

Study of structure and thermal properties of styrene-butylacrylate copolymer with OMMT nanocomposite emulsions

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Abstract

(St-co-BA) polymer through montmorillonite (MMT) nanocomposite emulsion is prepared by in situ intercalative emulsion polymerization of styrene (St), butyl acrylate (BA) in the presence of organic modified montmorillonite (OMMT) with different OMMT contents (0, 0.5, 1.0, 1.5, and 2.0 wt%). The synthetic compounds are characterized by FTIR, XRD. The nanocomposite emulsions are characterized by applying FTIR, SEM, TEM, TGA and DSC techniques in order to investigate the structure and the thermal properties of the copolymer. The properties of the nanocomposite emulsions containing OMMT are better than styrene-acrylate emulsion. The study of monomer conversion versus time and different OMMT contents indicates that the polymerization rate is decreased by increasing the concentration of styrene and OMMT. Consequently, the properties of the nanocomposite emulsion containing 1 wt % OMMT are cbetter than other contents.

Keywords: Styrene; butyl acrylate; emulsion polymerization; nanocomposites; montmorillonite.

Introduction

The nanostructure of particles, the film morphology, and the properties of the resulting material have been considered under influence of the synthesis route in order to produce hybrid latex. The production of core-shell particles can be followed by two routes of seeded emulsion polymerization, either acrylic (or styrene) monomers in the presence of siloxane seed or siloxane onto the

polyacrylate seed latex [1-4]. Due to the outstanding mechanical, thermal, chemical and electrical properties over the pure polymers, polymers/clay nanocomposites (PCNs) became an interesting area of industrial and academic researches [5]. There are several kinds of nanofillers including layered silicates which include montmorillonite widely used as nano-clay [6,7]. Organic polymers, loaded

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with small amounts of montmorillonite (MMT) clay produce PCNs having a good resemblance in dielectric properties with respect to their structural properties [8,9].

Montmorillonite (MMT) is a natural type of clay which has been composed of triad triple layer nano platelets including two tetrahedral silica layers fused into an edge-shared octahedral layer of alumina, 1 nm to 100 nm thick. Montmorillonite is a kind of layered silicate which is usually used in forming effective polymer nanocomposite. It belongs to a smectite group of clay minerals with a 2:1 type of layer structure in which the central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets [10].

A low volume of the dispersed MMT in polymeric matrix can significantly improve the mechanical properties [11], thermal stability [12], and the barrier properties [13]. Various reports about polymer production processes and characterizations associated with the polymer-MMT nanocomposites are available in the related literature [14–17]

The adopted surfactants to organo-MMT (OMMT) are micro molecules which would degrade the thermal stability and durability of the fabricated nanocomposites through the electrostatic attraction to positive charges at crystal edges.

A compound of poly acrylate-OMMT nanocomposites which is made in situ polymerization has been reported [18].

Until 2011 the modified copolymer with macromonomer containing styrene and OMMT had not been reported. The thermal properties of nanocomposite emulsion, influence of different amounts of OMMT and organosilicon on the nanocomposite

emulsion are studied. The main goal of this research is the study of thermal properties of (St-co-BA) copolymer with OMMT nanocomposite emulsions *via* different concentrations of the nanocomposite.

Experimental

Materials

The styrene (St) (Aldrich) and butylacrylate (BA) (Aldrich) monomers are removed from the inhibitor through 10% aqueous NaOH by shaking, washing with distilled water and drying through Na₂SO₄. They are distilled under reduced pressure down to 10⁻⁴ atm at -15 °C to avoid thermal polymerization. The initiator ammonium persulfate, APS, (Merck), the buffer NaHCO₃ (Merck), the emulsifiers sodium laurylsulfoacetate (SLSA) and nonylphenol ethylene oxide-40 U (NP-40) are purchased from Henkel, Germany. The antifoam EFKA-2526 which is supplied by EFKA, Holland and Sodium montmorillonite (MMT) is supplied by Zhejiang Geologic Institute China. Cetyltrimethylammonium bromide (CTAB) sodium silicate (Na₂SiO₃), and ethylene glycol (inhibitor) are supplied by Merck. Polyvinyl alcohol (PVA, protective colloid) is supplied by Sichuan Vinylon Factory China. Double – distilled and deionized (DDI) water is used throughout the process.

Instruments

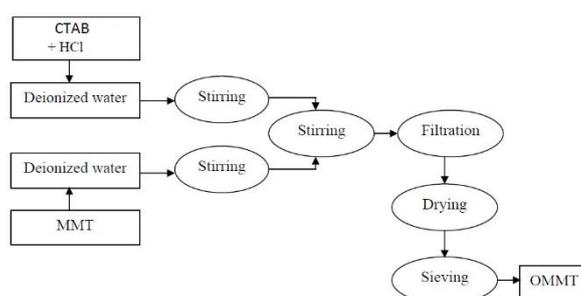
Fourier transform infrared (FTIR) spectroscopy analysis is performed with a Nicolet Impact 400 D Model spectrophotometer (Nicolet Impact, Madison, USA) using KBr pellets. Scanning electron micrographs are obtained by a JEOL-JXA 840 ASEM (JEOL, Boston, USA). The X-ray diffraction (XRD) analysis is performed using a Japanese D/ max-rA X-ray diffractometer (Cu K_α radiation, λ =

0.154 nm, 40 kV, 70 mA). The measured temperature is established at $(25 \pm 0.1) ^\circ\text{C}$. The TGA measurements of copolymers are carried out by a Dupont TGA 951 under nitrogen atmosphere at a $10 ^\circ\text{C}/\text{min}$ heating rate.

Preparation of OMMT

The required amounts of MMT and distilled water are added in the three necked flask and then sodium silicate is added to obtain $\text{pH}=11$. After stirring for 4 h, the mixture is allowed to stand

for 24 h at room temperature. The supernatant of the mixture is subsequently poured into another flask where the required amount of CTAB is added. The blend is heated up to $90 ^\circ\text{C}$ and stirred at the same temperature for 2 h. This blend is then washed by distilled water to make it free of bromide ions and then is filtrated through suction. The resistant solid is dried in a vacuum oven and grounded to 250 meshes (Scheme 1).



Scheme 1. Schematic illustration of surface modification of montmorillonite (OMMT)

Preparation of emulsion

The emulsions are prepared based on H. JavaherianNaghsh, et al [19]. The given amounts of St, BA, and OMMT are premixed for 24 h to get mixture I. The initiator is dissolved in distilled water in order to obtain 10 % solution. Two-thirds of the required distilled water volume, emulsifier, and total protective colloid and buffer agent are poured into a three-necked flask equipped with a stirrer, a thermometer, and a condenser. The mixture is heated up to $52 ^\circ\text{C}$, then, mixture I is poured into the flask. The blend is stirred at $52\text{--}55 ^\circ\text{C}$ for 10 min in order to obtain pre-emulsion. The 1/8 of the pre-emulsion is poured into another flask and heated up to $75 ^\circ\text{C}$. Afterwards, 1/3 of the given amounts of initiator

solution, emulsifier, and distilled water are added to the same flask. The blend for 30 min and a seed emulsion is obtained.

Results and discussion

FTIR spectrum of MMT and OMMT

FTIR spectra of (A) MMT and (B) OMMT have been illustrated in Figure 1. Non-modified MMT is evident from some groups of materials with absorption peaks lower than 1200 cm^{-1} . No specific difference is seen in absorption peaks at 1030 cm^{-1} that belong to Si-O in MMT or OMMT. In general, the vibration of -CH of alkyl ammonium ion is obvious at $2850\text{--}3000 \text{ cm}^{-1}$ and the $\text{N}^+(\text{CH}_3)_3$ cation peak is observed at 1487 cm^{-1} which indicates that MMT is modified to OMMT.

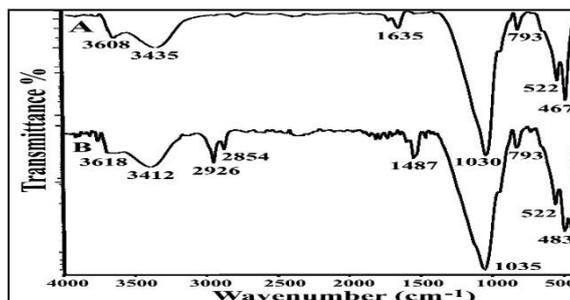


Figure 1. FTIR spectra of (A) MMT and (B) OMMT

Distance of MMT and OMMT layers

The distances between MMT and OMMT layers are calculated through Bragg law [20]:

$$2d \sin \theta = n\lambda \quad (1)$$

Where λ is the wave length of the X-ray ($\lambda = 0.154 \text{ nm}$), d is the interspaced distance, and θ is the angle of incident radiation (Fig.2). It can be deduced that the distance between MMT and OMMT layers are 1.262 and 1.471 nm, respectively. The results indicate that organic CTAB is intercalated between MMT layers.

FTIR spectrum of poly (St-co-BA) and MMT nanocomposite emulsion

The FTIR spectrum of (A) P (St-co-BA) and (B) P (St-co -BA) with OMMT have been illustrated in Figure 3. There are strong absorption peaks at 3027, 2939, and 1730 cm^{-1} which are ascribed to the vibration of =CH, -CH, and C=O, respectively, Figure 3 (A). After adding OMMT, a new sharp peak appeared at 1257 cm^{-1} which is attributed to the OMMT absorption, Figure 3 (B).

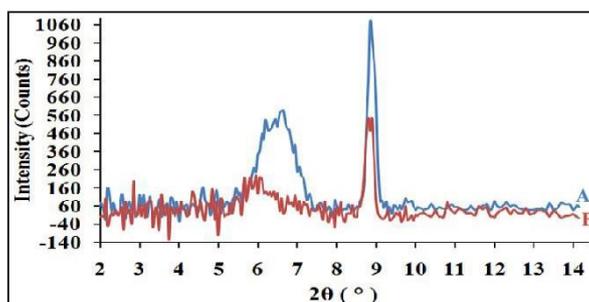


Figure 2. XRD patterns of (A) MMT and (B) OMMT

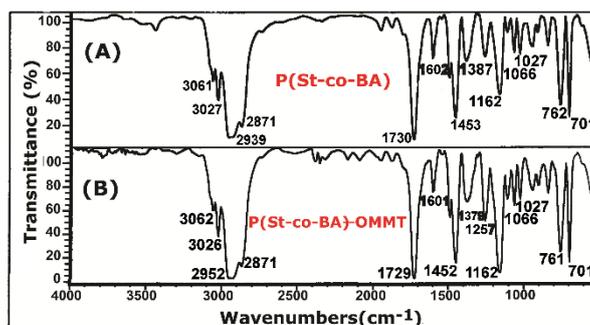


Figure 3. FTIR spectra of (A) P(St-co-BA) and (B) P(St-co-BA) with OMMT

Morphologies of the P (St-co-BA) and P (St-co-BA) with OMMT

The number of polymer particles per unit volume of water (N_T) is counted based on the monomer conversion X_M and the volume average diameter of the polymer particles d_v^3 is determined through a scanning electron microscope, using the following equations:

$$d_v^3 = \frac{\sum n_i d_i^3}{\sum n_i}$$

$$N_T = \frac{6M_0 X_m}{\pi d_v^3 \rho_p}$$

where, M_0 is the initial monomer concentration per mL and ρ_p is the polymer density (g/cm^3) [21, 22]. The

volume average diameter (d_v^3) of the lattices is found to be 1.2×10^{-14} and 8.1×10^{-15} mL for P (St-co-BA) and P (St-co-BA) with OMMT, respectively. The particle morphologies of the P (St-co-BA) and P (St-co-BA) with OMMT are examined by SEM and TEM, respectively. The micrographs of SEM are shown in Figure 4 (A–B) and data is shown in Table 1.

On the base of the previous works [23], by increasing OMMT percent, the particle size increases in a linear manner and their size distributions become narrower. It is obvious that the number of polymer particles is increased by increasing the conversion of monomers to copolymers (Table 1).

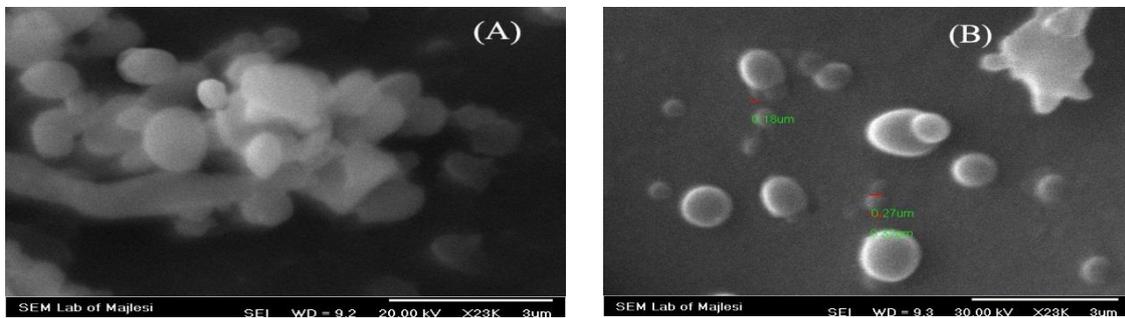


Figure 4. SEM micrographs of (A) P (St-co-BA), (B) P (St-co-BA) with OMMT at 81 °C

The conventional TEM can provide more information in real space in a localized area in a direct manner. On the morphology and determining of the defect structures, the nature of nanocomposites is necessary. Typical TEM image of P (St-co-BA) with OMMT nanocomposite with different magnifications is shown in Figure 5 (A–B) with the presence of several

OMMT layers in the P (St-co-BA) matrix which indicates the nanocomposites formation. TEM micrographs prove that most OMMT layers are dispersed homogeneously into the polymer matrix, although some clusters or agglomerated particles are detected.

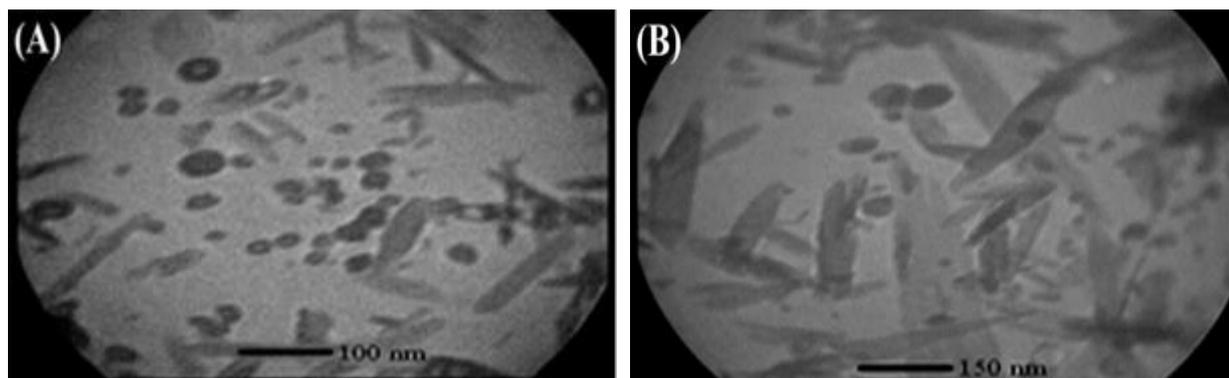


Figure 5. TEM micrographs of (A) P (St-co-BA), (B) P (St-co-BA) with OMMT at 81 °C

Thermal properties

The thermal properties of P (St-co-BA), P (St-co-BA) with OMMT with 1 wt % OMMT are evaluated through differential scanning calorimetric (DSC), and TGA/DTG, subjected to nitrogen atmosphere, respectively (Figures 6 and 7). DSC curve of the P (St-co-BA) reveals an endothermic shift about 102.04 °C, which corresponds to the glass transition temperature, T_g . T_g is about 81.21 °C for P (St-co-BA) with OMMT (Figure 5). T_g for P (St-co-BA) is high because the micro Brownian

motion is slow, and it becomes slower in the presence of silicone containing polymer chains. The TGA/DTG curve of P (St-co-BA) shows a stable situation up to 249.65 °C. The chemical decomposition will start after this temperature and the maximum decomposition is about 460.38 °C. P (St-co-BA) with OMMT emulsion. Moreover, it shows a stable situation up to 264.79 °C and the chemical decomposition would start after this point where the maximum decomposition is about 545.4 °C.

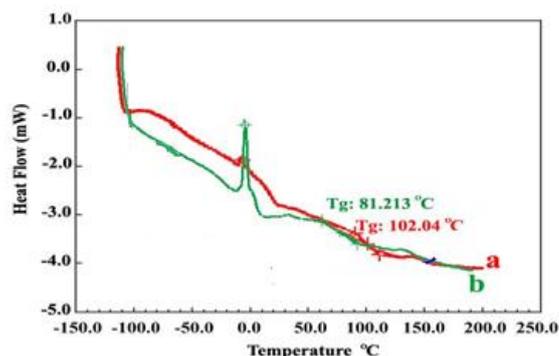


Figure 6. DSC curves of (a) P (St-co-BA), (b) P (St-co-BA) with OMMT

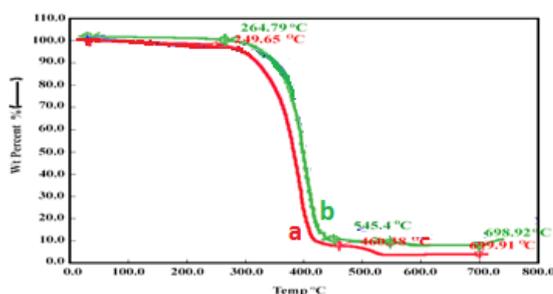


Figure 7. TGA curves of (a) P (St-co-BA), (b) P (St-co-BA) with OMMT

The effect of OMMT and its concentration

The effect of OMMT concentrations on the monomer conversion versus time are illustrated in Figure 8 where the initial initiator and total monomer concentrations are fixed at $I_0 = 8.4 \times 10^{-3}$ mole/L and $[M]_0 = 4.60$ mole/L. The figure shows that the rate of reaction

changes based on the OMMT concentration. According to Figure 8, the reaction rate decreases from St-BA to OMMT containing St-BA copolymers and the maximum rate is obtained by St-BA copolymers. Hence, the properties of the nanocomposite emulsion containing 1 wt % OMMT are better than other contents.

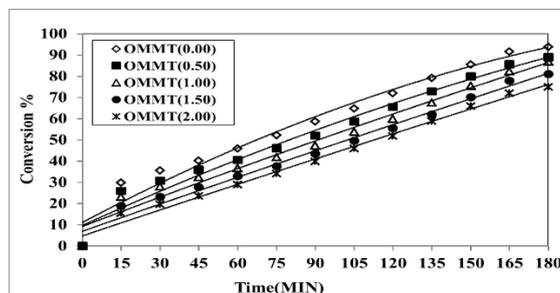


Figure 8. effect of OMMT concentration on the monomer conversion versus time

Conclusion

The Poly (styrene-co-butylacrylate) with organic modified montmorillonite nanocomposite emulsion were prepared by in situ intercalative emulsion polymerization of styrene (St) and butylacrylate (BA) in the presence of organic modified montmorillonite (OMMT) with different OMMT contents (0,0.5,1.0,1.5, and 2 wt %). The properties of styrene-butylacrylate emulsion were improved by the intercalative polymerization of butylacrylate-styrene in the presence of OMMT. OMMT layers are dispersed homogeneously into the polymer matrix. The property of nanocomposite emulsion containing 1 wt % OMMT possesses some of the best advantages including small particle size, rapid drying, and improved resistance against water by the incorporation of OMMT. The TGA/DTG curve of P (St-co-BA) shows a stable situation up to 249.65 °C.

Acknowledgments

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