Influence of Layered Silicate on Microemulsion Polymerization Kinetics of Butylacrylate with Alkoxylane

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Present paper refers to the possibility of obtaining nanocomposites through microemulsion copolymerization of butylacrylate (BuA) with vinyltriethoxysilane (VTES), in the absence/presence of some layered silicates. The maximal reaction rates of the BuA/VTES systems, with/without layered silicates, were evaluated through gravimetric technique. The products were characterized by FTIR spectroscopy, TGA and ESEM microscopy.

Keywords: microemulsion, layered silicates, sol-gel process

Microemulsion polymerization is a polymerization technique which allows to prepare ultrafine latexes particles with low particle size distribution (5…50nm), high molecular weight polymeric products and special dispersions with high-solids content [1]. A good control over heat transfer is also made possible during polymerization because of the low viscosity of the medium even at high solid contents [2]. A lot of previous studies present inorganic-polymer hybrid nanoparticles synthesis, polymer-layered silicates respectively [3,4,5,6], and also nanohybrid synthesis through sol-gel processes [7,8,9], but the obtaining of nanoparticles based on polymer-hybrid networks in the layered silicate presence and its kinetic, are not so often treated.

For this reason, the paper deals with the nanocomposites obtaining possibility through microemulsion copolymerization of butylacrylate (BuA) with vinyltriethoxysilane (VTES) in the absence/presence of some layered silicates with sodiumdodecylsulphate (SDS) as a surfactant. Through alkoxysilane presence, the aim was to generate a sol-gel process in order to increase the system reinforcement level. Premature hydrolysis and cross-linking reactions must be avoided to obtain stable latexes with good shelf stability. The hydrolysis of alkoxysilane was proved to be both acidic and base catalyzed. In order to avoid premature hydrolysis and condensation reactions, the polymerization process was driven at *p*H=7, since the minimum hydrolysis rate occurs at a neutral *p*H for most systems [7]. The sol-gel process took place at the end of reaction after *p*H modification. But, our first objective was to observe the kinetic behaviour of the system presented, in the presence of layered silicates, using the gravimetric technique. Another goal was to emphasize the presence of inorganic filler in the polymer matrix and to evaluate the particle size and the Zeta potential appeared at the particle-disperse media interface.

Experimental part

Materials

The monomers: butylacrylate (BuA) – was purified through rectification; vinyltriethoxysilane (VTES) – used without further purification; commercial products.

Buffer solution (natrium tetraboricum/kaliumdyhidrogenphosphate, *p*H=7) was used as dispersion media and 25% NH_3 solution to generate the sol-gel process. The surfactant, sodium dodecylsulphate (SDS) and the initiator, ammonim persulphate (APS), were used without other purifications. The LS were provided by Southern Clay Products Inc. and used in the sodium form (Cloisite ®Na) and organomodified with different ammonium salts (Cloisite® 30B, 20A and 15A).

Procedures

The latexes were obtained by using a three necks glass flask with round bottom, coupled to a thermostat bath with mechanical stirrer. A reflux refrigerator and a thermometer were also connected to the glass flask. In the first stage, the surfactant (15.44 g SDS) was solubilized in the buffer solution (77.28 g, *p*H=7) at 30^0C temperature. After that the layered silicate was added (0.956 g Cloisite). The mixture was mechanically stirred for 15 min. and ultrasonicated for 30 min. Monomer addition (6.912 g BuA, 1.536 g VTES) was followed by nitrogen bubbling. After oxygen removal, the reaction mixture was heated at 65^0C. The polymerization was started by adding the initiator (APS, 0.0056 g). The system was kept under mechanical stirring. Different samples were analyzed during the polymerization for conversion estimation. After 3 h the system was cooled and modified at *p*H=11 with a 25% NH_3 solution in order to generate the sol-gel process. A small amount of latexes were deposed on a polyethylene foil for water evaporation, which was done at room temperature for several days. The resulted material was washed from surfactant (through centrifugation) and analyzed through FTIR and TGA.

Measurements

Particles hydrodynamic diameters and Zeta potential were determined by Dynamic Light Scattering (DLS) with Zetasizer Nano ZS, ZEN3600, (Malvern International Ltd.) The samples were prepared using a 0.01M NaCl solution (0.1 mL latex/25 mL sol. 0.01M NaCl).

FTIR spectra of the final products resulted after water evaporation and surfactant removal, were recorded on a FTIR-Tensor 30 BRUCKER spectrometer from KBr pellets using 40 scans with 4 cm^{-1} resolution.

Thermogravimetric analysis (TGA) was carried out at a heating rate of $20^0C\ min^{-1}$ in air using a Du Pont 2000 instrument.

ESEM analyses were performed using a FEI Quanta 200, by scanning electron microscopy (SEM).

Results and discussions

Hybrid latexes based on butylacrylate (BuA) with vinyltriethoxysilane (VTES) in the absence/presence of some layered silicates were synthesized. In a first stage, maximal reaction rates were calculated. The results are

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presented in figure 1. The maximal reaction rate of the latex obtained in the absence of inorganic compounds was compared with the ones synthesized with layered silicates. It was observed that maximal reaction rates increased with the layered silicates addition, against the maximal reaction rates for pure latex; the presence of clay affected obviously the kinetic behaviour. Previous studies showed that layered silicates can be electron acceptors and/or electron donors in organic reactions. The electron acceptor sites are aluminium at crystal edges and transition metals in the higher valence state in the silicate layers; the electron donor sites are transition metals in the lower valence state [10,11]. Thus, layered silicate could catalyze or inhibit the polymerization and could possibly lead to an increase or decrease of maximal reaction rate [12,13]. Other studies explained that clay minerals also exhibit a wide surface chemistry that takes place at their layers' edges, including surface modification through ion exchange reactions and chemical modification with organosilanes. In the first case, the presence of cation exchange sites at the edges (approx. 10% of the total cation exchange capacity of the mineral) offers an easy route for accommodating charged entities with specific functionalities. In the second case, the organosilane is attached to the clay edges through condensation reactions between the surface hydroxyl groups and the chloro- or alkoxy- groups of the organosilane, thus affording Si-O-Si or Al-O-Al covalent bonds [14,15]. In conclusion, it is very possible that, the increase of maximal reaction rate in the presence of layered silicates, could be due to the silicate reactive sites.

In the case of the latexes prepared with Cloisite 30B, minimal value for reaction rate was observed. This value could be related with the double bond from the Cloisite 30 B structure. It is very possible that this double bond, promotes chain transfer reactions leading to a reaction rate decrease.

FTIR spectra for P(BuA-VTES) sample and P(BuA-VTES)-layered silicates samples are presented in figure 2 and showed the presence of polymer, silica and layered silicate specific peaks.

FTIR spectra of P(BuA-VTES) showed corresponding wavelength of C=O group, (stretching vibration) at 1737 cm^{-1} C-O-C 1163 cm $^{-1}$ (asymmetric stretching vibration) and 2960-2870 cm^{-1} for methyl groups (stretching vibration). The absence of characteristic band for vinyl group at 3066 cm^{-1} (stretching vibration), can be a proof that the copolymerization occurred [16,17]. A strong absorption band at 1165 cm^{-1} can be visualized; this is a characteristic band for Si-O-Si group and confirmed the sol-gel process.

In polymer-layered silicates nanocomposites case, silicates specific peaks were observed at 1045 cm^{-1} Si-O-Si (stretching vibration) and between 400-600 cm^{-1} Si-O (bending and stretching vibration), respectively [18]. Thus, the existence of P(BuA-VTES) and layered silicates peaks in extracted nanocomposites FTIR spectra, was ascribed to the inclusion of layered silicates in polymer matrix. The presence of silica and layered silicates in the polymer matrix was supported by TGA analysis, too. Thermal analysis showed a significant growth of hybrids samples residue (from 0 wt. % residue for PBuA sample, to around 11 wt. % for P(BuA-VTES) sample, and to 16-19 wt. % for silicates samples) against the samples without silicates. The maximum decomposing temperature grew with inorganic filler addition (from 392.07^{0}C for PBuA sample, to 428.02^{0}C for P(BuA-VTES) sample, and to around 436^{0}C for P(BuA-VTES)-(Cl 30, Cl 20A) samples). Therefore, the presence of inorganic partner brought up a significant thermal stability of polybutylacrylate.

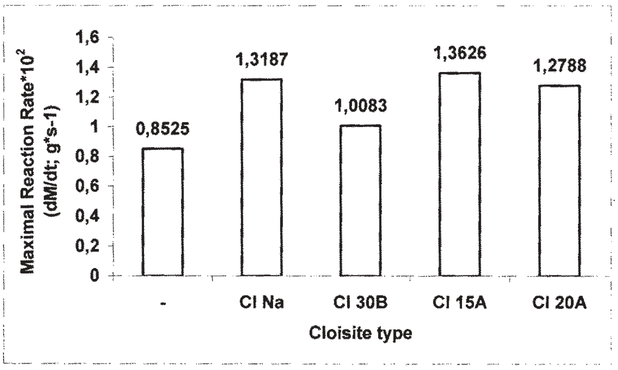

Fig.1 Maximal reaction rates calculated for P(BuA-VTES) system in comparison with maximal reaction rates of the systems with layered silicate (Cl Na, Cl 30B, Cl 15A, Cl 20A)

Additionally, the average hydrodynamic diameter of the particles and Zeta potential appeared at the particle-disperse media were determined, and are represented in figure 3. Greater average diameter values for the latexes obtained with inorganic compound were determined, with values situated in the (50...60 nm) range. This can be a proof for the polymer particle covering statement, but can't exclude the possibility of silicate layer localization into the polymer particle [19,21].

Zeta potential absolute values, shown in figure 4, increased in the presence of layered silicate, the filler leading to a possible latex stabilization. This increase can be explained by the electrostatic charge of the layered silicate [10,11,20]; this can contribute to the total charge on the particle surface leading to an increase of Zeta potential, if the silicate is located on the surface of the particle. The highest absolute value was determined for

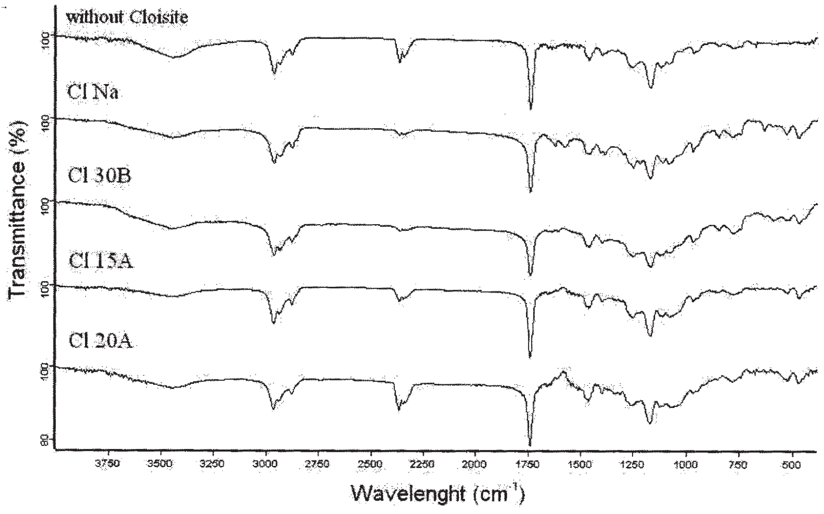

Fig. 2 FTIR spectra for P(BuA-VTES) sample and P(BuA-VTES)-layered silicates (Cl Na, Cl 30B, Cl 15A, Cl 20A) samples

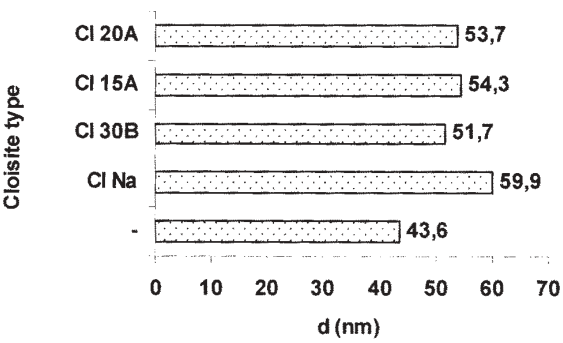

Fig. 3. The average hydrodynamic diameter of the particles of pure latex P(BuA-VTES) in comparison with diameters of hybrid latex polymer-layered silicates (Cl Na, Cl 30B, Cl 15A, Cl 20A)

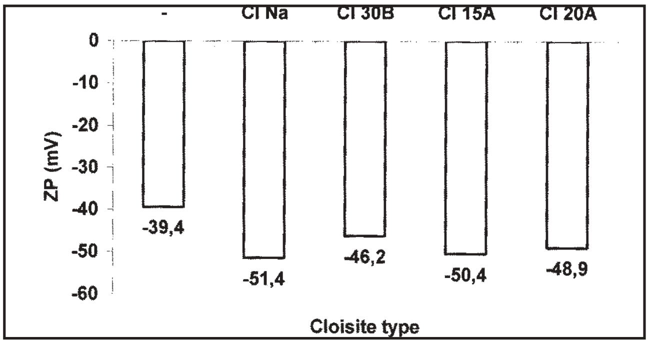

Fig. 4. Zeta potential of pure latex P(BuA-VTES) in comparison with Zeta potential of polymer-layered silicates (Cl Na, Cl 30B, Cl 15A, Cl 20A) hybrid latex

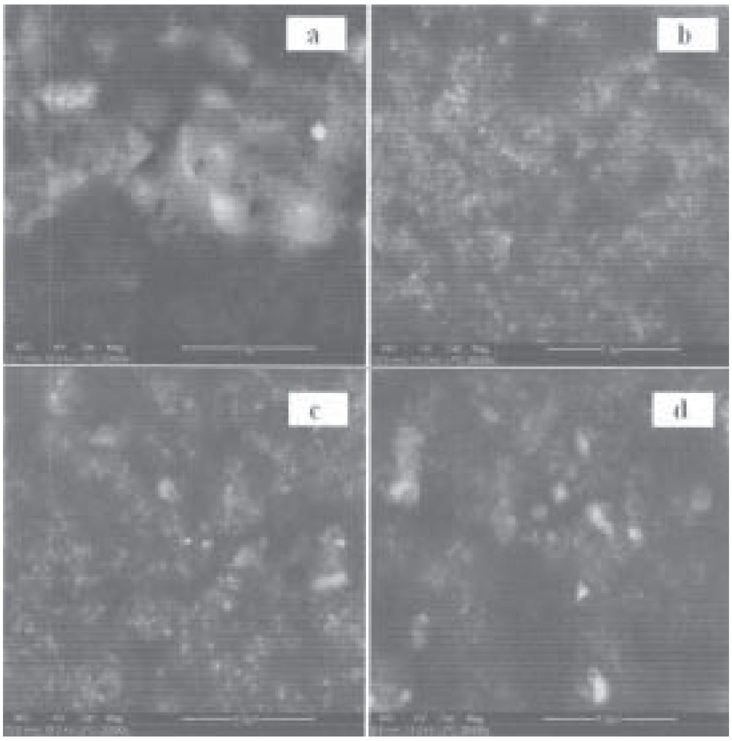

Fig. 5. ESEM micrograph for P(BuA-VTES) materials without Cloisite (a) and with Cl Na (b), Cl 30B (c) and Cl 20A (d)

Cloisite Na, the most hydrophilic layered silicate, this one being a viable partner for the polar monomer, as it was showed in our previous studies [22].

From ESEM images for polymer-layered silicate nanocomposites, we can observe a morphology modification in comparison with the pure latex; namely, aggregates areas of the silicate are very contoured. As we can see from figure 5, the individual hybrid particles are visualised easier, apparent morphology being strongly affected by the presence of inorganic partner.

Figure 5 ESEM pictures for P(BuA-VTES) materials without

Cloisite (a) and with Cl Na (b), Cl 30B (c) and Cl 20A (d)

Conclusions

Hybrid latexes based on butylacrylate (BuA) with vinyltriethoxysilane (VTES) in the absence/presence of several montmorillonite types of layered silicates were synthesized. From monomer conversions, it was observed that maximal reaction rates increased with the layered silicates addition, in comparison with the maximal reaction rates for pure latex, the presence of clay affecting obviously the kinetic behaviour.

FTIR spectra for P(BuA-VTES) sample and P(BuA-VTES)-layered silicates samples showed the presence of polymer, silica and layered silicate specific peaks. Thermal analysis showed a significant growth of hybrids samples residue against the samples without inorganic filler and its presence brought up a significant thermal stability of polybutylacrylate.

DLS analysis showed higher particle dimensions and Zeta potential absolute values increased with the silicates presence.

From ESEM analysis it was observed that the apparent morphology has been strongly affected by the presence of inorganic partner.

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Manuscript received: 7.02.2008