomposites were measured by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC 7 calorimeter. Samples of 10 mg masses were heated to 150°C, then decreased to 0 °C and heated again to 150 °C at a heating or cooling rate of 10 °C/min under nitrogen atmosphere. The glass transition temperature, T_g , of the nanocomposites was determined from the respective second heating history. Dynamic mechanical properties were measured using a dynamic mechanical analyzer (Perkin-Elmer DMA 7) with a three-point bend fixture. The specimens (1mm \times 2.5 mm \times 20 mm) were cut from the center of the samples. A temperature sweep at 5 °C min⁻¹ from -25 to 110 °C at a frequency of 1 Hz was used to determine the dynamic modulus.

Results and discussion

The surface of pristine clay is hydrophilic. The small inorganic cations such as Na⁺ and Ca⁺² can be exchanged by organic cations to make the clay surface hydrophobic [25]. There are two advantages of using VDAC as an emulsifier instead of non-reactive surfactants. The first one is that VDAC-MMT organoclay has a cohesive energy density similar to that of styrene [15]. Similar cohesive energy densities between styrene and the organoclay can lead to extensive intercalation of styrene into clay gallery and expansion of the interlayer distance. The second advantage is the possibility of VDAC-MMT reacting with styrene to form covalent bonds, thus increasing the interfacial adhesion between polymer matrix and clay [15]. There is some evidence that clay dispersed in water at low concentration can be in a partially exfoliated state [26]. This provides an advantage of one-step emulsion polymerization approach to obtain exfoliated polymer nanocomposites. The loading of MMT for the one-step emulsion polymerization was varied in the range from 3 to 20 wt.% by weight of total styrene and MMT mixture.

Figure 1 compares XRD patterns of untreated Na-MMT, VDAC functionalized MMT (VDAC-MMT) by cationic exchange process and polystyrene-MMT nanocomposite. The XRD pattern of Na-MMT shows a broad peak centered at $2\theta = 8.9^\circ$. In contrast, VDAC-MMT, prepared by cationic exchange of Na-MMT with VDAC in aqueous solution [15], exhibits a sharp peak at $2\theta = 4.6^\circ$. The d_{001} spacing of VDAC-MMT increased from 0.99 nm of pristine Na-MMT [24] to 1.92 nm in dried state [15]. The d_{001} increment in VDAC-MMT corresponds to the distance between silicate layers separated by the insertion of VDAC cations. In the present study, VDAC was used for ion-exchange with Na-MMT in the presence of styrene droplets in water. As stated earlier, the amount of added VDAC was one half of the amount of MMT times

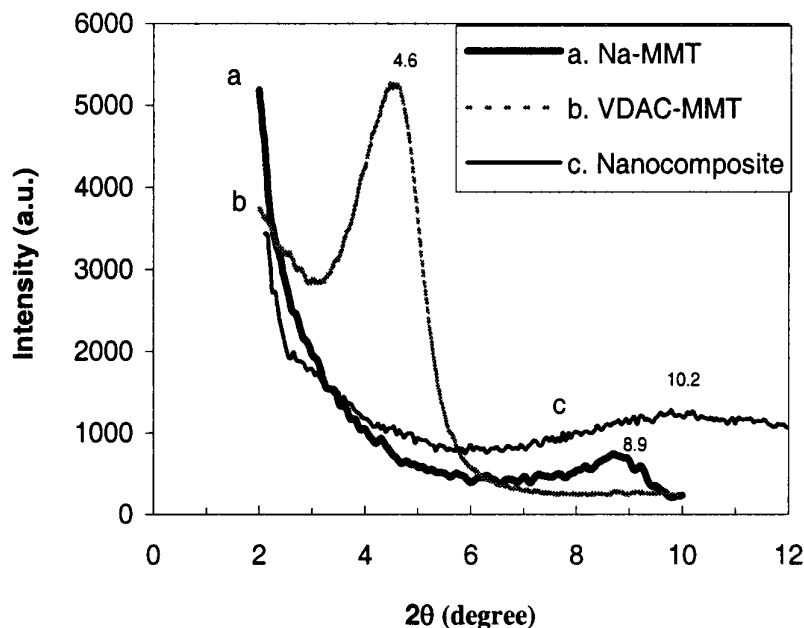


Figure 1. X-ray diffraction patterns of (a) Na-MMT, (b) VDAC-MMT, and (c) polystyrene-MMT nanocomposite with 5 wt.% MMT.

CEC/100 in order to avoid coagulation. The amount of surfactant for coagulation is less than but near the amount of clay times CEC/100 of MMT [27]. Thus, the XRD patterns a and b in Figure 1 depict the limiting cases of untreated and VDAC treated MMT. Curve c in Figure 1 shows the XRD pattern of a PS-clay nanocomposite containing 5 wt.% MMT. For MMT loading of 5 wt.% or less, there is no peak corresponding to Na-MMT or VDAC-MMT. However, there is a hump centered at $2\theta = 10.2^\circ$. Figure 1 suggests that partially exfoliated PS nanocomposites were obtained via one-step emulsion polymerization.

Figure 2 (a) illustrates typical morphology of PS-MMT latex particles prepared by one-step emulsion polymerization. The particles are spherical and there is some aggregation. The polymerization mechanism is not simple. Since the clay is not completely cationic exchanged, it is still negatively charged. Clay layers may be distributed inside monomer droplets or adsorbed to the monomer and water interface as speculated by Huang and Brittain [24]. The vacuum dried latex particles were molded into rectangular sheets by compression molding. TEM samples were prepared by cutting the molded nanocomposites with a diamond knife. Figure 2 (b) shows a TEM micrograph of molded polystyrene-VDAC-MMT (5 wt.% MMT) nanocomposite. Some layered structure exists, suggesting that there is only partial exfoliation. Partial exfoliation may be due to incomplete cationic exchange of clay with VDAC. This incomplete cationic exchange affects the compatibility between the surface of MMT and styrene, and also the intercalation of styrene in clay galleries.

The DSC thermogram in Figure 3 (a) shows that PS-MMT nanocomposite with 5 wt.% MMT has a higher glass transition temperature (103°C) than pure polystyrene (98°C). The increment of T_g may be attributed to various factors including higher molecular weight by emulsion polymerization, enhanced interaction between polymer and clay, and copolymerization of styrene with VDAC [15]. GPC measurement shows that PS nanocomposites containing 5 wt.% VDAC-MMT has a number average molecular weight (M_n) around 150,000. Figure 3 (b) shows DMA results of PS and

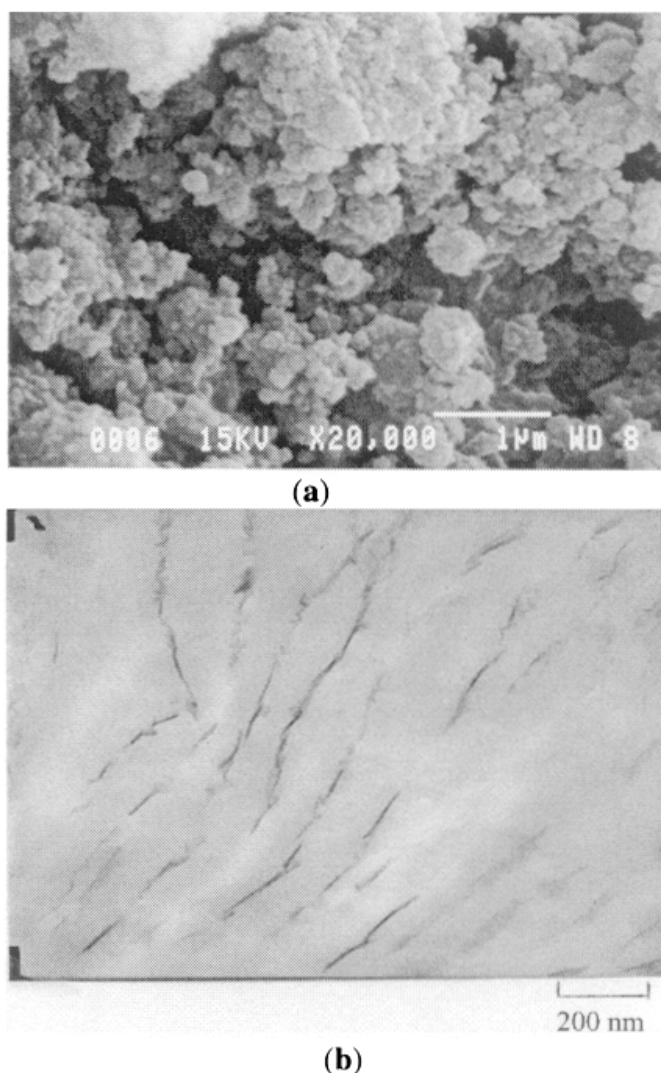


Figure 2. (a) Scanning electron micrograph of polystyrene-MMT nanocomposite latex particles, and (b) Transmission electron micrograph showing microstructure of molded polystyrene-MMT nanocomposite containing 5 wt.% MMT.

PS-MMT (5 wt.%) nanocomposites prepared by one-step emulsion polymerization. The dynamic modulus of the nanocomposites is higher than that of pure PS.

Conclusion

Partially exfoliated polystyrene-MMT nanocomposites have been synthesized via emulsion polymerization of styrene in the presence of clay and a polymerizable surfactant, VDAC. VDAC containing a vinyl benzyl group is effective in functionalizing and exfoliating MMT during the process of emulsion polymerization. Polystyrene-MMT nanocomposites show higher glass transition temperature and dynamic modulus compared with pure polystyrene.

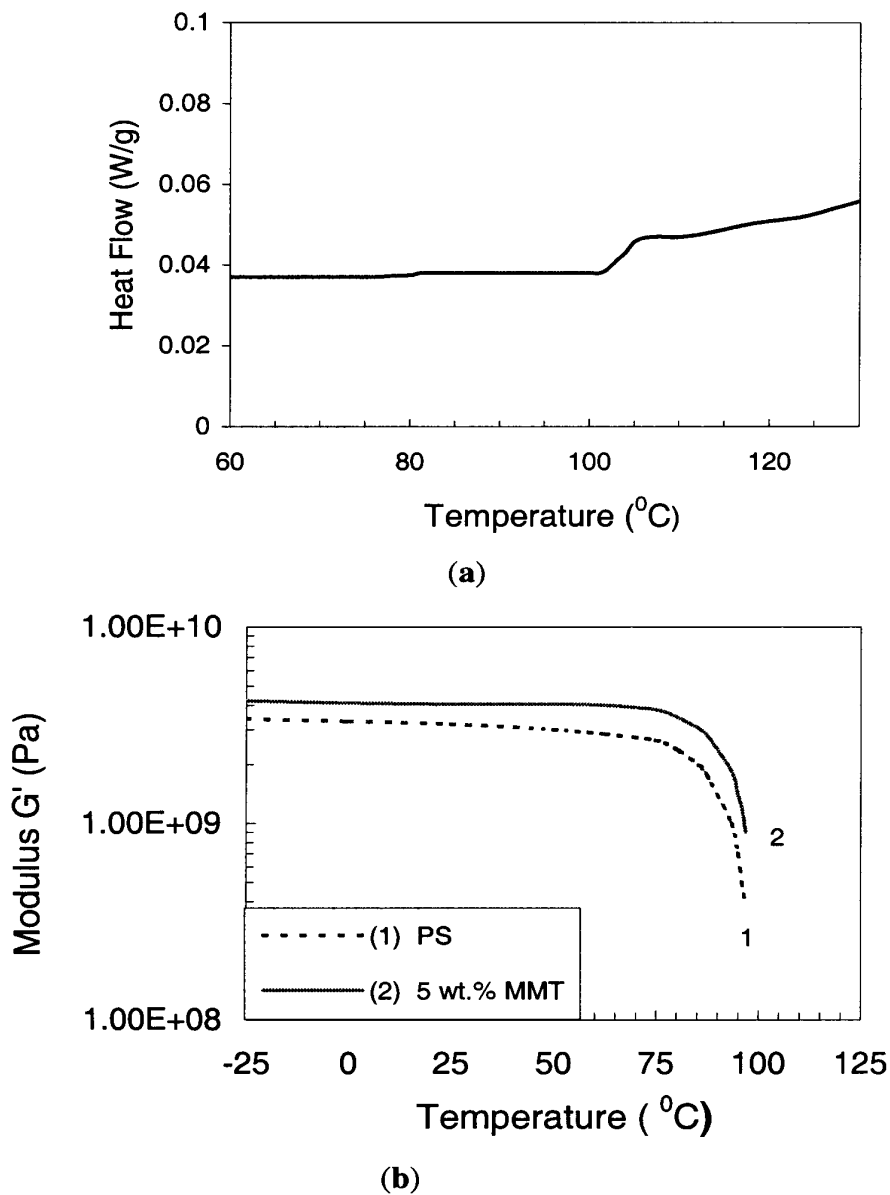


Figure 3. (a) DSC thermogram of polystyrene-MMT nanocomposite, and (b) DMA scans of pure polystyrene and polystyrene-MMT nanocomposite containing 5 wt.% MMT.

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References

1. Novak BM. (1993) Adv Mater 5:422
2. Giannelis EP (1996) Adv Mate. 8:29
3. LeBaron PC, Wang Z, Pinnavaia TJ (1999) Applied Clay Science 15;11

4. Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima A, Kurauchi T, Kamigaito O (1993) *J Mater Res* 8:1179
5. Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima A, Kurauchi T, Kamigaito O (1993) *J Mater Res* 8:1185
6. Lan T, Pinnavaia TJ (1994) *Chem Mater* 6: 2216
7. Messersmith PB, Giannelis EP (1994) *Chem Mater* 6:1719
8. Kojima Y, Fukushima A, Usuki A, Okada A, Kurauchi T (1993) *J Mater Sci Lett* 12: 889
9. Messersmith PB, Giannelis EP (1995) *J Polym Sci, Part A: Polym Chem* 33:1047
10. Gilman JW, Kashiwagi T, Lichtenhan JD, (1997) *SAMPE J* 33:40
11. Kato C, Kuroda K, Takahara H (1981) *Clay and Clay Minerals* 29:294
12. Doh JG, Cho I (1998) *Polym Bull* 41:511
13. Akelah A, Moet A (1996) *J Mater Sci* 31:3589
14. Qutubuddin S, Fu XA, Tajuddin Y (1999) In *Proceeding of SAMPE advanced composites conference*, Detroit, Michigan
15. Fu XA, Qutubuddin S (2001) *Polymer* 42:816
16. Weimer MW, Chen H, Giannelis EP, Sogah DY (1999) *J Am Chem Soc* 21:1615
17. Vaia RA, Ishii H, Giannelis EP (1993) *Chem Mater* 5:1694
18. Vaia RA, Giannelis EP (1997) *Macromolecules* 1997, 30:8000
19. Hasegawa N, Okamoto H, Kawasumi M, Usuki A (1999) *J Appl Polym Sci* 74:3359
20. Hoffmann B, Dietrich C, Thomann R, Friedrich C, Muhaupt R (2000) *Macromol Rapid Commun* 21:57
21. Lee DC, Jang LW (1996) *J Appl Polym Sci* 61:1117
22. Noh MW, Lee DC (1999) *Polymer Bull* 42:619
23. Laus M, Camerani M, Lelli M, Sparnacci K, Sandrolini F (1998) *J Mater Sci* 33:2883
24. Huang XY, Brittain WJ (2001) *Macromolecules* 34: 3255
25. Grim RE (1968) *Clay Mineralogy*, McGraw-Hill, New York
26. Ramsay JDF, Swanton SW, Bunce J (1990) *J Chem Soc Faraday Trans*, 86: 3919
27. Bongiovanni R, Chiarle M, Pelizzetti J (1993) *J. Dispersion Sci. & Tech.*, 14:255-268