



Characterization of styrene-co-butyl acrylate/Cloisite Na⁺ nanocomposite film synthesized via soap free emulsion polymerization



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ABSTRACT

The formation of stable armored styrene-co-butyl acrylate/Cloisite Na⁺ latex particles up to 250 nm which was synthesized by soap free emulsion polymerization method and thereafter, characterization of derived nanocomposite films was studied by many analysis such as transmission electron microscopy, low angle X-ray diffraction, Oxygen Transmission Rate (OTR), water vapor transmission rate (WVTR), water uptake and contact angle. The results of this research work revealed exfoliated nanoclay structure for the samples containing 6 and 8 wt% Cloisite Na⁺ and intercalated nanoclay structure for sample containing 10 wt% Cloisite Na⁺. The barrier properties of these clear films processed from aforementioned latexes was according to the well dispersion of clay layers within the nanocomposite matrix. Drastic reduction of OTR and WVTR were observed by increasing the clay loading up to 10 wt%. The increase in tensile strength and Young's modulus of nanocomposite films showed high effects of nanoclay on the film mechanical properties, mainly due to the presence of the delaminated clay layers regularly all within the styrene-co-butyl acrylate/Cloisite Na⁺ matrix. However, the contact angle values for the crude copolymer film (styrene-co-butyl acrylate film) and its' nanocomposites film (styrene-co-butyl acrylate/Cloisite Na⁺ film) did not show any distinguished changes and were almost equal in value.

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1. Introduction

In recent decades, synthesis of polymeric nanocomposites has attracted researchers all around the world. One favorable procedure for making nanocomposites is based on in-situ heterophase polymerization (emulsion, miniemulsion, suspension and dispersion) in which various amounts of surface active agents are used. The surface active agents or surfactants usually remain in fabricated product and may affect the final properties of the nanocomposites, adversely. One effective route in emulsion polymerization in which no surface active agent is used was introduced as Pickering emulsion polymerization. Pickering is a type of emulsion system in which solid particles play the role of low molecular weight surfactants in addition to their reinforcing effects on product final properties. This Pickering emulsion polymerization was first introduced by Ramsden in 1903 [1] and Pickering in 1907 [2]. In 1959, Wiley and coworkers reported Pickering suspension polymerization by using bentonite as a Pickering surfactant in suspension

polymerization of styrene-divinyl benzene [3,4]. Recently, many studies have been reported using different types of particles as solid surfactant including nanoclay, silica, titania, cerium oxide and zinc oxide [5–11].

In addition to nanoclay's ability for improving the thermal stability and mechanical properties of nanocomposites, they can lower the gas permeability and flammability of the final nanocomposite films, effectively [12–15]. Herrea et al. grafted mono and trifunctional silane on the surface of Laponite to modify its surface which was efficient for stabilizing the emulsion polymerization of styrene-butyl acrylate. They demonstrated those particles which were modified only by trifunctional silane, adhered together and therefore, were not appropriate for this kind of Pickering synthesis, while other particles which were modified by monofunctional silane were located very well at the surface of polymer particles [16]. Cauvin and coworkers applied laponite RD as a stabilizer in Pickering miniemulsion polymerization of styrene and synthesized armored latex particles with average particle size of about 145 nm [17]. Voorn and coworkers used Cloisite 20A in inverse Pickering emulsion copolymerization of acryl amide and 2-hydroxy ethyl methacrylate in cyclohexane. Hybrid latexes in a size range between 700 and 980 nm were obtained by using water-soluble

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(VA-086) and oil-soluble initiators (AIBN) [18]. Wang and coworkers prepared polymer nanoparticles showing armored structure of Laponite which were prepared by Pickering miniemulsion polymerization of *n*-lauryl acrylate. Also they observed by addition of small amounts of the “soft-hard” clay-armored PLA particles into the butyl acrylate-co-acrylic acid latex, increased tack adhesion energy was received which is an essential factor for production of waterborne pressure-sensitive adhesive [19].

Ianchis et al. investigated the influence of clay modification (which obtained through grafting of different mono functional alkoxysilanes) on the stability and morphology of styrene/acrylate nanoparticles that were synthesized by surfactant-free emulsion polymerization. They believed that in the presence of crude Cloisite, interaction between polymer particles and Cloisite platelets were so weak, therefore polymer particles kept their spherical shape and modified Cloisite were localized inside or outside of the polymer particles, regularly [20,21].

Zhang et al. managed to modify clay platelets by using poly [2-(dimethylamino)ethyl methacrylate] (PDMAEMA) brushes and then, employed these modified particles as a stabilizer in Pickering emulsion polymerization of methyl methacrylate. They revealed that these clay layers having PDMAEMA chains covered the PMMA polymer particles [22]. Bon et al. used Laponite as a sole stabilizer in Pickering miniemulsion polymerization of variety of hydrophobic monomers. They showed that the hydrophobicity of monomers is a crucial factor, as reactions performed on monomers with higher water solubility such as methyl acrylate were partially successful. Later they presented a new model for prediction of polymer particle sizes, too [23].

Dungen et al. described Pickering miniemulsion of styrene-co-butyl acrylate by using organically modified MMT through using cation exchange via sulfonic acid. They revealed these latexes were more stable compared to SDS stabilized latexes [24]. Later MMT clay layers were pre-modified via cationic amphiphilic block copolymer and were applied as a stabilizer in dispersion polymerization of styrene in ethanol/water medium by Greesh and coworkers. As they proved the formation of armored polymeric structures, declared this kind of materials should act as super-heat barrier materials, because of increased overall thermal stability of polymer in nanocomposite matrix [25].

Teixeira et al. by employing Laponite, prepared armored soft polymer latexes and asserted that the use of hydrophilic monomers should be restricted. The affinity between hydrophobic monomers and clay were improved by using small amounts of methacrylic acid (MAA) as an auxiliary comonomer [26]. Bonnefond and colleagues reported surfactant-free emulsion and miniemulsion polymerizations of styrene and butyl acrylate in presence of Na⁺ MMT which was modified via a macromonomer (Sipomer PAM100 as a stabilizer). They cited addition of Sipomer PAM100 into the latex containing clay, helped to make lower the water uptake and water vapor transition rates [27].

In our previous paper [28] we focused on the synthesis of aforementioned latex and proved that without using any surfactant or emulsifier our latex particles were stable for a long time. There we suggested that KPS molecules with dual actions (although it is an ionic initiator, but some part of it acts as surfactant or emulsifier) were responsible for stabilizing of the medium of polymerization in absence of clay. In presence of clay, KPS molecules not only have the above roles, but also work as an intercalant/chemical modifier of the clay surfaces (intercalant/chemical modifier of the clay surfaces is a material adsorbed between the clay platelets and binds with them to form an intercalated and/or exfoliated layered structure with individual clay platelets dispersed in the polymer matrix). Hence, in our opinion, KPS expanded the interlayer clay spacing and produced layered clay with improved interactions between the clay and the matrix. Finally these separated clay layers local-

ized mostly around monomer droplets and polymer particles and stabilized them very well.

By now, despite the extensive research works on the synthesis of armored latexes, a few papers have been published on the final properties and application of these latexes. In this study, the Cloisite Na⁺ (in presence of KPS) was examined as an exclusive and successful stabilizer in Pickering emulsion polymerization of styrene-co-butyl acrylate. Also the role of nanoclay loading in this in-situ Pickering emulsion was discussed based on the nanocomposites morphology/properties relationship. Then appropriate clear films were prepared showing mid-honeycomb like structure exhibited much better thermal, mechanical and barrier performances.

2. Experimental

2.1. Materials

Cloisite Na⁺ (Na⁺ MMT) was purchased from Southern Clay Product Inc. Monomers; styrene (STY) and *n*-butyl acrylate (BA) were obtained from Merck and Fluka companies, respectively. Styrene was used after removal the initiator by 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 kept on dried CaCl₂ at 0 °C prior to use, while butyl acrylate was used without washing. Potassium persulphate (KPS) was provided from Merck and was used as initiator without any purification. Sodium hydrogen carbonate (NaHCO₃) from Merck was used as a buffer. Twice distilled water with pH around 6–7 was prepared in our laboratory and used in all experiments.

2.2. Preparation of styrene-co-butyl acrylate armored latexes

Briefly, Cloisite Na⁺ (0.6 g) was magnetic stirred in distilled water (90 ml) for 72 h and then 0.1 g NaHCO₃ was added to this dispersion (pH of media was kept about 7.5) and further ultrasonication was done by the sonicator probe with a power of 80% amplitude for 5 min. Afterwards, mixture of monomers (totally about 10 g) containing *n*-butyl acrylate (5.57 g) and styrene (4.43 g) 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. The resulting emulsion was poured into a 250 ml glass reactor equipped with a reflux condenser, nitrogen inlet and a three bladed turbine stirrer, which was sealed by using a rubber seal and was bubbled through with N₂ for 20 min. The reaction mixture was heated to 80 °C to start the polymerization reaction under nitrogen atmosphere and mechanical stirring (300 rpm) until the end of the reaction (approximately 6.5 h). Various recipes including different clay concentrations were reported in Table 1.

Table 1

Samples made by Pickering emulsion polymerization: crude copolymer and its nanocomposites.

Sample	Solid content (wt%)	Clay/monomer (wt%)	NaHCO ₃ (g)	Initiator (g)
A ₀	10	0	0.1	0.15
A ₆	10	6	0.1	0.15
A ₈	10	8	0.1	0.15
A ₁₀	10	10	0.1	0.15

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