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NANODISPERSED SYSTEMS OBTAINED IN THE PRESENCE OF ALKOXYSILANE AND LAYERED SILICATES

Raluca IANCHIŞ[1], Dan DONESCU[2], Cristian PETCU[3], Marius GHIUREA[4],
Raluca ŞOMOGHI[5], Sever ŞERBAN[6]

Prezenta lucrare investighează posibilitatea de obținere a unor nanohibdride prin copolimerizarea în microemulsie a acrilatului de butil (BuA) cu metacriloiloxi propil trimetoxisilan (MPTS), în prezență de silicați stratificați şi ulterior, dezvoltarea unui process sol-gel la capetele alcoxisilanului. Latexurile finale au fost caracterizate prin DLS. Materialele solide obținute au fost analizate prin ATG, spectrometrie FTIR şi microscopie eletronică ESEM.

The present work investigates the possibility to synthesize nanohybrides through copolymerization in microemulsion of butylacrylate (BuA) with metacrylyloxy propyl trimetoxysilane (MPTS), in the presence of layered silicate, and subsequently the development of a sol-gel process through alkoxysilanes extremities. Final latexes were characterized by DLS. Solid materials were analyzed by TGA, FTIR spectrometry and ESEM electronic microscopy.

Keywords: alkoxysilane, layered silicate, dispersed systems

1. Introduction

A considerable attention has been devoted over the past decades to the preparation of nanocomposites [1,2,3]. In this case, the filler amount is lower than the classic composites. Also, the physical-chemical properties of polymeric nanocomposites are net superior to the classic polymer composites because of the increased specific surface between partners. Among the wide range of

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[1] Scientific researcher, National Research &Development Institute for Chemistry&Petrochemistry – ICECHIM, Polymer Department, Romania, ralumoc@yahoo.com

[2] Senior researcher, National Research &Development Institute for Chemistry & Petrochemistry– ICECHIM, Polymer Department, Romania

[3] Senior researcher, National Research &Development Institute for Chemistry & Petrochemistry– ICECHIM, Polymer Department, Romania

[4] Scientific researcher, National Research &Development Institute for Chemistry&Petrochemistry – ICECHIM, Polymer Department, Romania

[5] Scientific researcher, National Research &Development Institute for Chemistry&Petrochemistry – ICECHIM, Polymer Department, Romania

[6] Senior researcher, National Research &Development Institute for Chemistry & Petrochemistry– ICECHIM, Polymer Department, Romania

nanostructured materials, the effort has been recently focused on the elaboration of polymer-layered silicates nanocomposites [4-6]. Systems in which layered silicate is well dispersed in a polymer matrix generally exhibit positive effects on mechanical properties [4] at relatively low loadings, ca. 5 wt. %. Layered silicates' dispersing in the polymer is very difficult, that's why compatible agents are used. Their role is to enhance the dispersal into polymer. The most common are alkyl ammonium ions who can be easily replaced with inorganic ions located between layers, and they can reduce the electrostatic interactions between the multilayered silicates, in order that the diffusion of the polymer between layers be optimal. Generally, multilayered polymer-silicates composites are distributed in three categories: conventional composites, in which the multilayered silicates behaves as a conventional filler, intercalated nanocomposites, which consist in the common insertion of the polymer in the silica layers, and the exfoliated nanocomposites, where the silica layers of 1 nm thickness are dispersed in the polymer matrix [1].

On the other side, inorganic-organic materials obtained by sol-gel process are increasingly important due to their extraordinary properties, which arise from the synergism between the properties of the components [7-9]. Alkoxysilanes have two types of groups attached to a silicon atom: an organic nehydolizable group (alkyl, aromatic, organofunctionalized group, or a combination of these) which confers compatibility for organic compounds, and in this case with the monomer and the alkoxy group (methoxy or ethoxy) which can react with hydroxyl group resulting, in this way, silica networks. Through alkoxy group we can establish the bond with the inorganic layers and with the pigments, fillers, and the effect being the improvement of the adhesive and cover properties [10]. The problem which appears refers at the premature hydrolysis and crosslinking reaction. This can be stopped by controlling the reaction conditions (pH, temperature, surfactant amounts). It was demonstrated that alkoxy groups hydrolysis takes place in both acidic and basic medium, hydrolysis minimum rate for the most systems being at the neutral pH. Thus, the polymerization process will be driven at the neutral pH; hydrolysis and the condensation reactions will occur after the modification of the pH of the latex.

For the reasons presented, we tried to obtain advanced organic-inorganic materials, using two sorts of inorganic partner, layered silicate and silica from sol-gel process. Thus, our first objective was to perform a microemulsion copolymerization in the presence of layered silicate and subsequently, to perform a sol-gel process using alkoxysilane edges. Another goal was to evidence the presence of silica and layered silicates in the polymer matrix, and to observe the morphologies of solid materials.

2. Experimental

Copolymerizations in microemulsion of butylacrylate (BuA) with metacryloyloxy propyl trimetoxysilane (MPTS) in the presence of several layered silicates were performed.

2.1. Materials

The monomers: butylacrylate (BuA) – was purified through rectification; metacryloyloxy propyl trimetoxysilane (MPTS) – used as supplied; commercial products.

Buffer solution (natrium tetraboricum/kaliumdyhydrogenphosphate, pH=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, ammonium persulphate (APS), were used without other purifications. The LS were provided by Southern Clay Products Inc. and are used in the sodium form (Cloisite ®Na, 92meg/100g) and organomodified with different ammonium salts (methyl, tallow, bis-2-hidroxyethyl)-(Cloisite® 30B; 90 meg/100g),) and (dimethyl, dihydrogenatedtallow)-(Cloisite® 20A; 95 meg/100g) and (dimethyl, dihydrogenatedtallow)-(Cloisite® 15A; 125 meg/100g).

2.2. 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 glass flask. Compositions used for hybris syntheses are presented in Table 1. In the first stage, the surfactant was solubilized in buffer solution at 30^0C temperature, after that layered silicate was added. The mixture was mechanically stirred for 15 min. and ultrasonicated for 30 min. Monomers addition (BuA, VTES) was followed by nitrogen bubbling. After the oxygen removal, the reaction mixture was heated at 65^0C. The polymerization started by adding the initiator (APS). The system was kept under mechanical stirring. Different samples were analyzed during the polymerization for conversion estimation. After 3 hours the system was cooled and modified at pH=11 with 25% NH_3 solution in order to start the sol-gel process. A small amount of latexes was deposited on a polyethylene foil for water evaporation, which was done at room temperature for several days. The resulted materials were washed from surfactant (through centrifugation) and after complete water removal were analyzed by FTIR and TGA.

Table 1

Compositions used for hybrids syntheses

No. sample	Monomer (g)	MMT (g)	SDS (g)	Buffer solution (g)	APS (g)
1.	BuA (6.912)-MPTS (3.456)	-	15.44	77.28	0.15
2.	BuA (6.912)-MPTS (3.456)	Cloisite Na (0.956)	15.44	77.28	0.15
3.	BuA (6.912)-MPTS (3.456)	Cloisite 30B (0.956)	15.44	77.28	0.15
4.	BuA (6.912)-MPTS (3.456)	Cloisite 20A (0.956)	15.44	77.28	0.15

2.3. Instruments

Particles hydrodynamic diameters and Zeta potential were determined by Dynamic Light Scattering (DLS) with Zetasizer Nano ZS, ZEN3600, produced by 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 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).

3. Results and Discussions

In order to observe the influence of layered silicates over particle sizes and Zeta potentials, DLS analysis were performed. Fig. 1 and 2 presents the particle sizes and respectively, Zeta potential values for latexes of P(BuA - MPTS) and P(BuA - MPTS) – layered silicates.

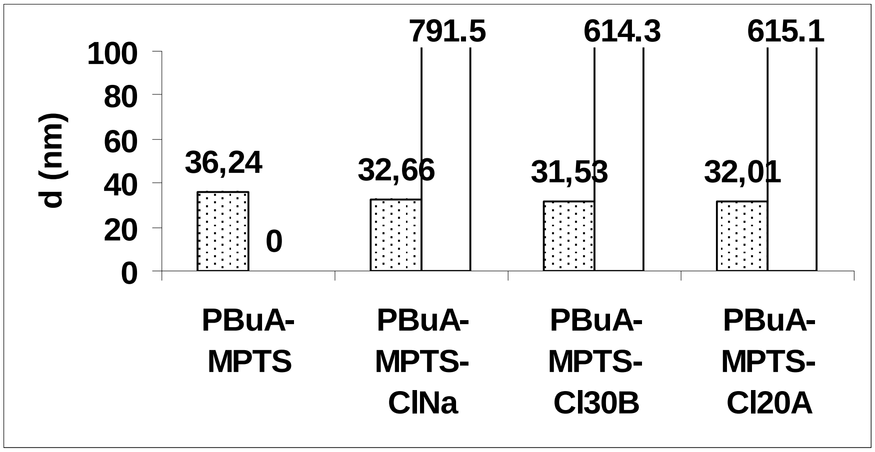

Fig. 1. Particle sizes for P(BuA - MPTS) in comparison with P(BuA - MPTS) – layered silicates

For P(BuA – MPTS) system, unimodal distribution was determined, the medium diameter being 36.24 nm. Not the same was observed for the systems with layered silicates. The medium diameters grow with the layered silicates addition and two particle generations were observed. The first peak, it was determined to be around 32 nm (ca. 77%) and the secondary around 700 nm (ca. 32%), for all Cloisite latexes. This is probably due to the association of silicate layers or stacking of the layers into a silica shell. It was shown, that trialkoxysilanes can link the clay sheet together, making them nondispersable [11]. The sol-gel process could involve the layer edges, leading to larger particles by association with polymer chains, until they reach their optimal stability. The absolute Zeta potential absolute values grow from 30 mV to 50-60 mV in the presence of clay, as it is presented in Fig. 3.

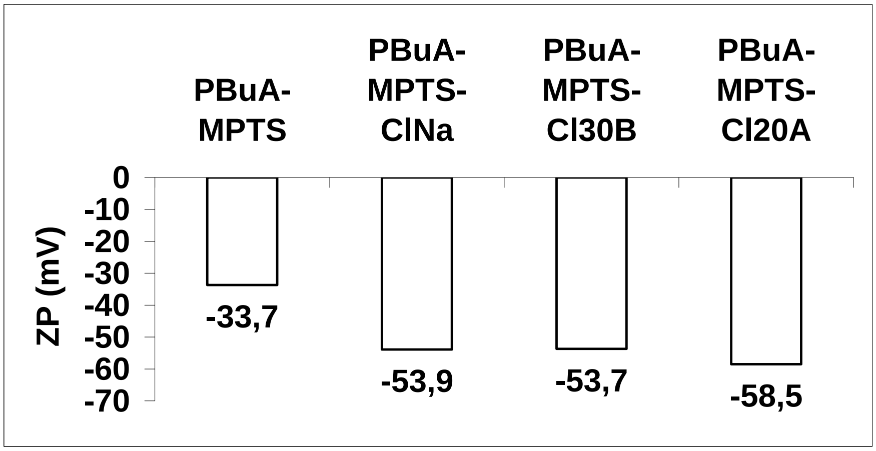

Fig. 2. Zeta potentials for P(BuA - MPTS) in comparison with P(BuA - MPTS) – layered silicates

According to Zeta potential measurements, the presence of layered silicates in the P(BuA-MPTS) latex increases the stability of the system. This increase could be explained by the electrostatic charge of layered silicate [12] which can contribute at the total charge, leading to an increase of Zeta potential. In conclusion, DLS analysis showed evident modifications of the latexes in the presence of layered silicates.

FTIR spectra of P(BuA-MPTS) from Fig. 3, showed corresponding wavelength of C=O group, (stretching vibration) at 1734 cm^{-1}, C-O 1167-1118 cm $^{-1}$ (asymmetric stretching vibration) and 2930-2850 cm^{-1} for CH_2 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]. Though, a weak peak at 1636 cm^{-1} C=C vinyl group (stretching vibration) can be observed which can be very probably from the unreacted monomer, taking into account that the conversions were established to be ca. 75%. In polymer-layered silicates nanocomposites case, silicates specific peaks were observed at 400-600 cm^{-1} Si-O (bending and stretching vibration) and 3634 cm^{-1} NH (stretching vibration). Thus, the existence of P(BuA-MPTS) and layered silicates peaks in extracted nanocomposites FTIR spectra, was ascribed to the inclusion of layered silicates in polymer matrix.

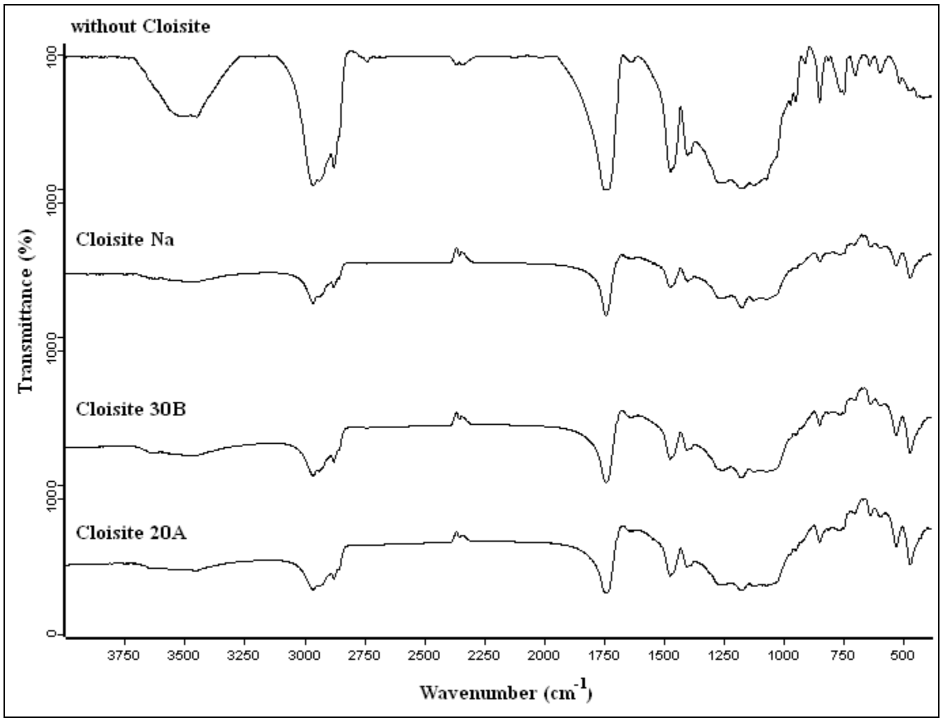

Fig. 3. FTIR spectra for the systems based on P(BuA-MPTS)

The presence of inorganic partner in the polymer matrix was supported by TGA analysis, too. Thermal analysis, presented in Fig. 4, showed a significant growth of hybrids samples residue (from 11 wt. % for P(BuA-MPTS) sample to ca. 17 wt. % for silicates samples) against the samples without silicates.

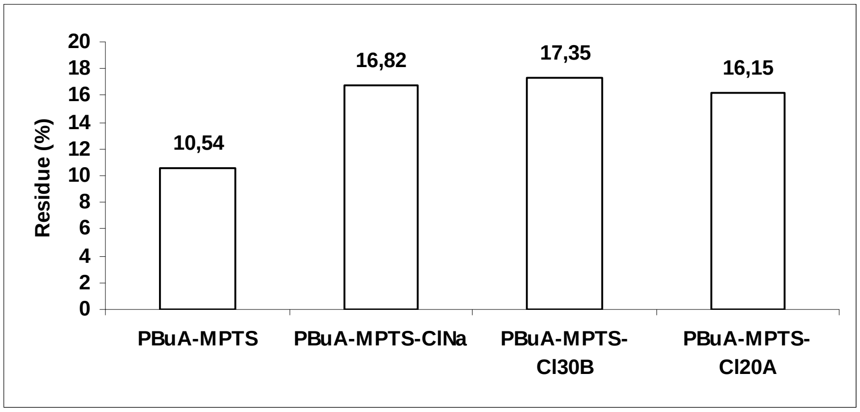

Fig. 4. Residue obtained at 700°C for P(BuA - MPTS) in comparison with P(BuA - MPTS) – layered silicates

The maximum decomposing temperature, presented in Fig. 5, showed no evident modification in the case of Cl Na (365.14^{0}C for P(BuA-MPTS) and 363.46^{0}C for P(BuA-MPTS)-(Cl Na)). For P(BuA-MPTS)-(Cl 20A) the maximum decomposing temperature decreases to 355.05^{0}C. In the case of Cloisite 30B the maximal decomposing temperature (370.19^{0}C) is bigger against the pure sample, the presence of silicate leading to an increase in thermal stability. These modifications are very probably due to the layered silicate amount. It was shown that the clay content can brought up significant increases or decreases in thermal stability related to the filler content [4].

ESEM pictures, presented in Fig. 6 and Fig. 7, showed evident changes of morphologies in the presence of clay.

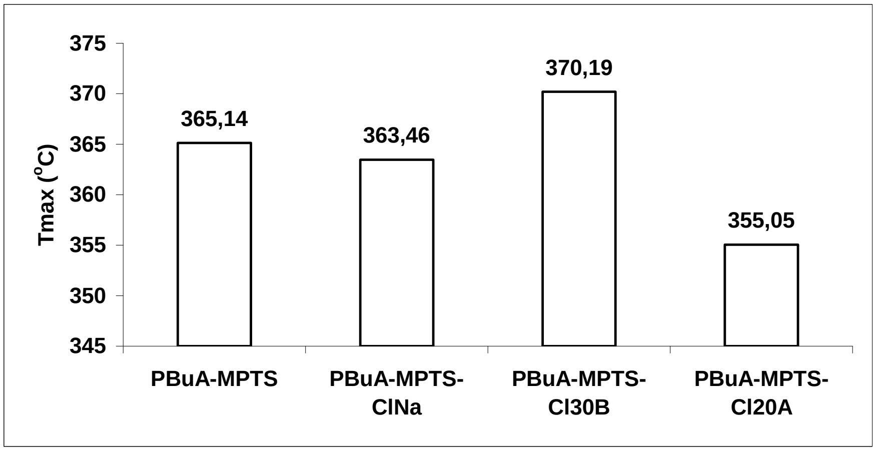

Fig. 5. Maximal decomposing temperature for P(BuA - MPTS) in comparison with P(BuA - MPTS) – layered silicates

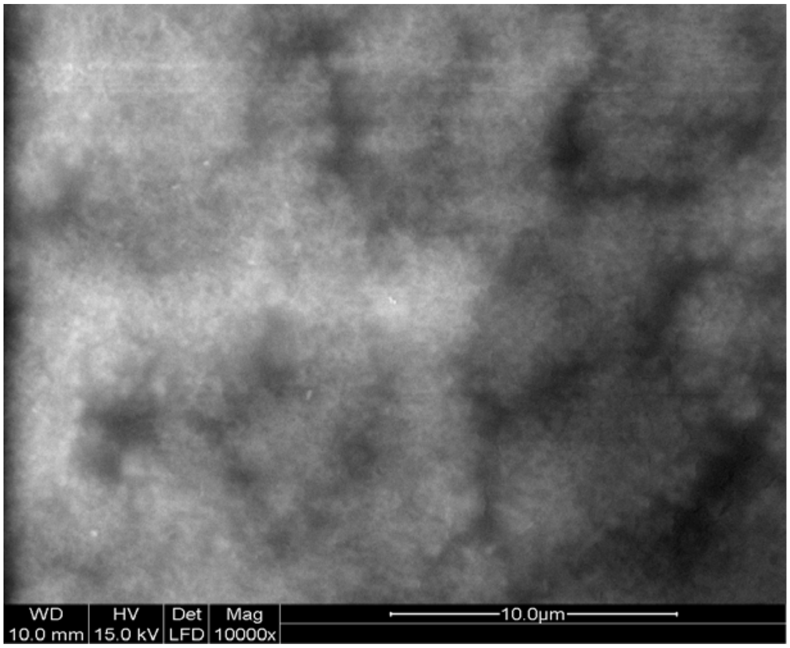

Fig. 6. ESEM pictures for P(BuA - MPTS) system

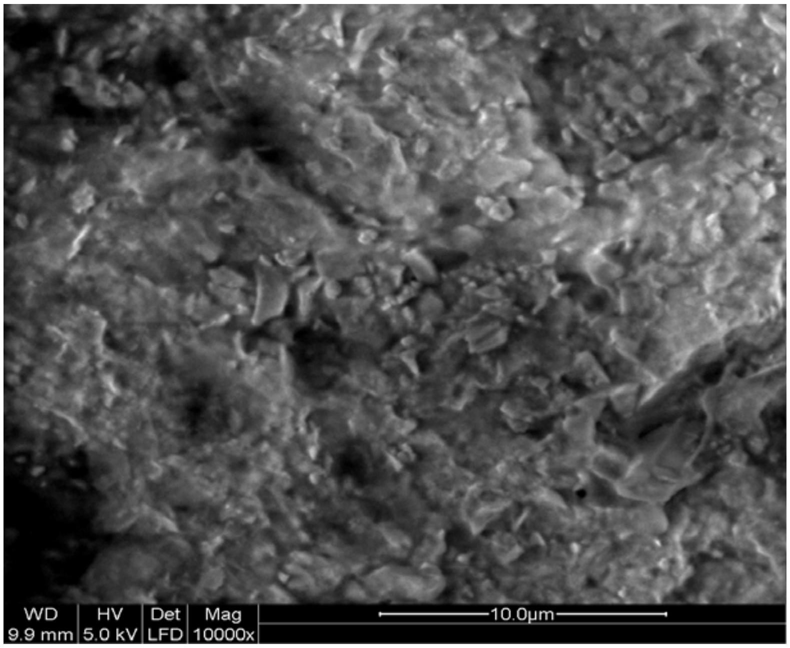

Fig. 7. ESEM pictures for P(BuA - MPTS) – ClNa system

5. Conclusions

Nanohybrids systems based on butylacrylate (BuA) with metacrylyloxy propyl trimetoxysilane (MPTS), in the presence of layered silicate were synthesized. DLS analysis showed evident modifications of particle sizes and Zeta potential in the presence of clays. FTIR spectra of final products resulted after water evaporation and surfactant removal from hybrid latexes showed the specific peaks of polymer and silicate which is ascribed to the inclusion of layered silicates in polymer matrix. Increase in residue, modification of maximum decomposing temperature and the morphology changes with clays presence, supported FTIR analysis.

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