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Pickering Emulsion Polymerization of Styrene-co-butyl Acrylate Nanoparticles by Using Cloisite Na$^+$ as Surfactant

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Abstract

Cloisite Na$^+$ was used as a solid surfactant (stabilizer) in Pickering emulsion polymerization of styrene-co-butyl acrylate in presence of oil soluble initiator, azobisisobutyronitrile (AIBN) and water soluble initiator, potassium persulfate (KPS). Fourier transform infrared (FTIR) spectrum approved the corporation of Cloisite Na+ layers within the polymer matrix. Effect of clay content was assessed on the particle size and polymerization rate for both kinds of initiators. Reduction of particle size (nearly 100 nm) and enhancement of polymerization rate (30% and 10% for formulation with KPS and AIBN respectively) was observed by adding clay material to the blank recipe. Morphology of the particles was investigated by SEM and TEM. Formation of armored latex particles (covered particles with clay layers) with approximately 200 nm in diameter was proved via these micrographs. Furthermore, exfoliated structure of nanocomposites was revealed by XRD for sample containing water soluble initiator (ionic initiator) and oil soluble initiator. Impress of Cloisite Na$^+$ structure on Tg of synthesized copolymer (soap free systems) was investigated by DSC as large changes was observed (approximately 10-15 °C). Effect of Tg on film formation of latexes was also evaluated.

Keywords: *Pickering emulsion polymerization, Cloisite Na+, nanocomposite, film formation, soap free system.*

Introduction

In recent years, many studies have been accomplished to fabricate polymer nanocomposites by using various methods and nanoclays [1–15]. Nanocomposites from these methods have outstanding mechanical [16] and

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thermal stability compared to the neat polymer [17–20]. But when the goal is reduction of the water absorption or impermeability, these methods are not entirely suitable due to the large amount of surfactant used for stabilizing the system. Therefore surface active agent free systems (soap free systems) are more demanded.

One idea is using solid particles instead of surfactants which is called as Pickering emulsion, as was done by Ramsden in 1903 [21]. In 1907, Pickering described emulsion system while various solids such as copper sulfate, iron sulfate and other metal salts were used as stabilizers. For this reason, these systems were called Pickering systems [22]. Then in 1959, Wiley used methyl cellulose and bentonite as stabilizers to prevent the adherence of the particles in suspension polymerization of vinylidene chloride [23]. In 1960, Bentonite was used in suspension polymerization of styrene - divinylbenzene [24]. In the past few years efforts for making organic- inorganic hybrids was resumed by variety of nanoparticles such as SiO_2 [25-30], TiO_2 [31], CNT [32], crystals of cellulose [33], Fe_2O_3 [34] and ZnO [35]. PMMA/Na-MMT nanocomposites were synthesized via a soap-free emulsion polymerization of methyl methacrylate (MMA) by using 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) [36]. Voorn and colleagues proved that surfactant-free inverse emulsion polymerizations of the hydrophilic monomers such as acrylamide or 2-hydroxyethyl methacrylate can be successfully carried out by using organically modified clay platelets like Cloisite 20A as solid stabilizer. Then particles with diameter of 700 to 980 nm were obtained [37]. Zhang and coworkers prepared poly [2-(dimethylamino) ethyl methacrylate] brushes on the surfaces of clay layers by in situ free-radical polymerization. Poly (methyl methacrylate) colloid particles which was stabilized and initiated by mentioned polymer brushes were prepared by Pickering emulsion polymerization. They indicated exfoliated structures of clay and proved that the clay layers with PDMAEMA chains covered the PMMA colloid particles [38]. Ianchis et al. reported surfactant-free emulsion polymerization of styrene [39] and acrylate monomers [40] by using five modified montmorillonite through grafting mono functional alkoxysilanes. In the presence of Na^+ MMT, interactions were so weak and the particles kept their spherical shape but modified montmorillonite particles were mainly localized inside and outside of the polymer particles [39]. They also explained based on surface hydrophobicity of Cloisite, less hydrophobic compounds tend to stabilize O/W emulsions, and hydrophobic modified particles worked as stabilizer for W/O emulsions [40]. MMT clay layers pre-modified with cationic amphiphilic block copolymer like poly (styrene-b-2-hydroxyethylacrylate) has also been used as a stabilizer in dispersion polymerization of styrene in alcoholic medium (ethanol/water). It was shown that colloidal polystyrene particles covered with MMT layers were obtained [40]. It was noted that armored structures for particles covered with the clay platelets can act as super-heat barrier and give raise the overall thermal stability of polymers so that degradation of nanocomposite contaning 10% and 7% clay incrased 60 °C relative to the neat polymer [41].

Dungen and coworkers has modified the clay surfaces and used it in Pickering miniemulsion of (styrene-co-butyl acrylate) [42]. Bonnefond and colleagues reported surfactant-free emulsion and miniemulsion polymerizations of styrene and butyl acrylate in presence of Na^+ MMT clay which was modified with a macromonomer (Sipomer PAM100 as a stabilizer). They cited addition of Sipomer PAM100 to the latex containing clay, helped to decrease the water uptake and water vapor transition rates [43]. Cavin and coworkers prepared polystyrene latex particles armored with Laponite RD clay particles using Pickering stabilization system. They believed that oil phase initiation is preferred as the clay particles could complicate the radical entry and exit from the polymer particles [44]. Negrete-Herrera et al. have synthesized polymer/Laponite nanocomposite latex particles via emulsion polymerization in presence of organically modified Laponite clay platelets. They reported that use of trifunctionalsilane makes the clay layer stick together, and hence not enable to redisperse into the water [45]. Solid-stabilized or Pickering miniemulsion polymerization by using Laponite clay discs as surfactant were reported by Bon and coworkers.

Armored latexes obtained from hydrophobic acrylate monomers in which the hydrophobicity of monomers was a crucial factor [46]. Wang and coworkers prepared polymer particles having armored Laponite-clay prepared by the Pickering miniemulsion polymerization of *n*-lauryl acrylate. They observed addition of small amounts of the “soft-hard” clay-armored PLA particles to poly (butyl acrylate-*co*-acrylic acid) latex for production of waterborne pressure-sensitive adhesive (PSA), increased tack adhesion energy was received [47]. Bourgeat- Lami et al. prepared high solids content poly [styrene-*co*-(*n*-butyl acrylate)] latexes armored with Laponite clay platelets prepared by soap-free emulsion copolymerization. The overall polymerization kinetics showed the effect of clay platelets on nucleation and stabilization of the particles as the majority of Laponite platelets were located on the polymer particle surfaces [48].

Most of the above researchers have used modified clay. Some of them have added additional chemical agents to induce stability into their system. But in this study, we prepared armored polymer particles of styrene-*co*- butyl acrylate only by inserting Cloisite Na^+ layers without applying any surfactant, modifier or auxiliary monomers, since natural Cloisite itself played the main role of stabilizer in our emulsion system. Effect of clay content on stability of latex, rate of polymerization, particle size, glass transition temperature, morphology of the polymer particles and finally, film formation process were also investigated here.

Experimental

Materials

Styrene and n-butylacrylate (BA) were purchased from Merck and Fluka companies, respectively. Styrene was purified by two times washing with 5 W/V% aqueous NaOH solution and subsequently rinsed with plenty of distilled water (until pH of the separated aqueous phase was reached to 7.0) and stored on dried $CaCl_2$ (Merck, Germany) at 0 °C prior to use to remove the inhibitor. Cloisite Na^+ (NA^+ MMT) was provided from Southern Clay Product Inc, U.S.A. Potassium persulphate (KPS) from Merck and 2, 2'-azobisisobutyronitrile (AIBN) from Fluka were used as initiators without any purification. AIBN was recrystallized in ethanol and was kept in fridge before using it. Sodium hydrogen carbonate ($NaHCO_3$) from Merck was used as a buffer. Twice distilled water was prepared in our laboratory and was used in all experiments with pH around 6-7. Hydroquinone, acetone and all other materials were analytical grade and were used as received.

Typical polymerization procedure

In a typical experimental procedure (sample code A-2), NA^+ MMT (0.6 g) was dispersed in distilled water (90 ml) for 72 hours, then 0.1 g $NaHCO_3$ was added to this dispersion (pH of media was kept about 7.5). Quickly, it was sonicated by ultrasonic homogenizer at pulsed mode with a power of 80% amplitude for 5 min, in order to improve the exfoliation of Na^+ MMT layers. Afterwards mixture of monomers (totally about 10 g) containing n-butylacrylate (56 % wt) and styrene (44 % wt) was added to aforementioned aqueous dispersion. This mixture was sonicated again for 5 min while was keeping in ice bath in order to prevent any undesirable polymerization reactions. Finally 0.15 g KPS was added to this as prepared emulsion. A 250 ml glass reactor equipped with a condenser and a three bladed turbine stirrer was bubbled with purified nitrogen about 20 minutes and was kept under nitrogen atmosphere and continuous mechanical stirring of 300 rpm until the end of polymerization reaction. Meanwhile, the polymerization temperature increased to 80 °C. Finally, the as prepared emulsion was poured inside the reactor and was heated for 6.5 hours. Various recipes including different clay concentrations were reported in Tables 1 and 2.

Table 1. Pickering emulsion copolymerization of Sty-BA using KPS as an initiator and varied amounts of Cloisite Na^+ as stabilizer.

Sample	H_2O (g)	Cloisite Na^+ (g)	Sty (g)	BA (g)	KPS (g)	Overall monomer content (wt%)	Clay / monomer (wt%)
A-1	90	--	6.42	3.58	0.151	9.98	---
A-2	90	0.6	6.42	3.58	0.153	9.92	6
A-3	90	--	4.43	5.57	0.15	9.98	---
A-4	90	0.6	4.43	5.57	0.15	9.92	6
A-5	90	0.8	4.43	5.57	0.151	9.90	8
A-6	90	1.0	4.43	5.57	0.152	9.88	10

Table 2. Pickering emulsion copolymerization of Sty- BA using AIBN as an initiator and different amounts of Cloisite Na^+.

Sample	H_20(g)	Cloisite Na^+(g)	Sty(g)	BA(g)	AIBN(g)	Overall monomer content (wt%)	Clay / monomer(wt%)
B-1	90	--	6.42	3.58	0.156	9.98	---
B-2	90	0.6	6.42	3.58	0.149	9.92	6
B-3	90	0.8	6.42	3.58	0.151	9.90	8
B-4	90	0.6	4.43	5.57	0.150	9.92	6
B-5	90	0.8	4.43	5.57	0.153	9.90	8
B-6	90	1.0	4.43	5.57	0.149	9.88	10

Characterization

Sonication was done by SONOPULS ultrasonic homogenizer; model HD 2200 from BANDELIN electronic GmbH & Co. KG (Germany). ZE 76 titanium probe was used in all experiments. Gravimetric conversion was made as follows: at different time intervals, small amounts of latex were taken from the reactor and then one droplet of hydroquinone solution in acetone was added to it. Then the sample were dried at 1 to 6 hour in oven of 70°C.

Stability measurements of the final latexes were done by LUMI Reader separation analyzer (Germany). The principle of this instrument is measuring the light which is transmitted from the dispersion within a day (256 intervals, each interval is about 338 Sec; intensity of light is 125 %).

Particle size distribution and average particle size of polymer particles were measured by light scattering on a SEM 633 from SEM Tech Co, France. Samples were prepared by diluting the latex in distilled water, while Scattering angle was fixed at 90° under laser beam (λ = 633 nm) at temperature of 25 °C.

Fourier transforms infrared (FTIR) spectra were recorded by EQUINOX 55, Bruker (Germany) using 16 scan s^{-1} in the form of KBr pellets. XRD analysis were carried out on X'Pert Pro MPD PAN analytical from Netherlands with Cu radiation source (λ = 1.54184). SEM images and energy dispersive X-ray microanalysis (EDX) were taken by TESCAN model VEGAII XMU from Czech Republic (20 kv). Latex sample was diluted sixty times and then one droplet of it was casted on a sample holder, dried at room temperature and coated with gold. DSC was carried out by using Mettler Toledo DSC1 (Switzerland), over a temperature range of -20 to 400 °C at the scan rate of 20 °C/min under nitrogen atmosphere.

A Philips TEM CM30 (300 kV) transition electron microscope from Netherlands was employed for HRTEM analysis of the nanocomposite latex morphology. Sample was prepared by casting a droplet of sixty time diluted latex (by sonication in a Bandelin SONOREX Digital 10 p ultrasonic bath) onto a 200-mesh covered formvar/carbon coated copper grid at room temperature.

Results and discussion

FTIR spectra of Cloisite Na$^+$ and its nanocomposite

The presence of the Cloisite Na$^+$ in the polymer matrix was characterized by FTIR analysis. Figure 1 indicates FTIR spectra of Cloisite Na$^+$ (a) and its nanocomposite (b). In Figure 1-a, the peak at 1028 cm^{-1} corresponds to Si–O stretching vibration of silicate layers. The peak located at about 3438 cm^{-1} is related to –OH stretching of silicate layer and the peaks 531 and 461 cm^{-1} are due to the stretching of Al–O and bending of Si–O, respectively. Figure 1-b clearly shows the presence of main peaks of Cloisite Na$^+$ in poly (styrene-co-butyl acrylate) spectra which proves the existence of clay particles inside the structure of nanocomposite's films.

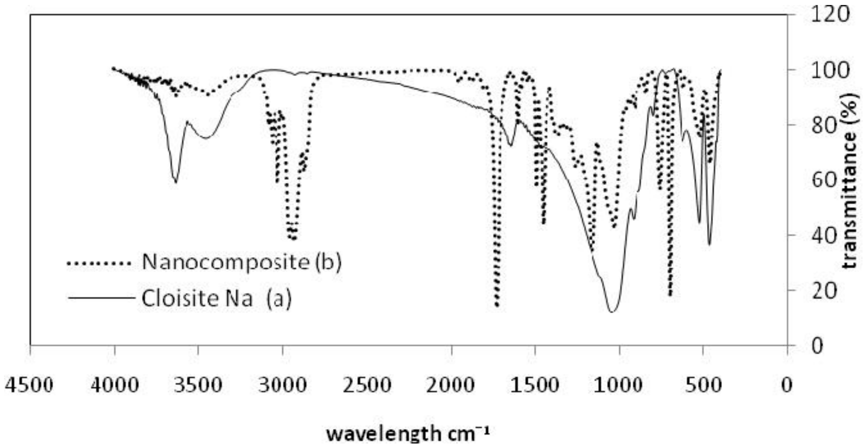

Figure 1. The FTIR spectra: (a) Cloisite Na$^+$, (b) Nanocomposite containing 6 wt% Closite Na$^+$ (A-2).

Stability of latex

Synthesized latexes (except samples A-1 and A-3) weren't stable upon storage. Sample without nanoclay (mother lacquered sample or A-3) was more stable than samples containing nanoclay. Due to data obtained from LUMI reader instrument (transmission versus position of cell at various time intervals is measured), showed that latex containing Cloisite Na+ (A-4) were precipitated during 24 h but again well dispersed after shaking it. As observed in Figure 2-a, the percentage of light transmitted from middle of tube increased from 12% to 90% in 24 hours which represents settling of latex with time (color change from red to green indicates the passage of time). This behavior for other samples containing clay was also similar. This phenomenon should be due to the high density of clay particles. Sample A-3 was stable (Figure 2-b) for 5 h but after sedimentation, couldn't be redispersed due to interfuse of nanoparticles into each other. In samples comprising nanoclay, clay platelets on the surface of particles (Pickering emulsion) prevent the interfuse of them and therefore no coagulation was observed. Similar results were also reported by Bon et al. [44] and Ianchis et al. [39].

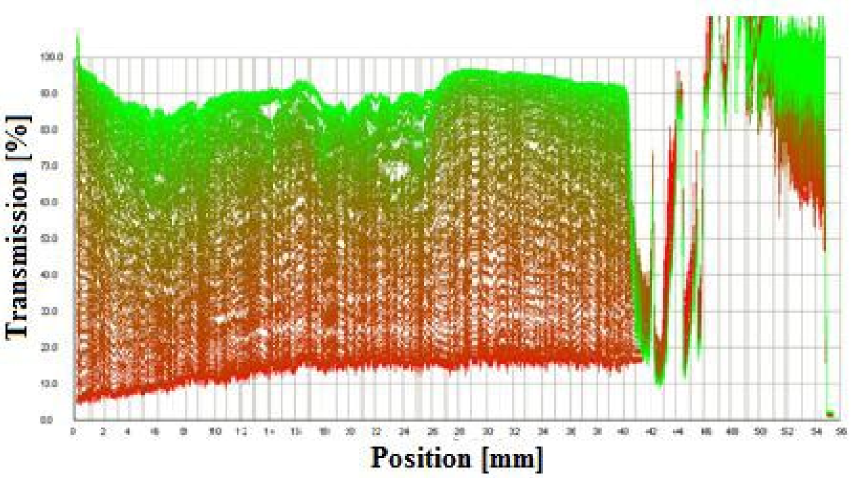

Figure 2-a. Transmission versus position of tube for sample A-4, Color change from red to green indicates the passage of time.

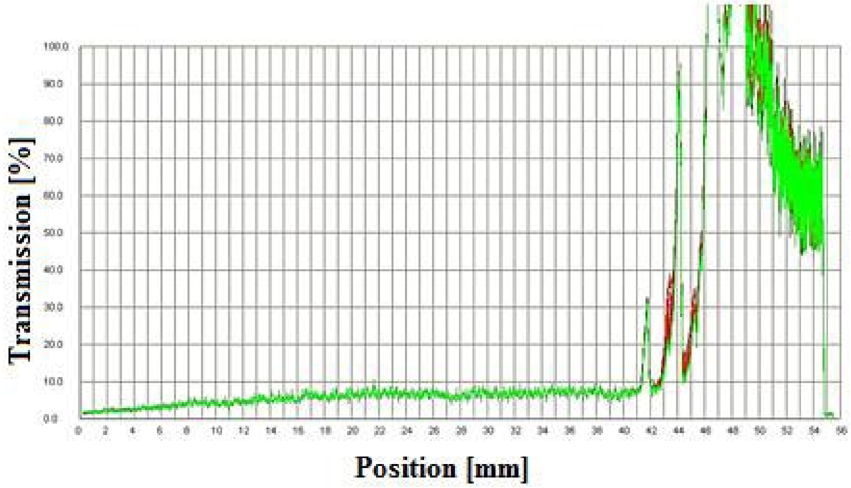

Figure 2-b. Transmission versus position of tube for sample A-3, Color change from red to green indicates the passage of time.

Rate of polymerization, particle size and polydispersity

Gravimetric analysis (Figure 3) was done and showed that polymerization rate in samples containing nanoparticles (A-4, A-5 and A-6) was higher than sample without nanoparticles (A-3).

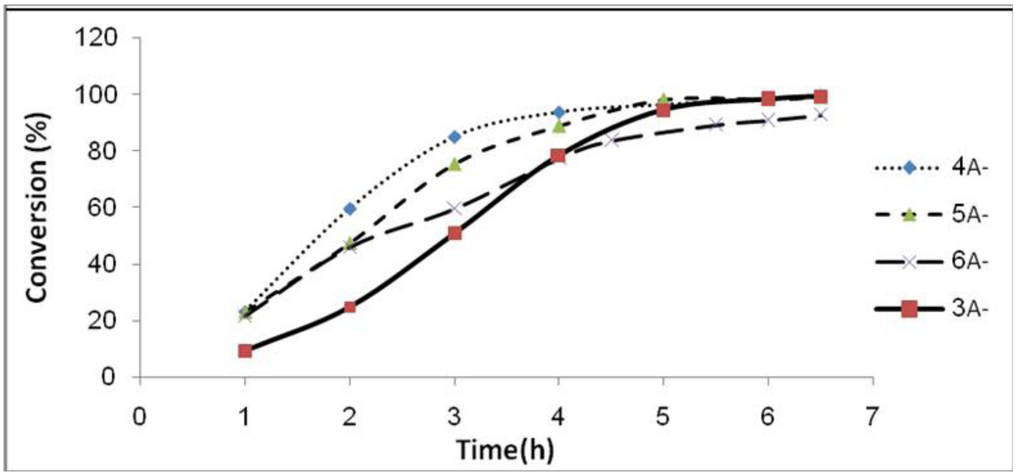

Figure 3. Conversion versus time for emulsion polymerization without clay (A-3), 6 wt% clay (A-4), 8 wt% clay (A-5) and 10 wt% clay (A-6) (respect to monomer).

In Figure 3 also it was observed that conversion decreased with increasing nanoparticle weight percentages. According to the ionic nature of KPS and electrostatic repulsion between initiator and clay layer, this reduction in rate and conversion can be expected since the initiator efficiency is reduced. Particle size and final conversion of polymerization were displayed in Table 3.

Table 3. Average particle size and final conversion.

Sample Code	Average particle size (nm)	Final conversion (%)
A-3	526.7	99
A-4	423.7	99
A-5	440.1	98
A-6	547.2	92
A-2	432.4	93
B-4	753.6	89
B-5	664.7	87
B-6	671.8	92

Average particle size for sample containing 6 wt% clay (A-4) is smaller than mother latex (A-3). Also particle size increased by increasing the weight ratio of Cloisite from 6 wt% to 10 wt % as was shown in Table 3 and definitely confirmed the data obtained from the gravimetric analysis. This increase in particle size was due to the particle coagulation and hence, instability in the system as no encapsulation was observed by further experiments. In other words, micro coagulation happened via increasing the weight ratio of clay in the recipe. Plot of particle size distribution for A-3 to A-6 series was shown in Figure 4.

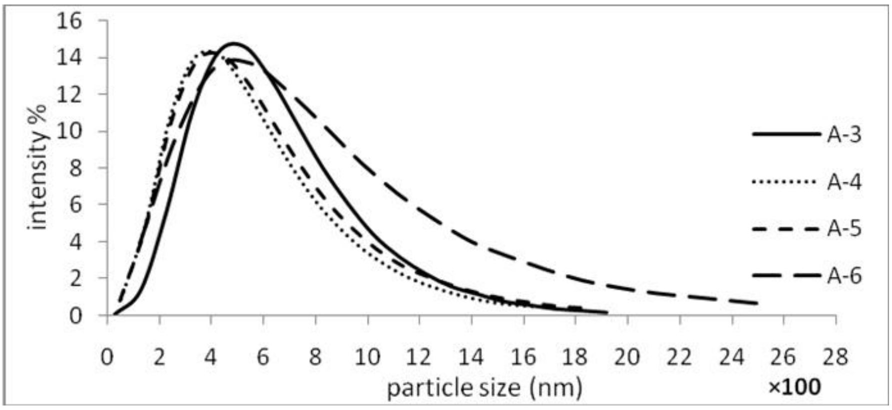

Figure 4. Particle size distribution for A-3 (blank), A-4 (6%wt clay), A-5 (8%wt clay) and A-6 (10%wt clay) samples for KPS initiator.

Enhancement of polymerization rate and reduction of particle size plus increasing the population of smaller particles can be attributed to the monomer droplets stabilized by Cloisite particles or nuclei created by their. Major part of polymerization proceeded and stabilized by clay particles, than homogenous nucleation. To omit the homogenous nucleation, AIBN (nonionic initiator) were used. Latex synthesis without clay in the presence of AIBN (B-1) led to coagulation of the system. Furthermore this result was not obtained for the latex which synthesized without clay in the presence of KPS initiator (A-3), where homogenous nucleation preceded during the polymerization. For these samples (Table 2) was suggested that the emulsion was stabilized by nanoclay particles; as solid particles or exfoliated layers. From gravimetric analysis was found that by increasing the amount of nanoclay, rate of polymerization was also increased (Figure 5).

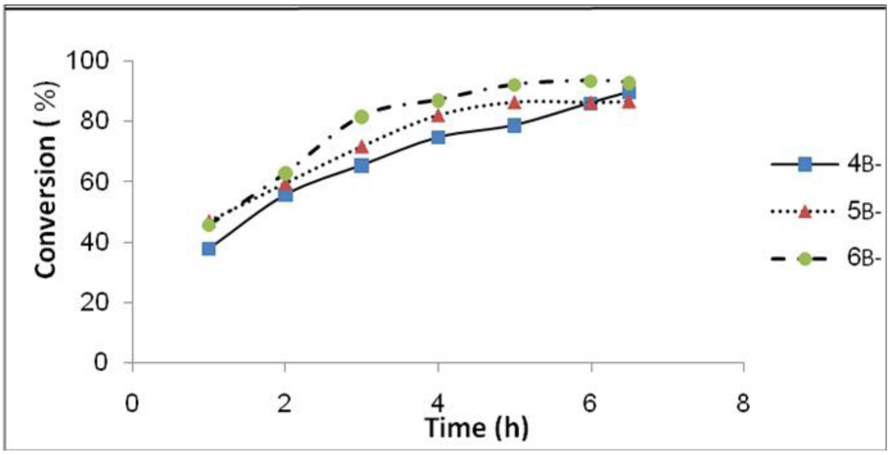

Figure 5. Conversion versus time for samples containing 6 wt% clay (B-4), 8 wt% clay (B-5) and 10 wt% clay (B-6).

Also light scattering measurements showed that by increasing the amount of clay percentage, reduction of particle size was happened (Table 3, B-4 to B-6 series). These observations confirmed that weight percentage of clay has a significant effect on nuclei formation during the polymerization, as increase in amount of clay led to reduction of particle size and accordingly decrease of particle size caused the increase in polymerization rate. Similar effects were observed by Teixeria et al. as they have expressed enhancement in overall polymerization rate upon increasing amounts of Laponite clay, which was due to an increase in the total amount of particles [49]. Others reported that particle size of nanocomposites was decreased as the clay loading increased. This effect was explained by stabilization mechanism of the nucleated particles at the early stage of the polymerization via adsorption of the partially modified clay [41].

Morphology of the nanocomposite latex revealed by SEM and TEM

Figure 6 shows SEM images of particles synthesized by two different initiators. When KPS was used as initiator and clay as stabilizer (Figures 6-a, 6-b), the polymer particle size was more uniform than when AIBN was applied as an initiator (Figure 6-c and 6-d).

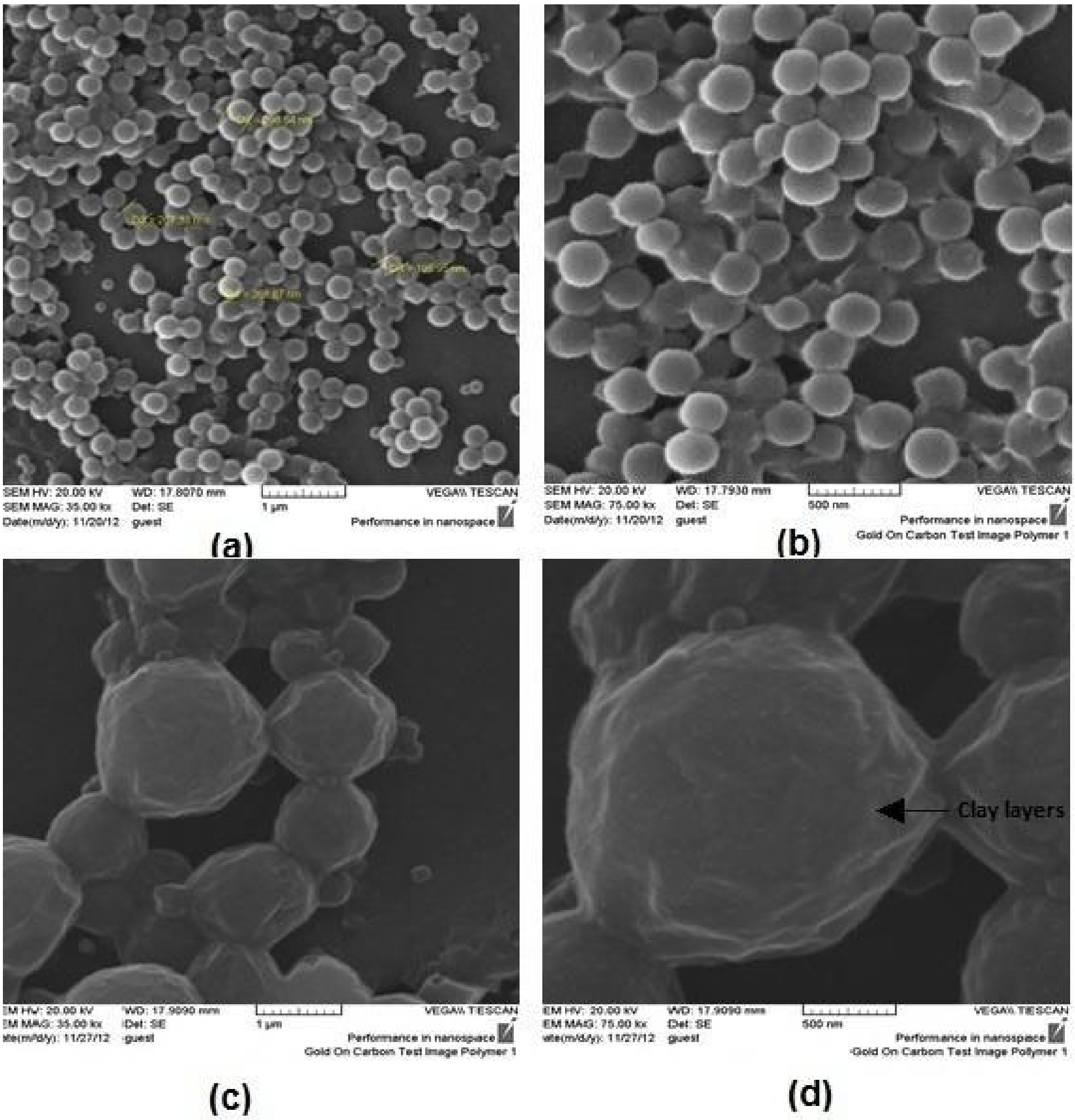

Figure 6. SEM images of sample A-2 (KPS as initiator) with magnification 35000 (a) and 75000 (b), sample B-2 (AIBN as initiator) with magnification 35000 (c) and 75000 (d).

Also it was observed that polymer particle size for sample containing KPS was smaller than samples prepared with AIBN. According to these images one can conclude that negative charges of monomer droplets in presence of KPS gave more stability to the emulsion polymerization system. As was evident in Figure 6-b, most of the particles was hexagonal in shape and a few of them were spherical, these received shapes were due to settling the clay platelets mostly on the surface of polymer particles. In Figures 6-c and 6-d clearly observed that clay layers perch on the surface of particles, therefore, particles weren't completely spherical in shape. Dispersion of clay layers in polymer matrix was proved by detecting the Si element through EDX measurements. EDX images showed homogeneous dispersion of clay layers (red point) within polymer matrix (Figures 7-a, 7-b).

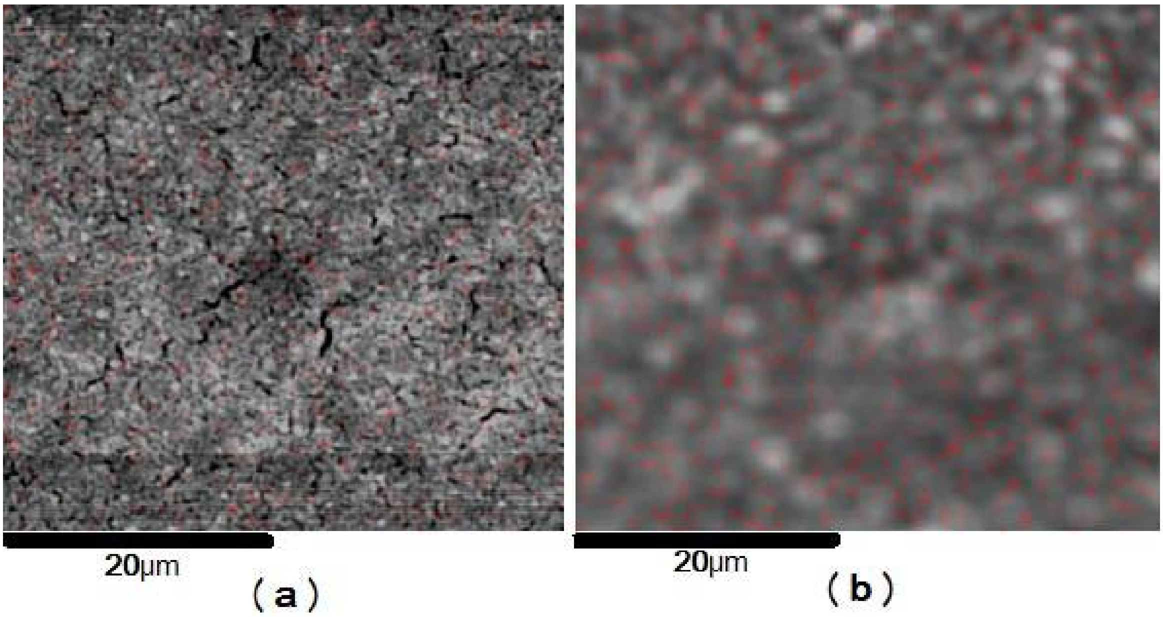

Figure 7. EDX images with 5000 magnification, dispersion of Si element (clay) in sample A-2 (a) and sample B-2 (b).

These images confirmed that our method was applicable for polymerization of STY-BA in aqua medium systems. TEM images for sample A-2 proved that hexagonal shape of the polymer particles in Figure 6-b was due to the presence of the clay layers at the surface of particles (Figures 8-a, 8-b).

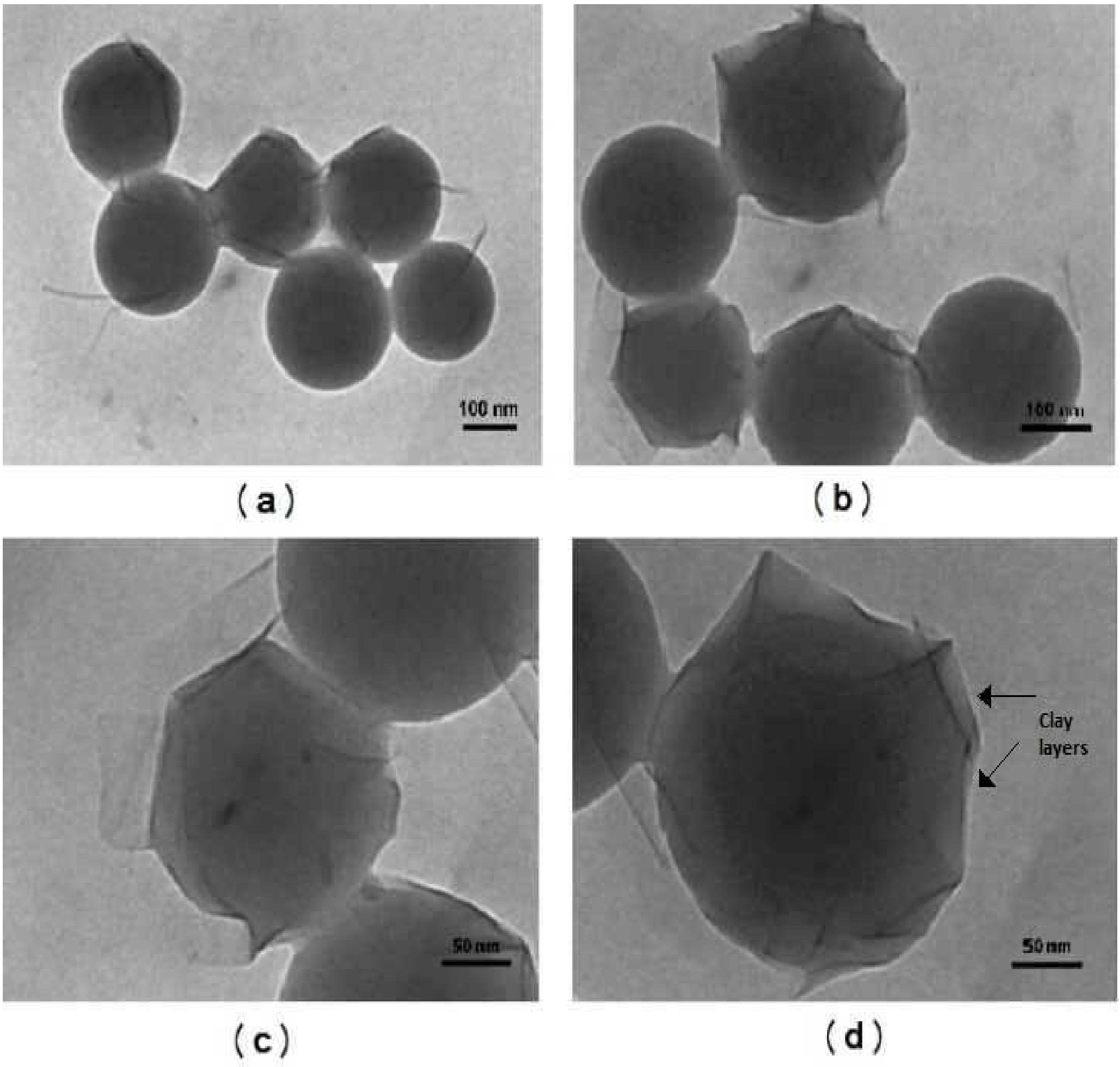

Figure 8. TEM images of sample A-2 containing 6wt% clay and KPS as initiator; scale bar 100 nm (a and b) and 50 nm (c and d).

As it was seen in these Figures, clay layers were exfoliated and located on the surface of polymer particles (Figures 8-c and 8-d). TEM images showed some of particles had not clay particles on their surfaces, maybe these particles were made by homogenous nucleation while other particles with more population were formed by Pickering emulsion. Our TEM images were compared with what Bonnefond et al. had presented [43], as they have noted Cloisite Na$^+$ alone, couldn't stabilize their system. They believed polymerization reaction proceed by homogeneous nucleation and Cloisite Na$^+$ hadn't appropriate affinity faced to the surface of the polymer particles and hence, instead of standing at the interface of polymer particles, were dispersed in aqua phase, but when Sipomer PAM100 was added by them, the wettability of the clay with the polymer mixture was improved and Pickering morphology was observed [43]. Results of the other researchers were also similar to Bon's work as they declared pristine Cloisite was not quite adequate for this kind of polymerization while reactions including modified clay have a better impression [39, 41].

XRD analysis

XRD pattern for A-4 sample (containing 6 wt% nanoclay and was synthesized with KPS initiator) showed that full exfoliation of clay layers was happened (Figure 9-a), since main peak of Cloisite Na^+ (at 2θ = 7.8, d is d = 1.17 nm in Figure 9-c) has disappeared completely and also there were no peak in areas smaller than this 2θ, which proved full exfoliation of clay platelets, but when AIBN was applied as initiator (B-4), exfoliation of clay layers did not observe (Figure 9-b) and the resulting nanocomposites had only intercalated structure (at 2θ = 5.51 and d = 1.61 nm).

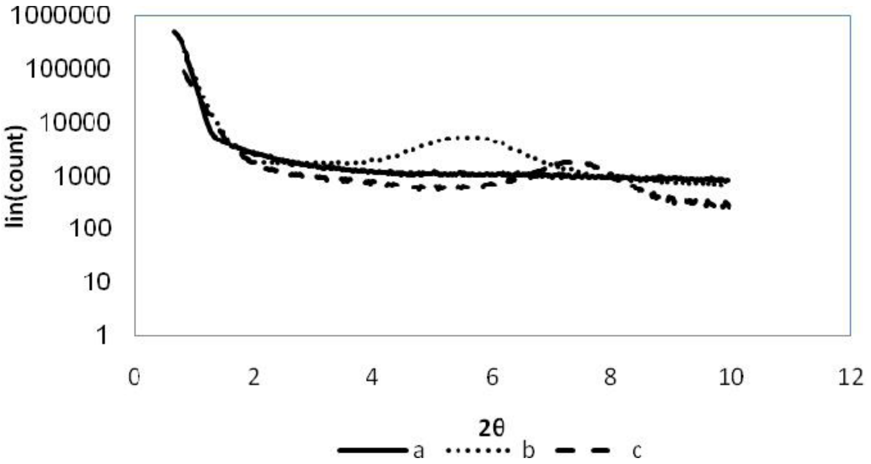

Figure 9. XRD pattern for: a) nanocomposite of A-2 sample (6%wt clay respect to monomer and synthesized with KPS), b) nano composite of B-2 sample (6%wt clay respect to monomer and synthesized with AIBN) and c) crude Na MMT.

Based on these results and TEM images can concluded that polymer synthesis in the presence of ionic initiator leads to the formation of polymer particles which their surfaces are more hydrophilic and has better compatibility with the hydrophilic surface of Cloisite Na^+ particles. This good affinity between surfaces caused more exfoliation of clay layers in comparison to polymer synthesis through other initiators such as AIBN.

Effect of clay on Tg

Tg measurements for all recipes was reported in Table 4 as calculated Tg (based on Fox equation) and experimental Tg based on DSC measurements as follows:

$$\frac{1}{Tg} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2} \qquad (1)$$

It was obvious that Tg, greatly increased by increasing nanoclay amounts. In other words, Tg for the samples containing clay (A-2, A-4, A-5 and A-6) were more than of corresponding neat copolymers (A-1 and A-3). This is attributed to the homogeneous dispersion of Cloisite Na^+ within the polymer matrix hence the polymer chains trapped between the clay layers and their mobility is restricted.

Table 4. Calculated Tg and experimental Tg for sample A-1 to A-6.

Sample Code	Calculated Tg from Fox Equation (°C)	Experimental Tg from DSC (midpoint) (°C)
A-1	25.00	25.40
A-2	25.00	44.00
A-3	-5.00	5.50
A-4	-5.00	16.70
A-5	-5.00	16.50
A-6	-5.00	17.20

SEM Investigation

SEM images were collected in Figure 10 (one droplet of diluted latex was dried at room temperature on the sample holder). Due to their high Tg, process of film formation for samples A-1 and A-2 were so weak at room temperature (Figures 10-a, 10-b). Therefore more butyl acrylate respect to styrene was used in next recipes for reducing the latex's Tg and therefore film's Tg. Then we observed that the film formation processed much more rapidly. This was confirmed through SEM images of samples A-3 to A-6, as indicated in Figures 10 (c, d, e and f), particles interfused together and formed a continues film without any crack or cavities. It was proved again that one of the main parameters for film formation is Tg and Cloisite layers at the surface of particles couldn't restrict it's film formation process while Tg was very low [50].

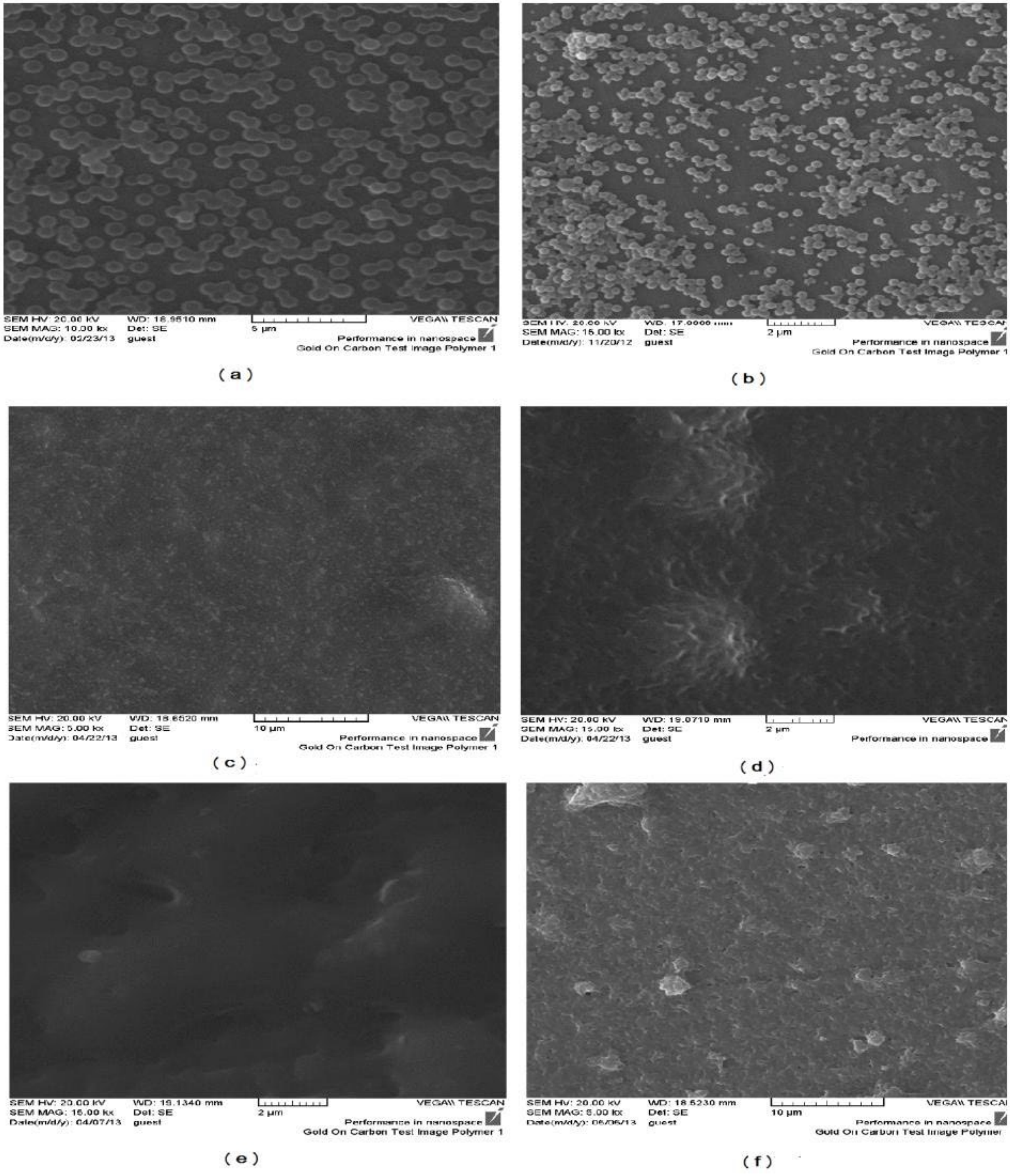

Figure 10. SEM images of all samples.

Conclusions

In this study, armored latex nanoparticles were prepared by Pickering emulsion polymerization wherein Cloisite Na+ played the essential role of surfactant. When AIBN was used as initiator, particle size reduced and polymerization rate increased by increasing the clay loading. It was concluded only Pickering emulsion was the dominant mechanism of nucleation in this recipe. When KPS was used with enhanced amount of clay, particle sizes increased and rate of polymerization reduced. Nice dispersion of exfoliated clay layers within polymer matrix was confirmed by SEM and EDX for latexes synthesized by Pickering emulsion polymerization. Presence of the clay layers on the surface of polymer nanoparticles was proved mostly by TEM images and exfoliation of layers were confirmed by XRD technique. Film formation was improved by reducing the Tg of latex through applying more butyl acrylate. This type of hybrid polymer nanoparticles represent outstanding potential for packaging films with better mechanical, thermal and especially barrier properties which will be presented in our next paper.

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