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Synthesis of polystyrene encapsulated nanosaponite composite latex via miniemulsion polymerization

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Abstract

The synthesis and characterization of polystyrene encapsulated nanosaponite composite suspension via miniemulsion polymerization are reported in this study. The particle size of nanoclay and its pre-modification are critical to successfully producing a stable complex suspension. The final products were characterized by X-ray diffraction spectra, transmission electron microscopy (TEM), scanning electron microscopy (SEM), thin window energy dispersive spectroscopy (EDS), and light scattering. The results show that ar-vinylbenzyltrimethylammonium chloride (VBTAC) modified nanosaponite could be fully exfoliated and encapsulated inside the polystyrene latex via in situ miniemulsion polymerization. When the concentration of hexadecane (a co-stabilizer used in the miniemulsion polymerization) was high, the final composite particles are composed mainly of spherical particles with size less than 100 nm, and a small number of hemispherical or bowl-structured particles of size ∼100 nm to 1000 nm. The phase separation due to the existence of large amounts of hexadecane accounted for the formation of a variety of morphologies.

Keywords: Miniemulsion; Nanocomposite; Exfoliation

1. Introduction

Polymer–nanoclay composites have attracted considerable attention due to their unique properties and broad applications [1–4]. Polymer encapsulated inorganic particles with submicron scale have wide applications in cosmetics, pharmaceuticals, catalysis, optics, agriculture, coating and painting areas [5–7]. The composites in an aqueous suspension form have many unique advantages over their bulk or solvent form [8] in terms of environment concern, energy saving, product control, etc. Miniemulsion polymerization is an in situ method for preparing encapsulated particle suspensions. Tiarks [9] and other authors studied the encapsulation of carbon black by miniemulsion polymerization. Erdem et al. [10–12] prepared polystyrene encapsulated TiO_2 particles using miniemulsion polymerization in the presence of hydrophilic TiO_2 particles. Landfester and Ramirez [13,14] encapsulated magnetite particles in polystyrene matrix using a miniemulsion polymerization process. Zhang et al. [15] synthesized a mono-dispersion silica–polymer core-shell microsphere via surface grafting and emulsion polymerization. Zhang et al. [16] synthesized SiO_2–polystyrene nanocomposite particles via miniemulsion polymerization by using methacryloxy (propyl) trimethoxysilane modified silica particles. Although the encapsulation of inorganic particles using miniemulsion polymerization has been extensively studied, most inorganic particles are spherical with a narrow size distribution. It is well known that nanoclay particles have a platy morphology with a broad size distribution, resulting in more difficulties in the dispersion and the encapsulation of these particles in monomer droplets and polymer latex in miniemulsion polymerization. Several researchers [17–19] have attempted to synthesize polymer encapsulated nanoclay composite via suspension, emulsion or miniemulsion polymerization methods. Xu et al. [17]

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described a method to synthesize intercalated poly(styrene-*co*-methyl methacrylate)–clay nanocomposites through an emulsion polymerization by using a reactive surfactant, 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS). Huang and Brittain [18] synthesized the PMMA–layered silicate nanocomposites by suspension polymerization and emulsion polymerization. They simply mixed the unmodified clay into the aqueous phase or added the clay in the post-polymerization step. The nanoclay particles were not encapsulated and the final suspension was not very stable. Herrera et al. [19] synthesized the water-based polymer–clay nanocomposites by first chemically modifying the laponite clay minerals by silane agents (γ-methacryloxy propyl mono-, di-, trimethyl ethoxysilane) before the polymerization and then proceeding with seeded emulsion polymerization. However, the stability of the final latex was not reported. Our recent work indicated that a stable nanocomposite suspension can be prepared by the encapsulation of laponite in the polymer latex particle [20]. However, when montmorillonite with an average size about 400 nm (SEM estimation) was used, the encapsulation was unsuccessful because the plate size of montmorillonite is too big to be encapsulated by polymer latex particles. Instead of using montmorillonite, we recently reported that a stable composite suspension could be prepared by miniemulsion polymerization of styrene and saponite (200–300 nm plate size) [21]. Although the suspension prepared in that study was very stable, a large portion of the saponite particles only adhered on the polymer latex surface rather than having been encapsulated inside the polymer latex.

It was found from our previous research that the particle size, the size distribution and the surface properties of nanoclay play synergistic roles in encapsulation and exfoliation as well as the final product stability in a miniemulsion polymerization process. For example, a highly viscous solution or a gel of styrene was formed if the amount of the modified saponite in the monomer was higher than 4 wt.% because well dispersed nanoclay in the monomer significantly increased the oil phase viscosity, resulting in an unstable miniemulsion. For this reason, the stable composite suspension could not be prepared if the content of nanoclay is higher than 4 wt.%.

In this paper, we report a method to synthesize stable polystyrene–nanoclay composite latex containing large amounts (up to 30 wt.%) of fully-exfoliated and encapsulated nanoclay. Contrary to our previous reports [20,21], two important improvements are taken into account. Firstly, instead of the saponite with a size of 200–300 nm (measured by light scattering; Source Clay Repository of the Clay Mineral Society, University of Missouri) used in previous study, a saponite sample with an average size of 50 nm (measured by light scattering; Kunimine Industries Co., Ltd., Japan) was selected. Secondly, as an alternative to using long chain cationic surfactant such as octadecyltrimethylammonium bromide (OTAB) for saponite modification, a short chain cationic surfactant with an unsaturated reactive group, (ar-vinylbenzyl) trimethylammonium chloride (VBTAC), was selected to pre-modify clay saponite. VBTAC can not only copolymerize with styrene, but also result in a low viscosity solution of nanoclay in the monomer phase.

2. Experiment

2.1. Materials

Na-saponite clay was supplied by Kunimine Industries Co., Ltd., Japan. It was synthesized by a hydrothermal reaction with an ideal formula of $(Na_{0.49}Mg_{0.14})^{0.77+}[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4]^{0.77-}$. The cationic exchange capability of Na-saponite is 0.997 equiv/kg. Its average particle size is ∼50 nm (measured by light scattering) when dispersed in water. 2,2′-Azoisobutyronitrile (AIBN) was a product of Waco Chemicals USA, Inc., and used as received. (ar-Vinylbenzyl) trimethylammonium chloride (VBTAC, 99%), octadecyltrimethylammonium bromide (OTAB), Triton 405 (TX-405, $4\text{-}(C_8H_{17})C_6H_4(OCH_2CH_2)_{40}OH$, 70% solution in water), hexadecane (99%), and styrene (99%) were purchased from Aldrich Chemical Inc. Styrene was purified by washing with 5 wt.% NaOH solution followed by de-ionized water until a pH of 7 was reached, and then distilled under reduced pressure and stored in the refrigerator prior to use. All other reagents were used as received.

2.2. Surface modification of saponite clay by VBTAC

In a typical procedure, a suspension of 5 g of saponite in 400 ml of water was continuously stirred at room temperature for 2 h until a transparent aqueous solution was obtained. Then, an aqueous solution of 1.2 g of VBTAC in 100 ml water was added to the solution. After continuous stirring of the suspension overnight at room temperature, a white precipitate was collected by centrifugation and washed with water and ethanol to remove the excess VBTAC until no chloride can be detected by silver nitrate. The sample was then dried in a vacuum oven at room temperature.

2.3. Miniemulsion polymerization of styrene in the presence of the modified saponite

In a typical run, as indicated by the recipe in Table 1, oil phase A composed of 1.2 g of co-stabilizer hexadecane and 0.24 g of AIBN, 12 g of the monomer styrene, and varied

Table 1
The basic recipe for the miniemulsion polymerization of polystyrene–clay nanocomposite latex particles

Mixtures	Component	Amount added (g)	Percentage in total (wt.%)	Percentage in monomer (wt.%)
Oil phase A	Styrene	12.0	10.4	100.0
	Organosaponite	0.48–3.6	0.4–3.0	4.0–30.0
	Hexadecane	1.2	1.0	10.0
	AIBN	0.24	0.2	2.0
Water phase B	TX-405	1.0	0.9	8.3
	D.I. water	100.0	87.0	833.3

amounts of saponite (4–30 wt.% of the weight of the monomer styrene), was subjected to magnetic stirring at room temperature for 30 min. The mixture was then exposed to ultrasonification for 4 min. Following that, oil phase A was poured into an aqueous phase B comprising of 1 g of TX-405 in 100 ml of water under vigorous mechanical stirring in an ice bath for 30 min. The miniemulsion composed of A and B was thus prepared by homogenization under ultrasonification for another 3 min and was ready for subsequent polymerization.

The miniemulsion polymerization was carried out by degassing with N_2 at room temperature for 30 min first, and then increasing the temperature to 80 ± 2 °C and keeping at this temperature for more than 6 h under continuous mechanical stirring (∼600 rpm). The reaction was terminated by adding one drop of 2% 4-methoxyphenol solution into the miniemulsion.

2.4. Characterization

FTIR spectra were recorded on a Magna System 560 from Nicolet Company, with samples in pellet form from KBr. Thermogravimetric analysis (TGA) was performed using a Seiko TG/DTA 320 at a heating rate of 20 °C/min under an air stream. X-ray powder diffraction patterns were recorded on a PW 1800 X-ray diffractometer (Philips, USA) using Cu Kα ray ($\lambda = 1.54056$ Å) as the radiation source. A step size of 0.04° and a scan step time of 0.5 s were adopted. The d (001) basal-spacing of the original clay and the exfoliated clay were calculated using the Bragg equation:

$$d = \lambda / 2 \sin\ \theta$$

The particle size and polydispersity were measured by a dynamic light scattering on a BI-200 SM Gohio-meter from Brookhaven Instrument Co. at a fixed angle of 90°, under laser ($\lambda = 632.8$ nm) and with an aperture of 100 µm. The transmission electron microscopy (TEM) observation was conducted on a JEOL 100C transmission electron microscope at an accelerating voltage of 100 kV and a beam current of 70 µA. The scanning electron microscopy (SEM) analysis was carried out on a LEO 1530 thermally-assisted field emission (TFE) scanning electron microscope in combination with a thin window energy dispersive spectrometer (EDS) for microanalysis at an operating voltage of 3 kV and a working distance from 6 to 10 mm. The ultrasonification was conducted on a W-385 sonicator from the Heat System-Ultrasonics Inc., USA, at an output power level of 5 with a continuous mode, and a duty cycle of 70%. Centrifugation was conducted using Beckman 20 centrifuge at 10,000 rpm for 30 min at room temperature.

3. Results and discussion

3.1. Modification and dispersion of nanosaponite

The pristine clay is hydrophilic and requires pre-modification to be dispersed in the monomer. It was found in our previous research that when long carbon-chain surfactant OTAB was used as a modifier, the saponite can change from hydrophilic to hydrophobic and be well dispersed in organic phase. However, the viscosity of styrene monomer increased rapidly with the increase of the modified saponite content. Consequently, stable miniemulsion could not be obtained if the saponite content is higher than 4 wt.% in the oil phase. In order to reduce the viscosity of the oil phase, a short carbon-chain cationic surfactant (ar-vinylbenzyl) trimethylammonium chloride (VBTAC) was selected as the modifier in this research. This surfactant has an unsaturated group on one end that can react with the monomer styrene, and a cationic ammonium group that can be absorbed on the surface of hydrophilic clay to form organophilic clay. The experimental result shows that when VBTAC-modified saponite was dispersed in styrene monomer, the viscosity of the styrene phase was much lower than that of OTAB modified saponite in styrene. Miniemulsion was stable up to 30 wt.% of VBTAC-modified nanoclay in the monomer phase. The composite latex obtained after polymerization was very stable and no remarkable precipitate was observed even after centrifugation at 10,000 rpm for 20 min. In addition, when a certain ratio (>30%) of VBTAC was replaced by OTAB, the viscosity of the monomer phase increased remarkably and the total nanoclay content in the monomer phase had to be reduced in order to obtain a stable miniemulsion.

The absorption amount of VBTAC on the clay saponite was measured by TGA. It was shown that 78.6 wt.% of the total weight of VBTAC-modified saponite remained until temperature was up to 463.8 °C, which agrees well with the maximum cationic exchange capability of saponite (99.7 mequiv/100 g, 78.9 wt.% remained). This agreement means that the cationic ion exchange of saponite with VBTAC is complete.

The viscosity of the mixture of styrene with organoclay modified by VBTAC is much lower than that modified by OTAB. FTIR spectrum, as shown in Fig. 1, clearly demonstrated that both VBTAC and OTAB can enter the galleries and bond to saponite. The presence of the C–H stretching of OTAB at 3000–2840 cm^{-1} and the double bond C=C stretching 1667–1640 cm^{-1} of VBTAC, indicates the existence of OTAB or VBTAC in the pretreated saponite samples. The intercalation of the organosaponite before and after polymerization was investigated using XRD. The dispersion of organoclay in styrene after 4-min ultrasonification and the final latex obtained from miniemulsion were freeze-dried, and then the powder of samples was used for XRD measurement. As shown in Fig. 2, the VBTAC-modified saponite powders dried from water and from styrene have the interlayer spaces of 1.47 nm and 1.48 nm, respectively. Fig. 2 also clearly shows that the peak of the saponite disappears after the polymerization, which suggests a full exfoliation structure of the saponite nanoparticles in the final composite suspension.

3.2. Morphology of polystyrene encapsulated organosaponite composite latex

The SEM and TEM images shown in Fig. 3(a) and (b) indicate that particles with various morphologies are presented

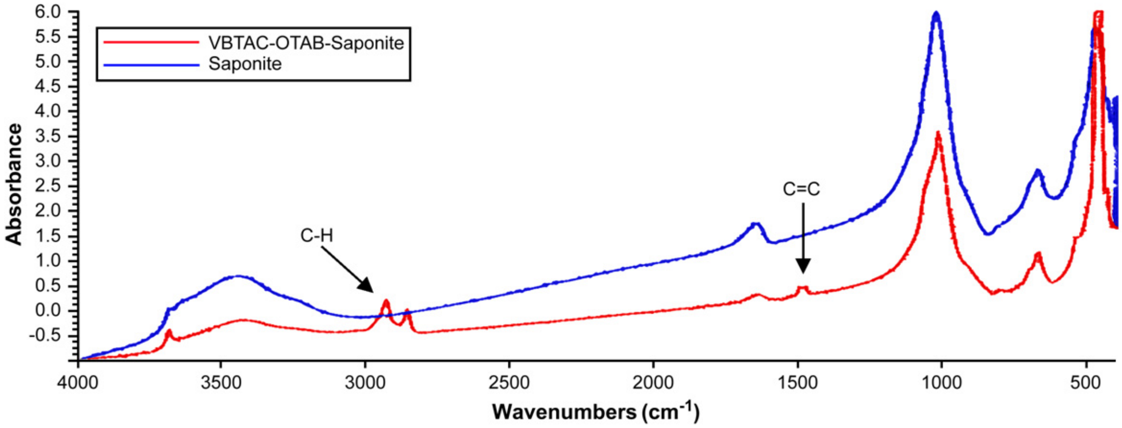

Fig. 1. The FTIR spectra of the unmodified saponite and VBTAC/OTAB modified saponite with KBr pellets.

in the final product of the polystyrene–saponite composite suspension. The final composite mainly consists of spherical particles less than 100 nm in size. However, some particles of size ∼100 nm to 1000 nm with hemispherical or bowl morphologies exist in the final product. The surfaces of both types of particles are smooth, and no clay particles can be observed. Furthermore, as shown in Table 2, the average particle size (measured by light scattering) of the final product in the presence of organoclay was larger and had a broader particle size distribution in comparison to that in the absence of organoclay.

In order to clarify the morphology of saponite particles inside the polymer latex, a dilute latex suspension was dropped on a TEM grid and dried at room temperature. The dried composite particles were then heated to high temperature (160 °C) to allow the polystyrene spreading on the TEM grid to form a thin film. TEM images of Fig. 4 show the morphologies of the polystyrene–organosaponite composite latex (a) before and (b) after melting. The TEM pictures show that the particles are uniformly dispersed on TEM grid with no organosaponite observed before melting. Thus, the organosaponite particles must be encapsulated inside the final latex particles made by miniemulsion polymerization. Fig. 5 shows the elemental composition of final polystyrene–nanosaponite composite particles. This EDS spectrum provides further evidence that the silicon is within the final latex particles although it could not be seen from the latex surface, suggesting the encapsulation of the saponite by polymer particles.

Fig. 6 shows the polystyrene–nanosaponite composite film after melting in the presence of the unmodified saponite (a) and the modified saponite (b). When the unmodified saponite was used, the platy saponite particles with an un-exfoliated morphology were observed. However, exfoliated saponite nanolayers are uniformly dispersed in the polystyrene matrix of the polymer thin film made from VBTAC-modified saponite. This result further proves that the organosaponite particles are not only encapsulated but also exfoliated inside polystyrene latex particles.

3.3. Morphologies of final latex particles

As shown in Fig. 3, the final polystyrene–saponite composite particles via miniemulsion polymerization using an oil-soluble initiator AIBN and non-ionic surfactant TX-405 are composed of two groups of particles: a spherical particle with a size less than 100 nm and hemispherical or bowl-structured particle with a size from ∼100 nm to 1000 nm. In order to understand the role of nanoclay in the formation of the hemispherical and bowl-structured particles, more experiments were conducted in the absence of organoclay. The results indicate that pure polystyrene latex is composed of similar morphologies under the same polymerization conditions. It has been known that the initiation inside a droplet is the dominant reaction mechanism in a miniemulsion polymerization. It is also known that almost no new particles are

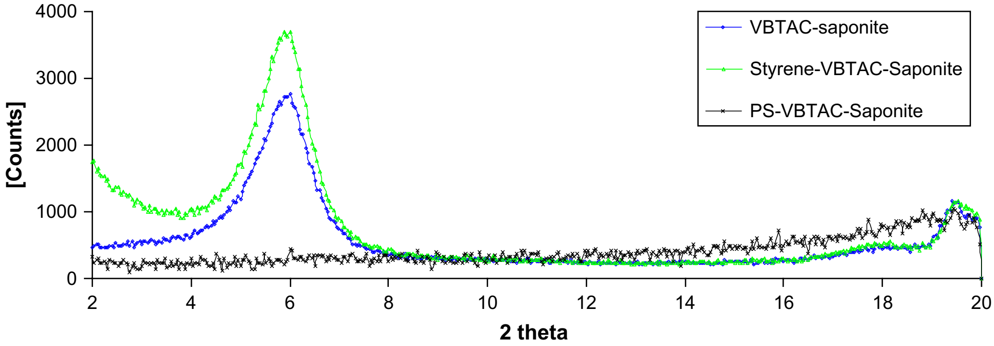

Fig. 2. XRD spectra of VBTAC-modified saponite, styrene dispersed VBTAC-saponite, and polystyrene exfoliated VBTAC-saponite.

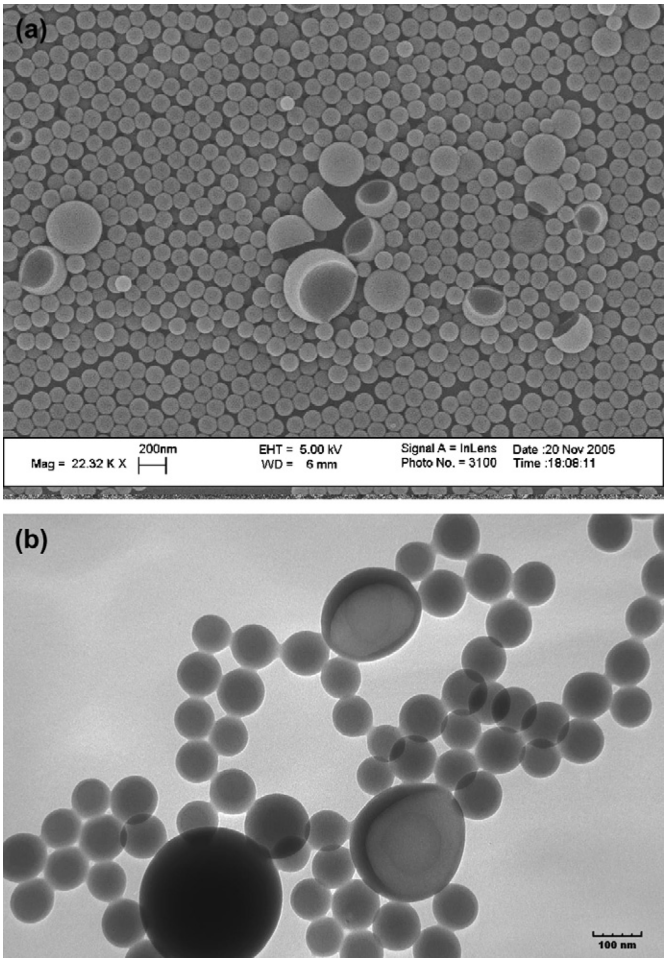

Fig. 3. SEM and TEM images of polystyrene–nanosaponite composite latex particles via miniemulsion polymerization in the presence of 10% organosaponite based on the weight of the monomer styrene: (a) SEM, (b) TEM.

produced during polymerization if 1–2% co-stabilizer is used in a miniemulsion polymerization [22] because co-stabilizer can effectively suppress the coalescence of droplets and retard Oswald ripening. Therefore, the traditional miniemulsion mechanism does not make a reasonable explanation for the formation of the particles with the varied morphologies.

Table 2
The particle size and its distribution of polystyrene latex particles in the presence and absence of modified saponite measured by light scattering

	Average diameter (nm)	Polydispersity index	Particle size distribution
Polystyrene latex without clay	161.4	0.117	Below 218.31 nm: 96%; between 218.31 nm and 2000 nm: 4%
Polystyrene latex with 4 wt.% clay	208.7	0.232	Below 232.40 nm: 81%; between 232.40 nm and 2000 nm: 19%

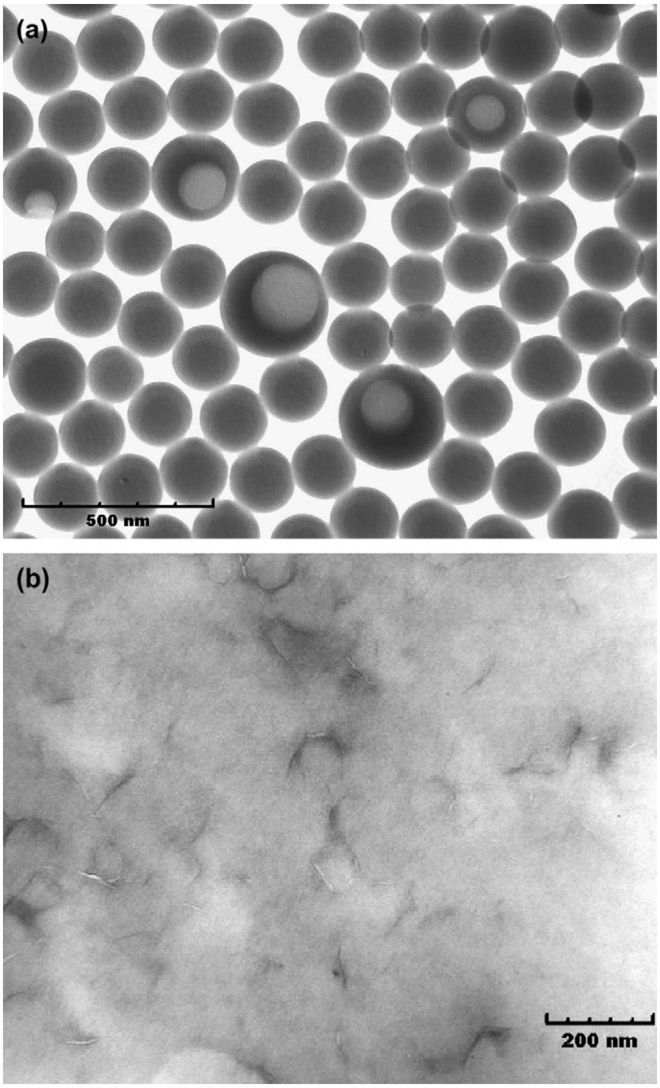

Fig. 4. TEM images of the polystyrene–organosaponite composite latex: (a) before melting, (b) after melting.

Fig. 7 shows the SEM images of the final latex particles prepared in the absence of hexadecane (co-stabilizer in miniemulsion polymerization) and saponite. It can be seen that the spherical latex particles are uniform with a diameter less than 100 nm. Compared to the SEM image of the latex prepared with 10% of hexadecane (Fig. 3), it can be concluded that co-stabilizer hexadecane plays an important role in the formation of various morphologies such as large hemispheres or bowls. Furthermore, the experiment in the absence of hexadecane but with nanosaponite indicates that the final latex particles have a uniform size, size distribution and morphology, as shown in the SEM image in Fig. 7, which suggests that the nanoclay is not the main factor for affecting the particle size and size distribution. Landfester et al. [23] reported similar morphologies when large amount (>10%) of hexadecane co-stabilizer were used in miniemulsion polymerization. Because polystyrene is insoluble in hexadecane, the phase separation of polystyrene and hexadecane inside the miniemulsion droplets occurred if hexadecane concentration in the latex is high. It is believed that the hexadecane was removed by high vacuum in SEM sample preparation, resulting in polystyrene hemispheres or bowls. The emulsion

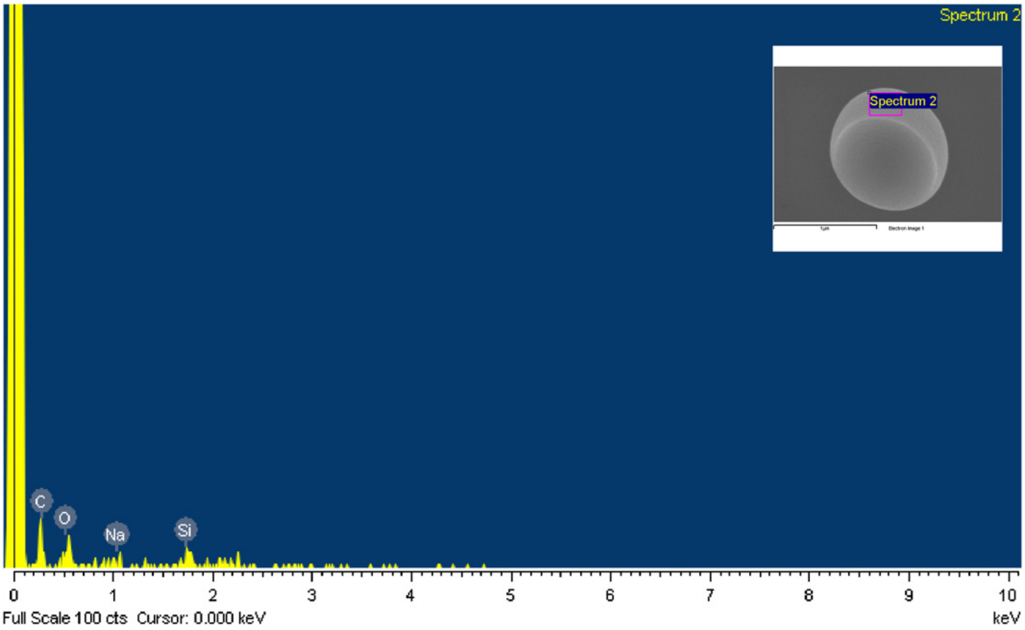

Fig. 5. EDS spectra of polystyrene–nanosaponite composite latex particles.

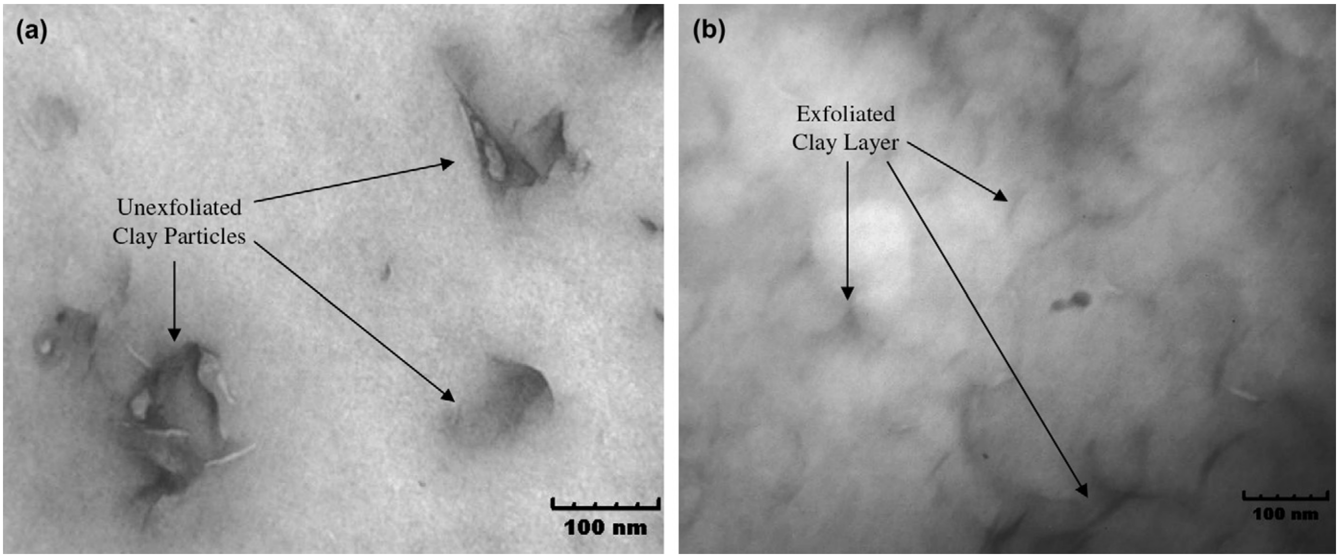

Fig. 6. TEM images of the polystyrene–nanosaponite composite film after melting. (a) Unmodified saponite and (b) modified saponite in polystyrene matrix.

coalition during polymerization was believed to account for the formation of some large particles in the final products.

4. Conclusion

This paper presents a one-step method to synthesize polystyrene encapsulated nanoclay composite latex via miniemulsion polymerization. The particle size of nanoclay and its pre-modification are two important factors for preparing stable miniemulsion before polymerization and latex after polymerization. The correct pretreatment chemistry is also one of the critical factors for encapsulation and exfoliation of nanoclay inside the latex particles. For the saponite with an average particle size of 50 nm and pre-modified by a monomer reactive cationic surfactant VBTAC, polystyrene latexes containing large amounts (up to 30 wt.%) of organosaponite were obtained. The final polystyrene–nanoclay composite particles were composed of two groups of particles, the majority of which were spherical particles with a size less than 100 nm, and the minority of which were hemispherical or bowl-structured particles with a size from ~100 nm to 1000 nm. Furthermore, the morphologies of final latex particles in the presence of the unmodified and the modified nanoclay and its melting film above 160 °C were investigated. The results further proved that VBTAC-modified nanoclay was exfoliated and encapsulated inside the polymer latex particles, while the

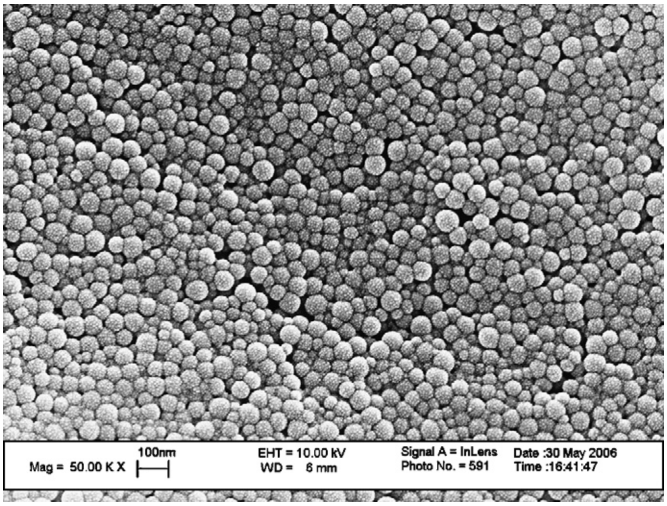

Fig. 7. SEM images of polystyrene latex in the absence of hexadecane.

unmodified nanoclay platelet was not exfoliated. In addition, the mechanism to form a variety of morphologies and broad size distribution for final polystyrene latex particles was investigated. Consequently, the mechanism can be clarified by the phase separation of polystyrene in high content hexadecane.

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