

# Synthesis of exfoliated acrylonitrile–butadiene–styrene copolymer (ABS) clay nanocomposites: role of clay as a colloidal stabilizer

Yeong Suk Choi<sup>a</sup>, Mingzhe Xu<sup>b</sup>, In Jae Chung<sup>b,\*</sup>

<sup>a</sup>Fuel-Cell Program Team, SAIT (Samsung Advanced Institute of Technology), Mt. 14-1, Nonseo-Ri, Giheung-Eup, Yongin-Si, Gyeonggi-do, South Korea

<sup>b</sup>Department of Chemical and Biomolecular Engineering, KAIST (Korea Advanced Institute of Science and Technology), 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea

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## Abstract

Acrylonitrile–butadiene–styrene copolymer (ABS) clay nanocomposites were synthesized using two clays (sodium montmorillonite, laponite). Both colloidal stability and mechanical properties of the nanocomposites were dependant on aspect ratios of clays. Laponite, a low aspect ratio clay, reduced particle sizes of ABS clay nanocomposite latexes, enhanced colloidal stabilities, and increased viscosity of the latexes. The colloidal stability of ABS clay latexes may result from four factors. Firstly, the electrostatic repulsion forces originated from surface charges of clays and anionic surfactant contribute to colloidal stability. Secondly, laponite layers separate sodium montmorillonite layers and polybutadiene latex particles preventing the coagulation. Thirdly, the laponite layers adsorbed on latexes act like steric barriers against coagulation. Fourthly, increased viscosity reduces latex mobility, lowering collision possibility among latex particles. Resultant ABS clay nanocomposites showed exfoliated structures, and their mechanical properties related to the relative weight ratio of sodium montmorillonite to laponite: as portions of sodium montmorillonite increased, dynamic moduli of the nanocomposites increased, because sodium montmorillonite has higher aspect (length/thickness) ratio than laponite.

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**Keywords:** Nanocomposites; Laponite; Sodium montmorillonite (Na-MMT)

## 1. Introduction

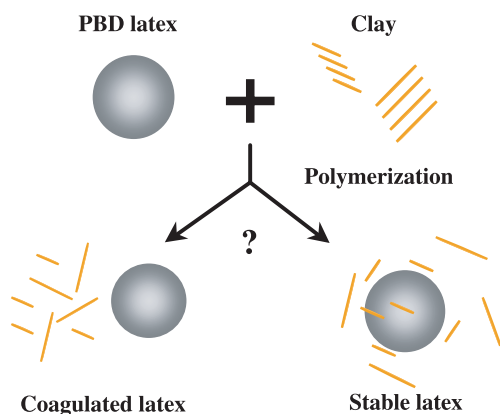
Solid particles such as silica, clay, carbon, hydroxides, metal oxides, basic salts of metals, colloidal silver, solid organic materials had been used for stabilizing emulsion droplets in oil-in-water (O/W) or water-in-oil (W/O) systems since early 1900s [1–21]. Stabilizing emulsion droplets by solid particles involves several mechanisms. Solid particles stabilize emulsion droplets by creating barriers around dispersed droplets, which keep the droplets from cohering [5,12], and they also build up three-dimensional network in aqueous phase. The emulsion droplets confined in three-dimensional network reduce their mobility [18,20]. Ionic surfactants are commonly used as stabilizers for preventing emulsion droplets from

coagulation via electrostatic repulsion between colloidal particles, while block copolymers or nonionic surfactants also act as a stabilizer by steric repulsion after being adsorbed on oil droplets. Most articles on emulsion polymerizations consider electrostatic stabilization, steric stabilization, and electrosteric stabilization by ionic stabilizers, block copolymers, and poly(acrylic) acid [22–29,34].

Acrylonitrile–butadiene–styrene copolymer (ABS) is a well-known commercial thermoplastic polymer for excellent mechanical properties [30,31]. In spite of industrial significance, ABS clay nanocomposite has not been intensively researched except few articles. Lee and co-workers reported that intercalated ABS sodium montmorillonite nanocomposites were developed with emulsion polymerization [32]. Wang et al. prepared intercalated–exfoliated structure of nanoABS by melt blending ABS and an organically modified clay [33].

If clay layers are added to polybutadiene (PBD) latex as shown in [Scheme 1](#), will flimsy clay layers make latex

\* Corresponding author. Tel.: +82 42 869 3916; fax: +82 42 869 3910.  
E-mail address: [chung@kaist.ac.kr](mailto:chung@kaist.ac.kr) (I.J. Chung).



Scheme 1. A schematic representation of possible colloidal states of ABS latexes after polymerization.

particles dispersed or coagulated after polymerizations? Usually clay layers will deter colloidal stability of the latex, but, when clay layers have surface charge, they may stabilize the latex. ABS clay nanocomposite latex will be a good example for the question. This article elucidates the role of clay on stabilizing ABS latex in emulsion polymerization. Two variables were adopted for the polymerization of ABS clay nanocomposites: (1) surfactant weight was varied at a fixed total weight percentage and ratio of clays during emulsion polymerizations, (2) sodium montmorillonite/laponite ratio in mixed clays was changed under a fixed surfactant weight during polymerizations. Colloidal properties of ABS clay nanocomposites such as particle sizes, viscosity, and colloidal stability in salt solution were examined and compared with neat ABS latex. Structures and mechanical properties of synthesized ABS clay nanocomposites were also investigated.

## 2. Experimental

### 2.1. Materials

The clays were sodium montmorillonite (Na-MMT,

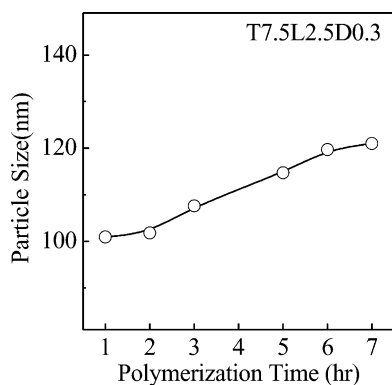


Fig. 1. Particle size evolution of an ABS clay nanocomposite latex (7.5L2.5D0.3) with respect to polymerization time.

Kunipia-F) from Kunimine Co. and laponite (a synthetic clay, Laponite RDS) from Southern clay Co. Na-MMT and laponite have cation exchange capacities (CEC) of 119 and 73 meq/100 g, respectively. Primary particle sizes of Na-MMT and laponite are about 50–500 and 20–30 nm. Acrylonitrile (AN), cumene hydroperoxide (initiator), styrene (S), 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), dodecylbenzenesulfonic acid, sodium salt (DBS-Na) were purchased from Aldrich and used without further purification. PBD latex (40 wt% in water, average particle size is about 100 nm) was kindly supplied by LG chemistry Co. The clays were dispersed in deionized water with ratios of 5 g/145 g (Na-MMT/water) and 2 g/145 g (laponite/ water) for 24 h at ambient temperature before polymerization. DBS-Na was selected for the surfactant because of its well-known structure and molecular weight compared with rosin soap.

### 2.2. Polymerization of ABS clay nanocomposites

Aqueous clay dispersion (variable), AMPS (0.3 g), AN (3 g), cumene hydroperoxide (0.05 g) dissolved in AN (0.5 g), deionized water (120 g) were added into a 1-L four-neck reactor equipped with a baffle stirrer, a reflux condenser, a nitrogen inlet, a rubber septum. DBS-Na (variable) and PBD latex (10.6 g) were successively injected into the reactor through the rubber septum by using a glass syringe. The mixture was stirred at 200 rpm for 1 h under nitrogen atmosphere at room temperature. Initial polymerization was performed at 85 °C for 1 h, and then 12.75 g of mixed monomers (S/AN = 60 g/30 g) was fed at a rate of 0.16 cc/min into the reactor through the rubber septum by using a syringe pump. After monomer feeding was completed, the polymerization temperature was increased to 95 °C, and maintained for 3 h for further polymerization. The sample was recovered from the reactor and dried with a freeze-dryer for 6 days and further dried under a high vacuum oven at 50 °C for 3 days.

### 2.3. Characterization

Characterizations using wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMA) for dried ABS clay nanocomposites were carried out with the same methods described in the other paper [36]. Average particle size (< 500 nm) of latex was estimated by using a dynamic light scattering (DLS) (Zeta plus, Brookhaven), with the constant scattering angle of 90° at room temperature, after ABS latex was diluted with de-ionized water. Large particle size (> 500 nm) was determined with a centrifuge particle size analyzer (CPSA). Average particle size and elemental compositions of latex were determined by a TEM (TECNI F-20) and an online energy dispersive X-ray system (EDAX PV-9900). A sample for TEM analysis was prepared by diluting ABS clay

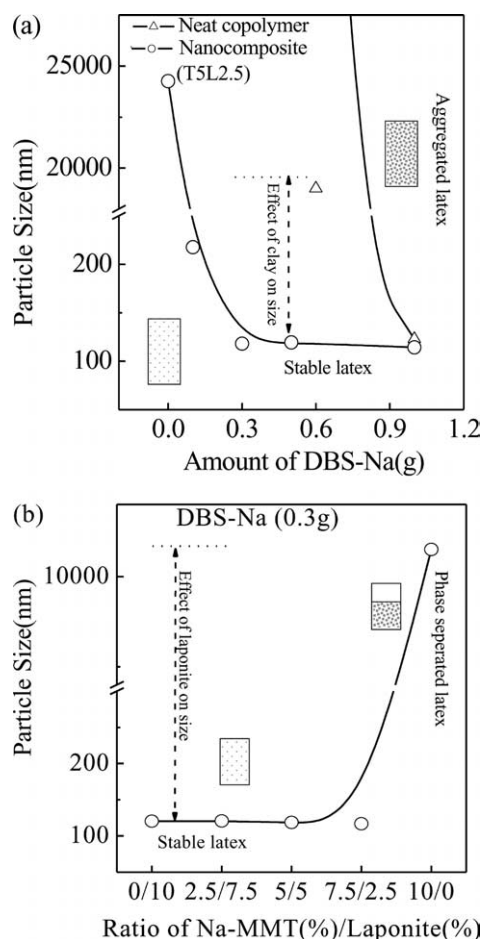


Fig. 2. Particle sizes of ABS clay nanocomposite latexes synthesized (a) with different DBS-Na weights, (b) with different ratios of Na-MMT to laponite in 10 wt% of mixed clays.

nanocomposite latex with deionized water, following the addition of ammonium acetate (1 ml, 3 wt%) and PVOH (1 ml, 3 wt%) aqueous solutions. The sample was sonicated for 30 min to obtain homogeneous dispersion, and then a

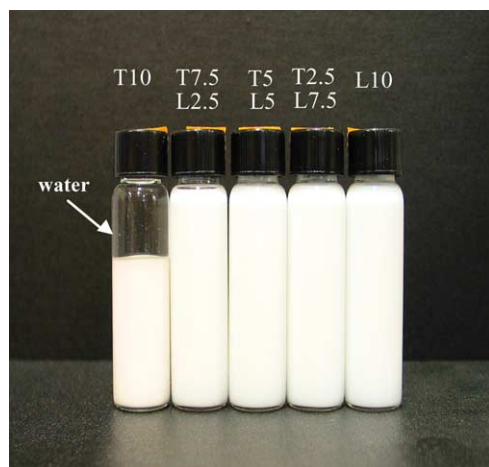


Fig. 3. Quiescent state photographs of ABS clay nanocomposite latexes synthesized with different ratios of Na-MMT to laponite in 10 wt% of mixed clays left for 4 months after polymerization.

drop of the sample was deposited on a carbon coated copper grid and blotted up by a filter paper to form a thin deposition and evaporated the water slowly. Viscosity of latex was measured on a Rheometric Scientific ARES rheometer equipped with a cone-and-plate geometry (cone radius and angle = 5 cm and 0.04°) at 25 °C.

### 3. Results and discussion

Fig. 1 shows particle size evolution of ABS clay nanocomposite latex with respect to polymerization time. The sample code T7.5L2.5D0.3 indicates the total clay (Na-MMT + laponite) of 10 wt%, Na-MMT of 7.5 wt%, laponite of 2.5 wt%, and DBS-Na of 0.3 g. As polymerization time elapsed, the particle size of the nanocomposite latex increased slowly until 2 h, and then reached rapidly about 120 nm.

Fig. 2(a) shows particle sizes of ABS latexes synthesized with various surfactant (DBS-Na) weights. Neat ABS latex polymerized without DBS-Na aggregated and became a lump of polymer soon after polymerization initiated. But the latex size decreased exponentially with DBS-Na added. Whereas ABS clay nanocomposite latex (T5L2.5D0) showed big particles visible in naked eyes, and the latex particle size decreased as DBS-Na content increased. Above 0.3 g of DBS-Na, the particle size was reduced to about 120 nm and the colloidal dispersion becomes stable. Particle size distribution of the nanocomposite latex was about 0.09–0.1, which is similar with neat ABS latex synthesized with 1 g of DBS-Na. Fig. 2(a) reveals that the clays (Na-MMT, laponite) as well as DBS-Na serve as a colloidal stabilizer, which prevents ABS latex from coagulation. Fig. 2(b) shows clay aspect ratio effect on ABS nanocomposite latex size. To avoid surfactant or mixed clay effect on the latex particle size, the DBS-Na weight and the total clay weight ratio to monomer in nanocomposites were fixed at 0.3 g and 10 wt%, respectively. Nanocomposite latexes containing laponite above 2.5 wt% in the 10 wt% clay showed about 120 nm in particle sizes, but T10L0D0.3, a latex synthesized with only Na-MMT, showed a particle size larger than 10,000 nm. The particle size data illustrate that laponite is more efficient than Na-MMT for stabilizing ABS clay nanocomposite latex. It may result from small layer size (<30 nm) or low aspect ratio of laponite. Furthermore, decreasing particle sizes by small amount laponite indicates that laponite layers separate Na-MMT and PBD particles, preventing the coagulation of them.

Fig. 3 shows photographs of ABS clay nanocomposite latexes left for 4 months after polymerization. The nanocomposite latexes synthesized with mixed clay (Na-MMT/laponite) exhibited no precipitation of particles and stable states, but the nanocomposite latex synthesized with only Na-MMT settled to the bottom of a vial and showed separated phases due to its big particle size. These

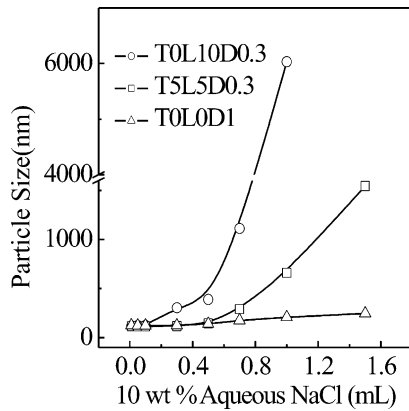


Fig. 4. Effect of NaCl addition upon the particle sizes of ABS latexes.

photographs explain that laponite improves the dispersion stability of ABS clay nanocomposite latexes.

The colloidal stability of latex is strongly affected by addition of salt, if latex particles are dispersed by electrostatic repulsion force. Fig. 4 shows the aggregation tendency of latexes with addition of aqueous NaCl solution

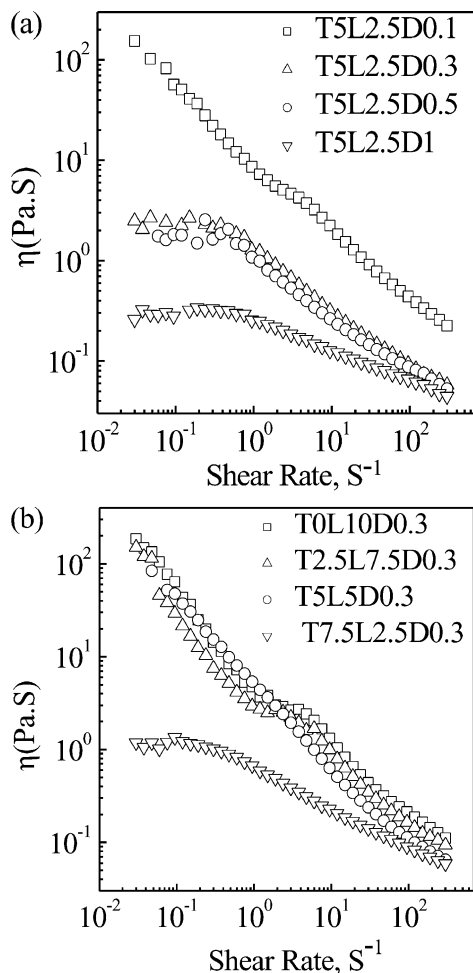


Fig. 5. Shear viscosities,  $\eta(\dot{\gamma})$ , of ABS clay nanocomposite latexes synthesized (a) with different DBS-Na weights, (b) with different ratios of Na-MMT to laponite in 10 wt% of mixed clays.

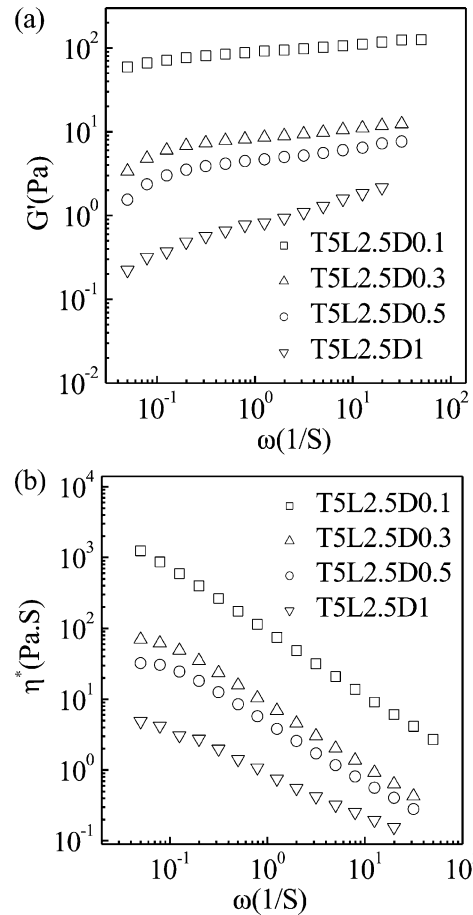


Fig. 6. (a) Storage moduli  $G'$  and (b) viscosities  $\eta^*$  of ABS clay nanocomposite latexes (T5L2.5 series) synthesized with different DBS-Na weights.

(10 wt%). As the NaCl solution was added, all latexes showed increases in particle sizes, indicating the latex coagulation by NaCl. The particle size result reveals that the ABS clay nanocomposite latexes are stabilized by electrostatic repulsion between particles [28,29,35]. The coagulation is affected very sensitively by laponite content. It is recognized that ABS clay nanocomposites can be easily recovered from the latexes by adding salt.

Fig. 5(a) shows viscosities of ABS clay nanocomposite latexes (T5L2.5 series) synthesized with various DBS-Na contents. The latexes except T5L2.5D0.1 exhibited a Newtonian behavior in a low shear rate region but the shear-thinning behavior above a moderate shear rate region. These latexes have nearly the same particle size, 120 nm, so the Newtonian behavior is related to the small particle size. The particle size became small as confirmed in Fig. 2(a), when the large amount of DBS-Na was added. Fig. 5(b) shows viscosities of ABS clay nanocomposite latexes synthesized with different ratios of Na-MMT to laponite. T7.5L2.5D0.3 (low portion of laponite) showed a Newtonian behavior in a low shear rate region, but the others showed shear thinning behaviors, although all the latexes had the same particle sizes as shown in Fig. 2(b). In a high

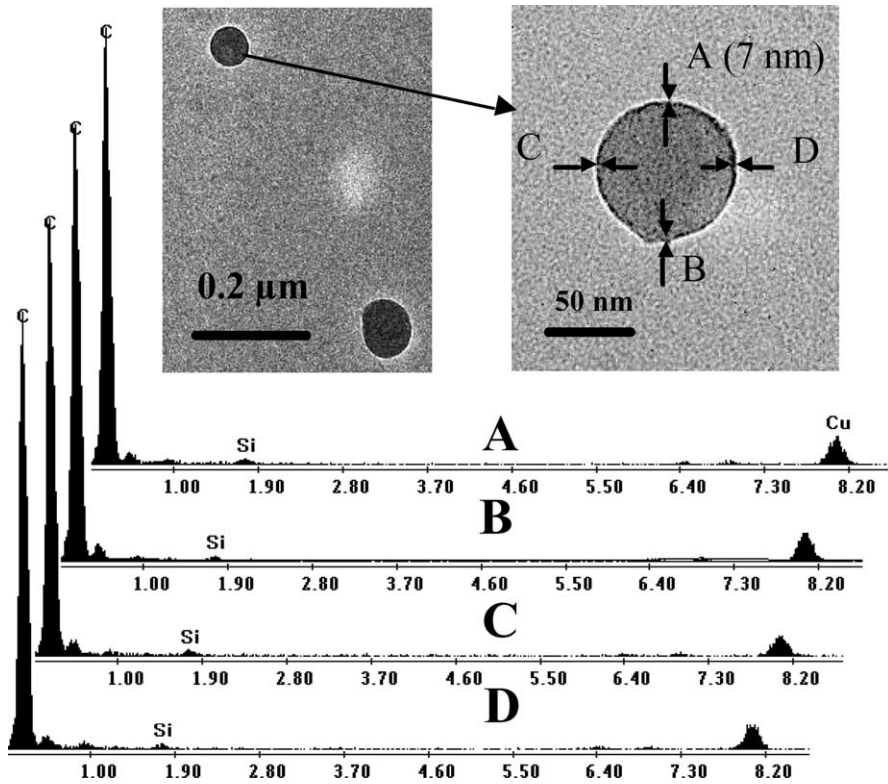


Fig. 7. Transmission electron microscopy of an ABS clay nanocomposite latex (TOL10D0.3) and EDAX spectra depicting elemental compositions of the edge areas.

shear rate region, latex viscosity increased proportionally with laponite content. Since the number of laponite layers is much higher than Na-MMT in unit volume, laponite may increase the viscosity like a thickener.

The storage modulus of the latex increased as the content of DBS-Na decreased in Fig. 6(a). T5L2.5D0.1 with 0.1 g of DBS-Na shows a non-terminal behavior at a low shear rate. It had the largest particle size as shown in Fig. 2(a) and acted

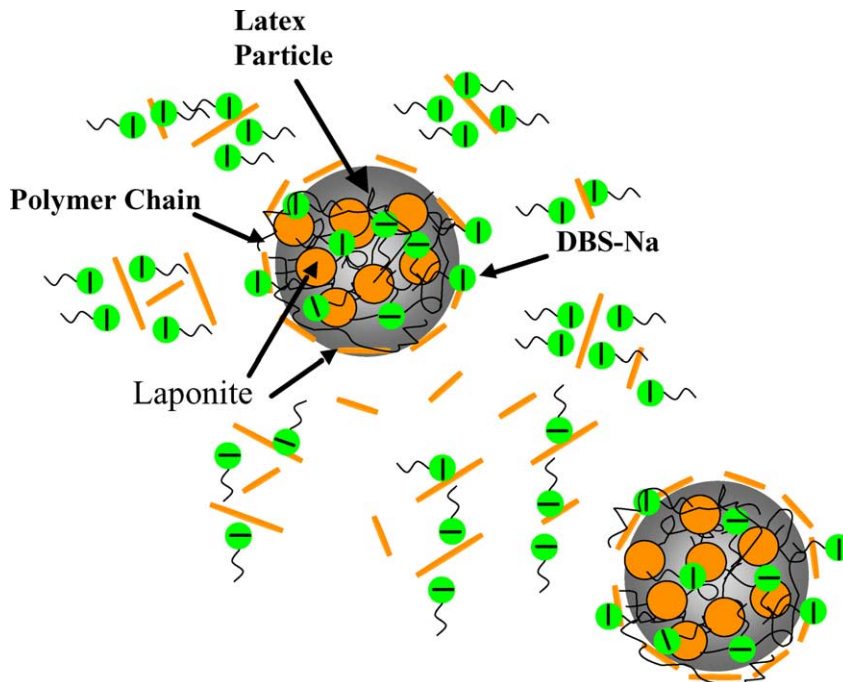


Fig. 8. A schematic representation for the colloidal stability of an ABS clay nanocomposite synthesized with mixed clays (Na-MMT/laponite).

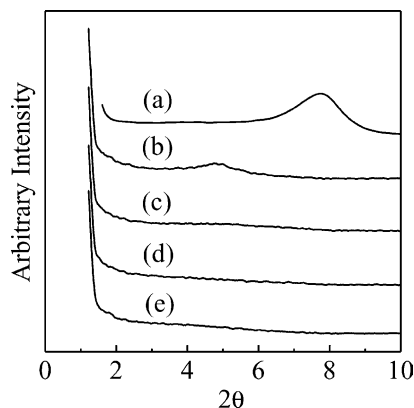


Fig. 9. X-ray diffraction patterns of ABS clay nanocomposites synthesized with different ratios of Na-MMT to laponite: (a) pristine Na-MMT, (b) T7.5L2.5D0.3, (c) T5L5D0.3, (d) T2.5L7.5D0.3 and (e) T0L10D0.3.

like a solid in the low shear rate region. The complex viscosity of the latexes decreased, as the DBS-Na content decreased in Fig. 6(b). Fig. 6 illustrates that DBS-Na acts like a lubricant for the ABS clay nanocomposite latexes.

PBD latex is a cross-linked rubber and it is very hydrophobic, but natural clays are hydrophilic. We expect that laponite or Na-MMT layers will not penetrate into PBD interior space. The particle sizes and elemental compositions of a ABS clay nanocomposite latex (T0L10D0.3) were examined using a TEM and an EDAX detector as given in Fig. 7. Four different areas of  $7\text{ nm} \times 7\text{ nm}$  (A, B, C and D) of the particle were selected, and the compositions were analyzed by using an EDAX detector. Cu peaks (8.1 keV) are from the copper TEM grid and C (about 0.2 keV) is from the ABS copolymer and the carbon black coated on the copper grid. The data from EDAX exhibit Si peaks, which indicate the adsorption of laponite layers on the latex surface. Na-MMT layers will have difficulty to be adsorbed on the PBD latex surface due to its stiffness and large layer width. For a ABS clay nanocomposite latex with only Na-MMT, Na-MMT layers seem to attract PBD latex and make big particles. Whereas, the laponite layers adsorbed on the

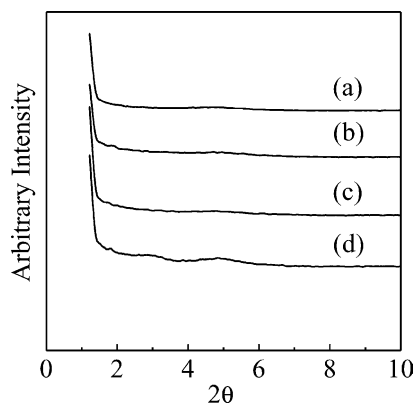


Fig. 10. X-ray diffraction patterns of ABS clay nanocomposites synthesized with different DBS-Na weights: (a) T5L2.5D0.1, (b) T5L2.5D0.3, (c) T5L2.5D0.5 and (d) T5L2.5D1.

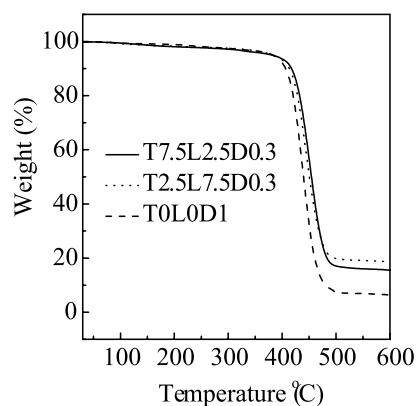


Fig. 11. Thermogravimetric analysis curves for ABS clay nanocomposites and neat ABS under a nitrogen atmosphere.

PBD latex work as a steric stabilizer and the laponite layers in aqueous phase separate Na-MMT layers from PBD latex.

From the above results and discussion, the ABS clay nanocomposite latexes obtain the colloidal stability via several mechanisms. Firstly, electrostatic forces from the clay layers and DBS-Na repulse ABS clay nanocomposite latex particles. Secondly, laponite layers separate Na-MMT layers and PBD particles preventing the coagulation. Thirdly, the laponite layers are believed to provide a steric barrier to latex particles. Fourthly, laponite, which has a large surface volume and a low aspect ratio, enhanced the viscosity of the latex as a thickener, so laponite reduces the mobility of latex particles and the possibility of particle collision. Fig. 8 shows schematic diagram for proposed colloidal stability mechanism of ABS nanocomposite latex.

The structures of ABS clay nanocomposites in dried states were analyzed with WAXD patterns. Pristine Na-MMT has an interlayer  $d$ -spacing of 1.14 nm in dry state. The  $d$ -spacing was obtained from the peak position ( $d_{001}$ -reflection) of WAXD traces by using Bragg equation:  $2d_{001} \sin \theta = \lambda$ , where  $d_{001}$  is the interplanar distance of (001) reflection plane,  $\theta$  is the diffraction angle, and  $\lambda$  is the wavelength. The thin film WAXD patterns of ABS nanocomposites synthesized with different ratios of Na-MMT to laponite are shown in Fig. 9. Actually laponite shows no peaks on WAXD pattern. Below 5 wt% of Na-MMT, a nanocomposite shows an exfoliated morphology. In the case of 7.5 wt% of Na-MMT, it shows an intercalated structure. Fig. 10 shows a series of thin film WAXD patterns obtained from nanocomposites with different DBS-Na contents. As DBS-Na increased in ABS latex, the nanocomposite showed an intercalated structure. Excessive DBS-Na may form additional micelles outside PBD particles, and the free micelles will competitively consume monomer with clay-surrounded ABS latexes or clay particles enveloped by DBS-Na. Then, the clay-surrounded ABS latexes will not have enough monomer to exfoliate clay layers.

TGA of ABS clay nanocomposites is shown in Fig. 11. The onset temperatures of thermal decomposition of

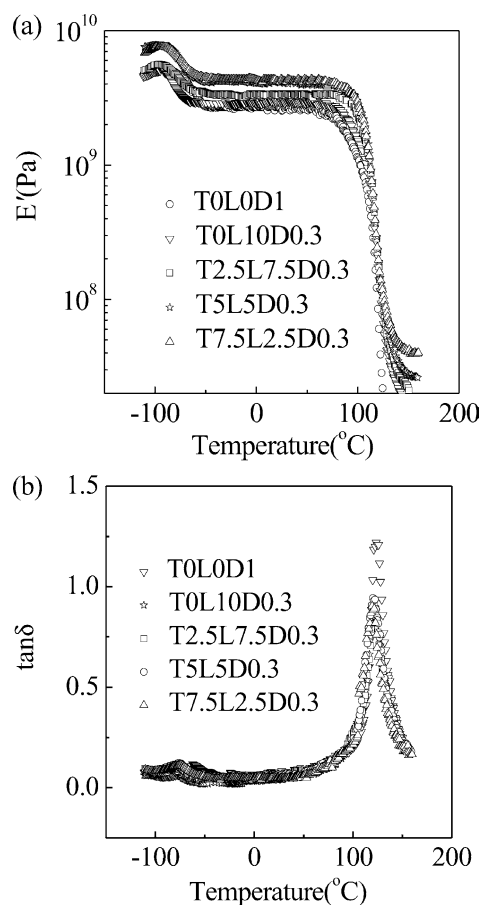


Fig. 12. Temperature dependence of (a) the storage Young's moduli  $E'$  and (b)  $\tan \delta$  for ABS clay nanocomposites and neat ABS.

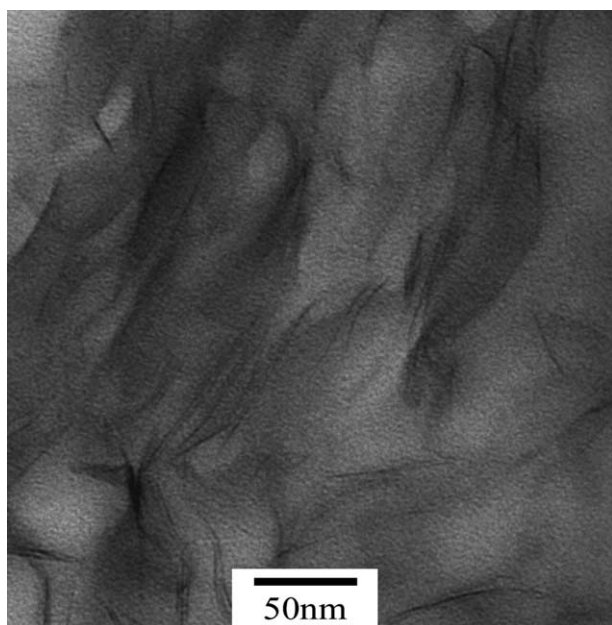


Fig. 13. Transmission electron microscopy of an ABS clay nanocomposite.

nanocomposites moved toward a higher temperature compared with neat ABS. The neat ABS showed 20% weight loss at 420 °C, but ABS clay nanocomposites decomposed at 13 °C higher temperature. This may result from the thermal barrier property of clay platelets in the ABS copolymer matrix.

Fig. 12 shows storage moduli,  $E'$ , and  $\tan \delta$  of samples including neat ABS. ABS nanocomposites (T0L10D0.3, T2.5L7.5D0.3, T5L5D0.3, T7.5L2.5D0.3) showed 9.3, 22.7, 57, and 60.8% enhancements of moduli over neat ABS (T0L0D1) at 40 °C. Interestingly, at a fixed weight of mixed clays to monomer, the storage modulus of nanocomposite increased with the content of Na-MMT. It is believed that, due to the high aspect ratio of Na-MMT, Na-MMT has a more pronounced effect on storage modulus than laponite. ABS clay nanocomposites had double glass transition temperatures ( $T_g$ ) at  $-80$  °C (PBD) and at 121 °C (styrene and acrylonitrile), which were obtained from the maximum peak temperatures of  $\tan \delta$  in Fig. 12(b).

Fig. 13 shows TEM micrograph of T5L0D0.5 nanocomposite. The dark lines in the figure correspond to the silicate layers. The clay layers were exfoliated in ABS matrix and large silicate particles (clay tactoids) were absent.

#### 4. Conclusions

From the above results, it can be summarized that clay works as a colloidal stabilizer due to several factors during ABS emulsion polymerization. Firstly, electrostatic repulsion force between ABS clay nanocomposite latex particles may contribute to stabilize the latex, because clays and DBS-Na have negative surface charges. Secondly, laponite layers separate Na-MMT layers and PBD particles, preventing the coagulation. Thirdly, the laponite layers adsorbed on latex particles may contribute to prevent latex from coagulating as a barrier. The clays are believed to provide a steric barrier against ABS latex coalescence so that it prevents coagulation of ABS latex particles. Fourthly, laponite layers, which have a large surface volume, increase the viscosity of latexes, reduce the mobility and the coagulation rate of the particles and contribute to stabilize the latex.

The ABS clay nanocomposite latexes consume less surfactant than neat ABS latex, and their production may need the small amount of surfactant. The storage moduli of ABS clay nanocomposites increase proportionally with Na-MMT content in the mixed clay (Na-MMT/laponite). It explains that a clay with high aspect ratio strongly enhances the mechanical properties of the nanocomposites.

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## References

- [1] Ramsden W. Proc R Soc London 1904;72:156.
- [2] Pickering SU. Emulsions. J Chem Soc 1907;91:2001.
- [3] Pickering SU. Über Latexen. Z Chem Ind Koll (Kolloid Z) 1910;7:11.
- [4] Briggs TR. Ind Eng Chem 1921;13:1008.
- [5] Finkle P, Draper HD, Hildebrand JH. J Am Chem Soc 1923;45:2780.
- [6] Schulman JH, Leja J. Trans Faraday Soc 1954;50:589.
- [7] Mukerjee LN, Srivastava SN. Kolloid Z 1956;147:146.
- [8] Mukerjee LN, Srivastava SN. Kolloid Z 1956;149:35.
- [9] Mukerjee LN, Srivastava SN. Kolloid Z 1957;150:144.
- [10] Mukerjee LN, Srivastava SN. Kolloid Z 1957;150:148.
- [11] Lucassen-Reynders EH, van den Tempel M. J Phys Chem 1963;67:731.
- [12] Levine S, Sanford E. Can J Chem Eng 1985;58:622.
- [13] Menon VB, Wasan DT. Colloids Surf 1986;19:89.
- [14] Tambe DE, Sharma MM. J Colloid Interface Sci 1995;171:456.
- [15] Yan N, Masliyah JH. Colloids Surf A 1995;96:243.
- [16] Puskás S, Balázs J, Farkas A, Regdon I, Barkesi O, Dékány I. Colloids Surf A 1996;113:279.
- [17] Zhai X, Efrima S. J Phys Chem 1996;100:11019.
- [18] Abend S, Bonnke N, Gutschner U, Lagaly G. Colloid Polym Sci 1998;276:730.
- [19] Midmore BR. Colloids Surf A 1998;132:257.
- [20] Lagaly G, Reese M, Abend S. Appl Clay Sci 1999;14:83.
- [21] Binks BP. Curr Opin Colloid Interface Sci 2002;7:21.
- [22] Gilbert RG. Latex polymerization: a mechanistic approach. London: Academic; 1995.
- [23] Valint PL, Bock J. Macromolecules 1988;21:175.
- [24] Piirma I. Polymer surfactants. Surfactant science series 42. New York: Marcel Dekker Inc.; 1992 p. 127.
- [25] Astafieva I, Zhong XF, Eisenberg A. Macromolecules 1993;26:7339.
- [26] Müller H, Leube W, Klaus Tauer K, Förster S, Antonietti M. Macromolecules 1997;30:2288.
- [27] Kukula H, Schlaad H, Tauer K. Macromolecules 2002;35:2538.
- [28] Coen E, Lyons RA, Gilbert RG. Macromolecules 1996;29:5128.
- [29] Vorwerk L, Gilbert RG. Macromolecules 2000;33:6693.
- [30] Kulich DM, Kelly PD, Pace JE. Encyclopedia of polymer science and engineering. New York, NY: Wiley; 1985.
- [31] Rubin II. Handbook of plastic materials and technology. New York: Wiley; 1990.
- [32] Jang LW, Chul MK, Lee DC. J Polym Sci Part B Polym Phys 2000;39:719.
- [33] Wang SF, Hu Y, Song L, Wang ZZ, Chen ZY, Fan WC. Polym Degrad Stab 2002;77:423.
- [34] Capek I. Adv Colloid Interface Sci 2002;99:77.
- [35] Lagaly G, Ziesmer S. Adv Colloid Interface Sci 2003;100–102:105.
- [36] Choi YS, Wang KH, Xu M, Chung IJ. Chem Mater 2002;14:2936.