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Poly(styrene-*co*-butyl acrylate)-Brazilian Montmorillonite Nanocomposites, Synthesis of Hybrid Latexes via Miniemulsion Polymerization

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Summary: In this work hybrid latexes of poly(styrene-co-butyl acrylate)/montmorillonite were synthesized via miniemulsion polymerization using a Brazilian organically modified montmorillonite. The natural clay was previously treated with Cetyltrimethyl ammonium chloride (CTAC) in order to increase the interaction between the clay and the monomer phase. Three different methodologies to modify the clay and their influence on the final properties of the composites obtained were evaluated in this work. The modified clays were characterized by X-ray diffraction (XRD). The films obtained after drying the latexes were characterized by dynamic-mechanical thermal analyses (DMTA), small amplitude oscillatory shear (SAOS), transmission electronic microscopy (TEM) and Cobb test. The X-ray diffractograms, showed an increase of basal spacing after organic treatment indicating the introduction of CTA^+ within the clay interlamelar space. This interlamelar space was further increased after polymerization for all of the three differently modified clays studied, indicating that *in situ* polymerization occurred. The introduction of organically modified clays did not influence the kinetics of polymerization. Stable latexes were obtained. The DMTA presented improved mechanical properties for the materials charged with two of the modified clays studied when compared to a conventional composite. SAOS analysis revealed that an exfoliated structure might have been obtained when adding one of the modified clays to the reacting medium. Cobb tests showed that the permeability to water was reduced by the incorporation of clays to the copolymer.

Keywords: butyl acrylate; hybrid latexes; miniemulsion; montmorillonite; nanocomposites; styrene

Introduction

Over the last 10 years, there has been great interest on the development of nanostructured composites. With structures on the length scale of nanometers, such materials present remarkable properties enhancements over standard microcomposites.[1] Polymer/layered silicates hybrid materials are one of the most important forms of organic-inorganic nanocomposites. These composites present the advantages of both, organic materials such as flexibility and good moldability, and inorganic materials such as high strength and heat stability.[1,2] They can be obtained dispersing montmorillonites (MMT)[3] which are interesting due to their high cation exchange capacity (CEC), swelling capacity and high surface area within the polymer. The resultant

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nanocomposite may present an intercalated structure, when the polymer is located within the clay layers but the layered structure is kept, or exfoliated structure, when the individual lamellas of the clay are totally dispersed within the polymer matrix.[4]

Polymer/layered silicate nanocomposites (PLSN) have been prepared by four main processes:[5] exfoliation-adsorption, template synthesis, melt intercalation and *in situ* intercalative polymerization. Several techniques such as solution,[6] suspension,[7] bulk,[8] emulsion[9] and miniemulsion[10] polymerizations have been used to prepare PLSN by *in situ* intercalative polymerization. When using either of these techniques the clay is normally first modified using quaternary ammonium (or others) salts to increase the interlayer spacing and turn its surface organophilic and consequently with better physico-chemical affinity with the monomer or polymer. Among all the techniques mentioned above, miniemulsion enables the formation of nanoparticles or 'nanoreactors' dispersed in a continuous medium, such as water. The concept of nanoreactors is based on the proposal that inside each miniemulsion droplet, generally in the order of 30–500 nm, a hypothetical bulk polymerization would take place, allowing in this way the performance of a whole variety of polymer reactions.[11] Among many different applications that have been developed for this technique, miniemulsion has been shown to be a powerful approach for the preparation of hybrid polymer nanoparticles such as polymer-polymer hybrids,[12] polymer-silica particles,[13] encapsulation of a liquid,[14] encapsulation of pigments,[15,16] and others.[11,17] However, when using miniemulsion to obtain polymer clay nanocomposites, the treatment of the clay is a determining factor to the formation of nanocomposite.[18,19] The interlayer spacing must increase and become hydrophobic to allow the transit of monomers and improve the chances of intercalation or exfoliation.

The incorporation of layered silicates (nanocharges) could generate products of remarkable improvements when compared to the matrix polymers alone or conventional microcomposites. Improvements can include superior storage modulus, in both solid and melt states, a decrease in permeability to liquids and gases, increased thermal resistance, and so forth.[20,21] In this work styrene/acrylate copolymers were synthesized by miniemulsion polymerization and the incorporation of a Brazilian MMT to this copolymer was studied. In particular, three different methods of clay treatment and their influences on the final properties of the composites obtained were evaluated.

Experimental

Materials

Sodium montmorillonite (Na^+-MMT) with a cation exchange capacity (CEC) of 75 meq/100 g was used in this work. This clay originates from a source of Campina Grande, State of Paraíba, Brazil and was supplied by Bentonite União Nordeste under the commercial name Brasgel. Cetyltrimethyl ammonium chloride (CTAC), from Clariant was used to modify the clay. Styrene was supplied by IQT. Butyl acrylate was kindly furnished by TEKNO. The initiator ammonium persulfate (APS) and the surfactant sodium dodecyl sulphate (SDS) were kindly furnished by RHODIA Brazil. The co-stabilizer n-hexadecane was purchased from Sigma-Aldrich. All reagents were used as received. Deionized water was used throughout the work.

Preparation of Organically Modified Montmorillonites

Na^+-MMT was ground and sieved so that only the granulometry less than 38 μm was selected. The measured specific surface area of the MMT particles was 76.9 m^2/g, determined in a Micromeritics ASAP 2010 instrument, using N_2 gas and BET method. The organically modified MMT were prepared as follows: 32 g of Na^+-MMT was dispersed in 800 mL of deionized water. The suspension was stirred for about 30 min

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(Methods A and B) or 48 hours (Method C). A water solution of Cetyltrimethyl ammonium chloride was slowly added to the Na^+-MMT suspension at room temperature (Method A) and at 60 °C (Methods B and C). The concentration of CTAC used was 1.3 CEC of the sodium montmorillonite. Then, the suspension was stirred for: 30 min at 1000 rpm (Method A), and 60 min at 200 rpm (Methods B and C). The organoclays were washed to eliminate free chloride anions. The clays were further dried at room temperature.

Polymerizations

Table 1 shows the formulation used in the experiments. Styrene (18 g) and butyl acrylate (22 g) were placed in a container with 2 g of hexadecane and 1.2 g of organically modified MMT and stirred for 20 h (swelling time). The organic phase was poured under strong agitation into another container with 190 g of deionized water and 0.8 g of SDS. The dispersion was later sonicated for 140 s, at an output of 9 (Sonics VC 375). To avoid polymerization by heating, the dispersion was placed in an ice-bath during sonication. Immediately after sonication, the miniemulsion was transferred to a 250-mL glass reactor equipped with nitrogen purging tube, condenser, temperature controller, and stirrer. To start the polymerization, the temperature was increased to 70 °C, and a solution of 200 mg of APS in 10 g of deionized water was added. The reactor was continuously purged with nitrogen during polymerization which was carried out for 6h. Samples of 5–6 g were removed periodically from the reactor with a syringe for conversion analysis. The same procedure was followed for the polymerization of the latex with Na^+-MMT and one experiment was carried out with no clay addition for reference.

Table 1.
Regular recipe.

Phase	Component	g
Organic	Styrene	18.0*
	Butyl Acrylate	22.0*
	Modified MMT	1.2**
	Hexadecane	2.0
Aqueous	SDS	0.8
	APS	0.2
	D.I. Water	200.0

* Sty/BuA ratio: 45/55 wt%.
** 3% based on the monomers.

Characterizations

All clay samples, hybrids and pure films were analyzed by X-ray diffraction (XRD) using a Philips X'Pert MPD diffractometer with Cu kα radiation and scanning rate of $1^\circ(2\theta)$/min. For the preparation of films of the materials after polymerization, 6 ml of latex were dried in an 80×35 mm glass surface at room temperature. Particle size measurements were carried out on a Malvern Zetasizer 1000 at 25 °C at a fixed angle of 90°. The diluent was an aqueous solution of SDS at the same concentration as the one used in all recipes. This procedure was adopted to reduce the dilution effect on particle stability.[17] Conversions were determined by gravimetric analysis. Coagulum contents were determined in relation to the theoretical solids total mass of each synthesis. The latexes were filtrated in a 270 mesh sieve, the coagulum retained was washed to withdraw the latex particles adsorbed on it and dried in a laboratory electric oven with air circulating system at 70 °C for 2 hours. Rheological tests were carried out using a controlled strain rheometer (TA Instruments ARES RLII). A parallel-plate configuration was used with a gap size of 0.70 mm and a plate diameter of 25 mm. The experiments were carried out at a temperature of 170 °C, under a nitrogen atmosphere. Strain and stress sweep tests were performed for all samples to define the linear viscoelasticity region. Dynamic frequency sweeps were performed for the hybrid and pure films. Dynamic-mechanical thermal analysis (DMTA) of films were carried out in a DMA-2980 TA-Instruments equipment with tension mode, from −50 to 150 °C with a heating rate of 3 °C/min, at 1 Hz of frequency. For the preparation of the sample films for SAOS and DMTA, the

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latexes were placed in silicon molds (125 × 80 × 5 mm) and heated in a laboratory electric oven with air circulating system at 30 °C for evaporation of the liquid phase of the latexes. The microstructure of films were characterized by transmission electron microscopy (TEM) using a Jeol JEM-1010. Thin films of latex samples were formed onto formvar/carbon-coated copper grid. Cobb tests were performed in a TESTE COBB, Regmed – Indústria Técnica de Precisão aparatus according to ABCP P.14/83 standard procedure. Films of 8–9 g/m^2 were prepared in a paperboard of 270–280 g/m^2 using a COATER RK 303, RK Print-Coat Instruments application desk, drying the latexes in a laboratory electric oven with air circulating system at 120 °C for 1 minute.

Results and Discussions

Clay Modification

Figure 1 presents the XRD patterns of the modified clays using the different methods reported above. Table 2 presents the basal spacing of the different clays.

It can be seen that the interlayer spacing was increased when using either of the three methods described above. It can also be seen that the organophilic MMT prepared by Method A presents a larger basal spacing than the one prepared using Method B indicating that increasing the reaction temperature does not result in an increase of basal spacing. The results presented in Table 2 seem to indicate that increasing the reaction temperature results in an increase of basal spacing only if the swelling time is increased. More details will be reported in another communication.

Table 2.
Basal spacing (d_{001}) values of montmorillonites before and after substitution of metal cations by organic cations.

Material	d_{001} (nm)
Na^+-MMT	1.42
CTA^+-MMT (Meth. A)	4.25
CTA^+-MMT (Meth. B)	2.76
CTA^+-MMT (Meth. C)	3.85

Polymerization and Latex Characterization

Figures 2 shows a comparison of the reaction conversion as a function of time during the reaction for the different samples studied. Table 3 presents total solid contents (TSC), particle diameter (DP), final conversion and coagulum contents of the latexes obtained after polymerization. It can be seen from Figure 2 that the addition of MMT does not seem to affect the reaction kinetics and final conversion and that large conversion % (larger

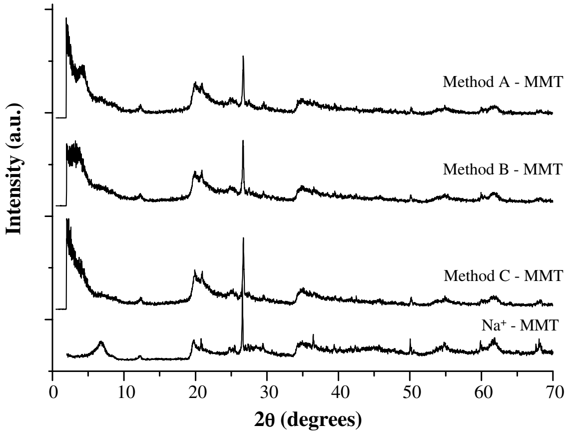

Figure 1.
XDR patterns of montmorillonites before and after substitution of metal cations by organic cations.

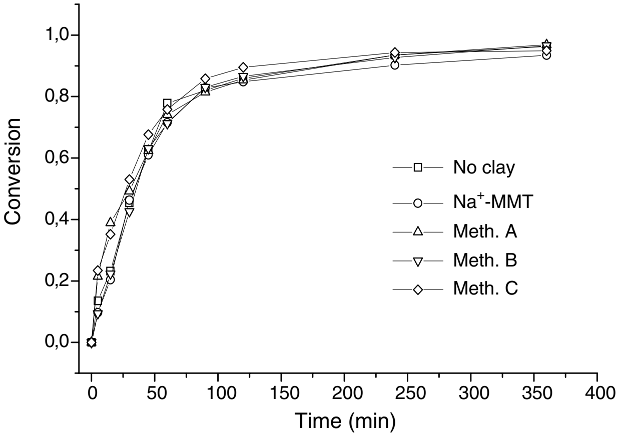

Figure 2.
Conversion *versus* time plot.

than 90%) are obtained for all the synthesis performed here.

The results presented in Table 3 show that an increase in particle size was observed when adding organophilic MMT to the reacting medium. This increase was not observed when adding Na^+-MMT. After organic modification the clay turns from hydrophilic to hydrophobic and most likely is located within the miniemulsion droplets explaining the increase of particle size. Na^+-MMT is hydrophilic and probably was dispersed in the water. The results presented in Table 3 also indicate that the particle size increased in a larger extent when adding the clays prepared using Methods A and C which correspond to the larger basal spacing (see Table 2).

Table 3.
Latex properties.$^{a)}$

Entry	TSC	DP	Conversion	Coagulum
	%	nm	%	%
No clay	16.3	118.9	96.3	0
Na^+-MMT	17.0	117.1	93.4	0.3
Method A	17.5	132.2	96.8	0.1
Method B	17.5	121.3	96.5	0.1
Method C	17.1	130.4	94.9	0.1

TSC – Total solid contents, DP – Particle diameter.
$^{a)}$ All data refer to the products obtained after 6h polymerization.

It can also be seen from the results presented Table 3 that the coagulum contents of the latexes obtained after polymerization were very small for all polymerizations indicating a good stability of the latexes.

Material Characterization

Figure 3 (a) presents the XRD patters of the materials obtained after polymerization in presence of the clays studied and Figure 3 (b) shows the detail of the region marked in (a).

It can be seen that only the film prepared with Na^+-MMT shows the peak corresponding to the basal spacing (Figure 3b): the interlayer spacing in that case increased from 1.42 (see Table 2) to 3.95 nm. This increase could probably originate from intercalation of polymeric molecules within the galleries of the hydrophilic silicate. Furthermore, when organophilic MMT was added to the system, the films presented much better clay dispersion, and an exfoliated morphology might be obtained.

Figure 4 shows the storage modulus $G'(\omega)$ for pure film and hybrid films containing sodium and organophilic MMT.

It can be noticed that for pure film, at low frequencies the storage modulus presents a typical terminal behavior. However, the storage modulus curves of the hybrid

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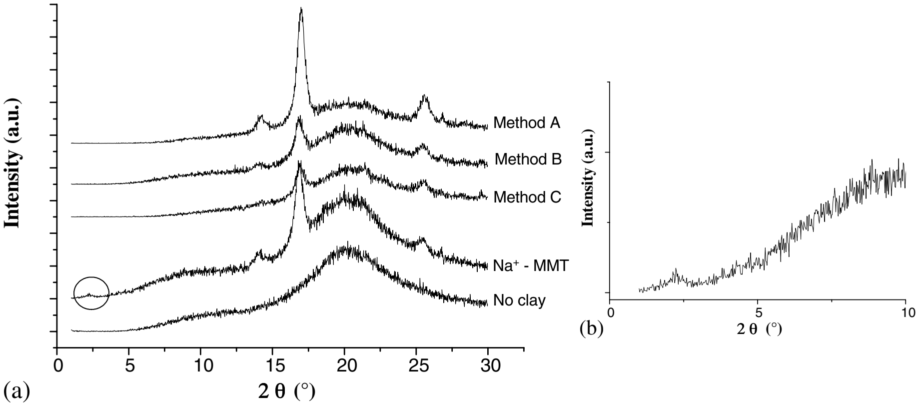

Figure 3.
(a) XDR patterns of polymeric materials obtained after polymerization in presence of montmorillonites, (b) the detail of the region marked in (a).

materials show a tendency of deviation from this terminal behavior, especially in the case of the material prepared using Method A-MMT. This increase of elasticity at small frequencies is normally observed for exfoliated nanocomposites. It has been shown in the literature that when exfoliated structures are obtained a deviation from the terminal behavior, which can result in the presence of a plateau at low frequencies, is observed.[22] This deviation from typical terminal behavior was explained by the formation of a tridimensional clay network which increases the elastic response of the molten polymer resulting in a material that may be considered pseudo-solidlike.[23] In the case of intercalated samples, this deviation is usually not observed.[23,24] Therefore, the results presented here indicate that the hybrid films prepared with Method A–MMT might present a predominantly exfoliated microstructure. The

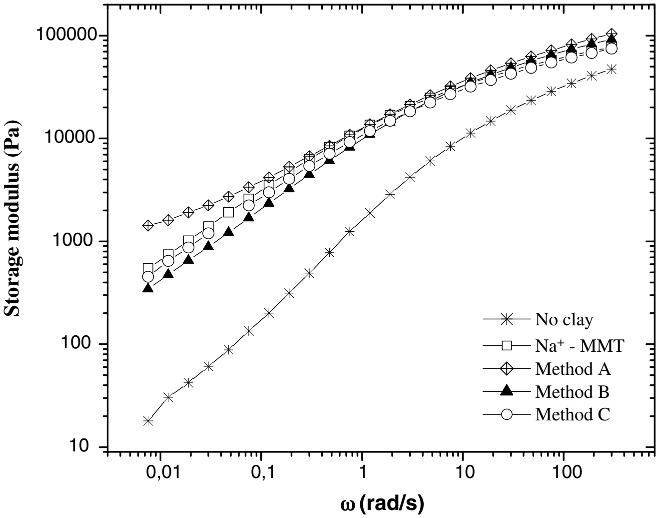

Figure 4.
Curve Storage modulus at a temperature of 170 °C for all materials studied.

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difference observed between the hybrid films prepared using the three different organophilic clays indicate that an efficient cation exchange is desirable to obtain exfoliated structure by miniemulsion polymerization.

Figure 5 shows storage modulus (E') as a function of temperature for the different samples studied. Table 4 presents E' at temperatures of -40 and $80\,^{\circ}\mathrm{C}$ and glass transition temperature (T_g) for the different samples studied.

It can be seen from Figure 5 and Table 4 that the addition of inorganic material always resulted in an increase of dynamic modulus. It can be also seen that when Method A-MMT and Method C-MMT were added to the copolymer larger increases of E′ (57.7 and 36.9% respectively) were observed than when adding $\mathrm{Na^+}$-MMT or Method B-MMT. Similar differences were also observed at temperatures larger than T_α. These results indicate that when Method A-MMT was added to the polymer a nanocomposite could have been obtained. These results are in good agreement with the results of SAOS presented above. It can also be seen in Table 4 that the addition of clay does not seem to affect the values of T_g.

Table 4.
DTMA data.

Entry	E’ at −40 °C (MPa)	E’ at 80 °C (MPa)	T_g (°C)[a]
No Clay	1110	0.2040	27.7
$\mathrm{Na^+}$-MMT	1290	0.4650	25.5
Method A	1750	0.6560	26.8
Method B	1100	0.4430	26.4
Method C	1520	0.9790	26.0

[a] Determined by temperature peaks of tan δ.

Figures 6–8 show typical morphologies of the copolymer films synthesized in the presence of clay for the different methods of clay modification. The micrographs indicate the presence of an exfoliated structure with the presence of small tactoids in the case of Figure 6, the absence of intercalation or exfoliation in the case of Figure 7 and an intermediate behavior in the case of Figure 8.

Cobb test is a standard test method to evaluate technologically the absorption of water by porous materials such as paper. In these tests the amount of liquid that is

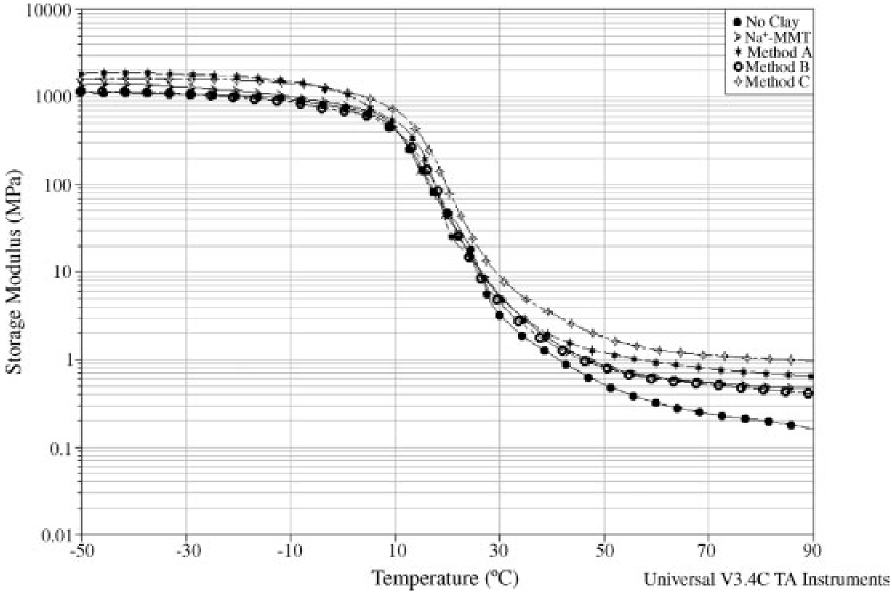

Figure 5.
Dynamic storage modulus of pure copolymer and composites as a function of temperature.

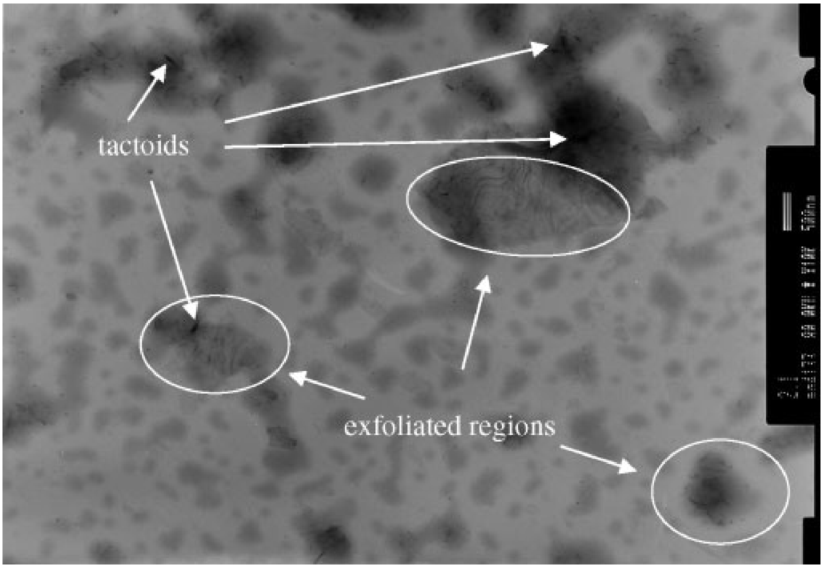

Figure 6.
TEM images of material obtained by polymerization in presence of MMT organically modified by Method A.

absorbed by a porous material in contact with that liquid for a certain amount of time is measured. The tests can be used as an indicator of hidrofobicity of a porous material. Table 5 presents the water absorption by Cobb tests of sheets of paper that were coated with the different films obtained here. It can be seen from Table 5 that once method A-MMT was incorporated to the copolymer a drastic decrease in water adsorption of the coated paper was observed.

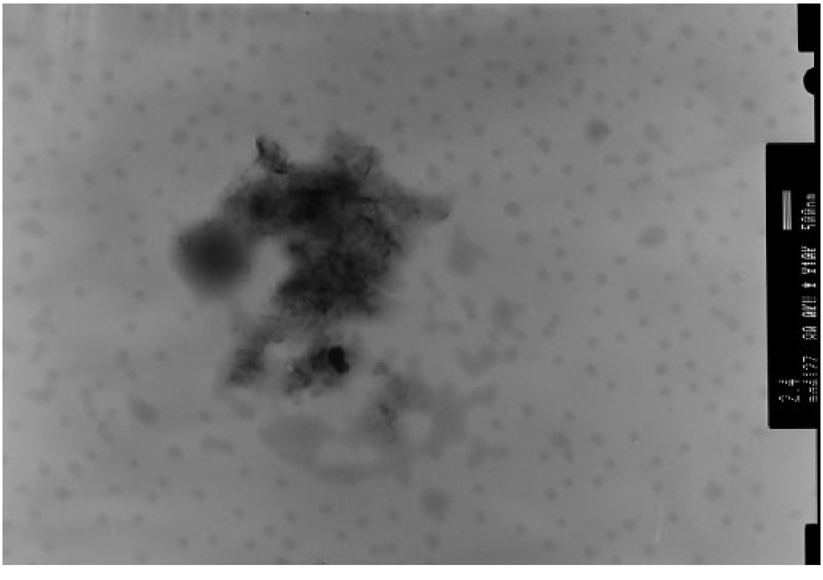

Figure 7.
TEM images of material obtained by polymerization in presence of MMT organically modified by Method B.

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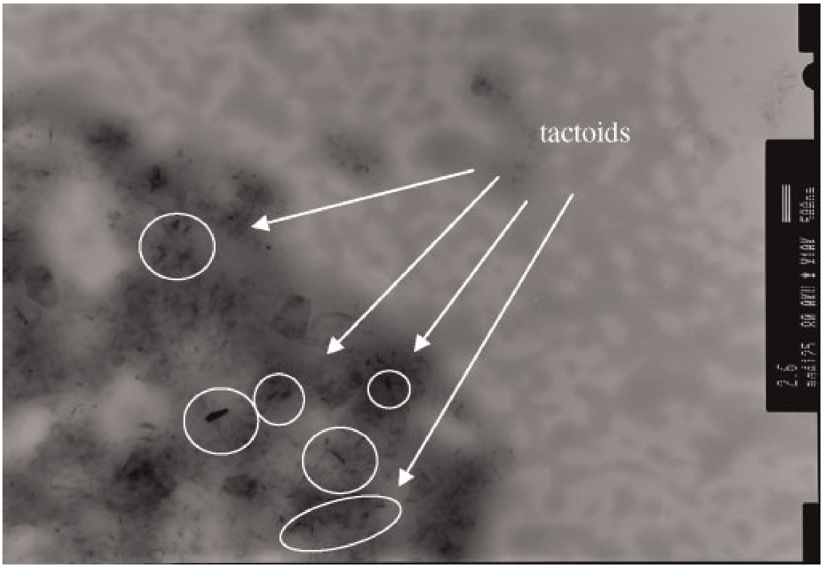

Figure 8.
TEM images of material obtained by polymerization in presence of MMT organically modified by Method C.

Table 5.
Cobb test results.

Sample	Paper absorption (g/m^2)	
	120 s	60 min
No Clay	23.5	116
Na$^+$-MMT	11.9	107
Method A	5.4	62
Method B	19.9	116
Method C	19.2	120

Conclusions

Hybrid poly(styrene-co-butyl acrylate) latexes to which 3 wt % organically modified MMT was added have been synthesized by *in situ* miniemulsion polymerization. Three different methodologies to modify the MMT were tested. Analysis of XRD showed an increase of MMT basal spacing after organic modification for all methodologies tested. The experimental results showed that the addition of clay did not influence the polymerization kinetics. Latexes with good colloidal stability were obtained. The XRD analyses indicated that the MMT basal spacing further increased after polymerization for all of the tree modified clays indicating that *in situ* polymerization occurred. The rheological characterization of the films indicated that one of the methodologies used to modify the clay might have led to an exfoliated structure. The DTMA results showed an improvement of mechanical properties for all the composites obtained. A larger increase in modulus was obtained when using the modified clay that might have led to an exfoliated structure. TEM images suggested intercalation or even exfoliation but clearly identify silicates tactoids evidencing limited dispersion of the silicate platelets in the polymeric matrix. The addition of clay reduced water permeability.

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