Influence of Granulometry and Organic Treatment of a Brazilian Montmorillonite on the Properties of Poly(styrene-*co-n*-butyl acrylate)/Layered Silicate Nanocomposites Prepared by Miniemulsion Polymerization

Raul P. Moraes,[1] Ticiane S. Valera,[2] Nicole R. Demarquette,[2] Pedro C. Oliveira,[1] Maria Lúcia C. P. da Silva,[1] Amilton M. Santos[1]

[1]*Departament of Chemical Engineering, Engineering School of Lorena, University of São Paulo, 12600-970, Lorena, SP, Brazil*
[2]*Department of Metallurgical and Materials Engineering, Polytechnic School, University of São Paulo, 05508-900, São Paulo, SP, Brazil*

ABSTRACT: The influence of granulometry and organic treatment of a Brazilian montmorillonite (MMT) clay on the synthesis and properties of poly(styrene-*co-n*-butyl acrylate)/layered silicate nanocomposites was studied. Hybrid latexes of poly(styrene-*co*-butyl acrylate)/MMT were synthesized via miniemulsion polymerization using either sodium or organically modified MMT. Five clay granulometries ranging from clay particles smaller than 75 μm to colloidal size were selected. The size of the clay particles was evaluated by specific surface area measurements (BET). Cetyl trimethyl ammonium chloride was used as an organic modifier to enhance the clay compatibility with the monomer phase before polymerization and to improve the clay distribution and dispersion within the polymeric matrix after polymerization. The sodium and organically modified natural clays as well as the composites were characterized by X-ray diffraction analysis. The latexes were characterized by dynamic light scattering. The mechanical, thermal, and rheological properties of the composites obtained were characterized by dynamical-mechanical analysis, thermogravimetry, and small amplitude oscillatory shear tests, respectively. The results showed that smaller the size of the organically modified MMT, the higher the degree of exfoliation of nanoplatelets. Hybrid latexes in presence of Na-MMT resulted in materials with intercalated structures. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1949–1958, 2009

Key words: hybrid latexes; clay; miniemulsion polymerization; nanocomposites; colloids

INTRODUCTION

Clay-containing polymer nanocomposites have gained both academic and industrial attention in the early 90's when Toyota research group[1] reported superior properties of these materials when compared with the ones of (micro) composites and unfilled polymers. Since then, clay-containing nanocomposites have been obtained using a large variety of polymers.[2,3] When working with clay-containing polymer nanocomposites, it is very important to obtain a good dispersion of the clay platelet within the polymer. This good dispersion will result in improved properties of the materials such as flame retardancy, heat and dimensional stability, barrier to liquids and gases, superior storage modulus in both solid and melt states among others.[4–6]

Clay-containing polymer nanocomposites can be obtained using different techniques, these include exfoliation-adsorption,[7–10] *in situ* intercalative polymerization,[11–14] and melt blending.[15–17] In the case of materials to be used as surface coatings, the product needs to be dispersed in water. These aqueous dispersions can be obtained either by emulsion[8,18–20] or miniemulsion polymerization.[9–12] Two main processes have been used to produce those dispersions; (i) *in situ* intercalative polymerization: in this case, the layered silicate is modified organically by cation exchange[11,12,14,18,21] or covalent bounding and later mixed with the reactants[14,20]; (ii) exfoliation-adsorption, when hydrophilic clays are delaminated in the aqueous phase prior to polymer intercalation. In the later case, the delaminated silicate layer may be attracted to the polymer particle surface by

electrostatic[8,10] or physical-chemical[9] attraction. When there is no attraction between the polymer particle and the delaminated silicate, the nanocomposite may be formed by solvent evaporation[7] or addition of a coagulant agent (heterocoagulation).[22]

The source of layered silicates (or clays) may be synthetic[8,14] or natural.[7,12] Hectorite,[8,14] saponite,[11,16] and montmorillonite (MMT)[7,12,21,22] are among the most used clays to produce nanocomposites. However, it is well known that MMT presents larger platelet size when compared with hectorite and saponite,[11,20] what may turn the production of hybrid latexes difficult.

In this work, polymeric dispersions (latexes), were synthesized using the miniemulsion technique to produce hybrid latexes of poly(styrene-co-butyl acrylate) reinforced with a Brazilian MMT. Experiments were carried out using either sodium montmorillonite (Na-MMT) or organically modified MMT (OMMT). The organic treatment was carried out by ion exchange using cetyltrimethyl ammonium chloride (CTAC), to improve the compatibility with the monomers and the polymer matrix. The influence of clay granulometry and clay treatment on the synthesis and properties of composites was evaluated.

EXPERIMENTAL SECTION

Materials

Natural Na-MMT with a cation exchange capacity (CEC) of 75 meq/100 g, from a source of Campina Grande, State of Paraíba, Brazil, was supplied by Bentonite União Nordeste, under the commercial name Brasgel PBS-50 (BUN). This clay exists in great abundance and therefore may be explored for a lower cost compared with commonly used commercial clays. CTAC, from Clariant, (Suzano, Satet of São Paulo, Brazil) was used to modify the clay. The monomers styrene (Sty, 99%) and butyl acrylate (BuA, ≥99%), the initiator ammonium persulfate (APS, ≥98%) and the costabilizer n-hexadecane (≥99%) were purchased from Sigma-Aldrich. Sodium dodecyl sulphate (SDS, 98.9%) was provided by RHODIA, Brazil. All reagents were used as received and deionized water was used throughout the work.

Preparation of organically modified MMTs

Na-MMT was ground and sieved in standard American Society for Testing and Materials (ASTM) sieves so that four granulometries were tested: smaller than 75 μm (ASTM #200 sieve), 53 μm (ASTM #270 sieve), 45 μm (ASTM #325 sieve), and 38 μm (ASTM #400 sieve). A colloidal size clay particle suspension was also obtained from the clay particles smaller than 38 μm. The clay particles were added to a graduated cylinder containing 1 L of deionized water. The suspension was stirred. Then, in 48 h intervals, colloidal suspensions, corresponding to a volume of 200 mL, were continually colleted. 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. A water solution of CTAC was slowly added to the Na-MMT suspension at room temperature. The concentration of CTAC used was 1.3 CEC of the Na-MMT. Then, the suspension was stirred for 30 min at 1000 rpm. The organoclays were washed to eliminate free chloride anions. The clays were further dried at room temperature.

The nomenclature used for the MMT in the text is as follows: Na#X corresponds to Na-MMT with particle size smaller than ASTM sieve #X opening, and CTAC#X corresponds to the MMT organically modified with CTAC, with particle size smaller than ASTM sieve #X opening.

Hybrid latexes synthesis

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 (3% based on the monomers) 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 6 h. Samples of 5–6 g were removed periodically from the reactor with a syringe for conversion and particle size analyses. Films of the materials after polymerization were prepared depositing 6 mL of latex on a 80 × 35 mm^2 glass surface and dried at room temperature.

Characterizations

All clay samples, hybrids, and films were analyzed by X-ray diffraction (XRD) using a Philips X'Pert MPD diffractometer with Cu kα radiation (λ = 1.54056 Å) and scanning rate of 1° (2θ)/min. Particle size distribution of the clays was determined using a Malvern Mastersizer E instrument. For those measurements, the clay was dispersed in water under heavy agitation. No dispersing agent was added to the dispersion and agglomeration may have occurred during the measurements. Specific surface area (SSA) of the clays

was also determined using a Micrometrics ASAP 2010 instrument using the BET method with N_2 gas.

The latex particle sizes were determined using a Malvern Zetasizer 1000. To reduce the dilution effect on particle stability during the analyses, an aqueous solution saturated with monomers and containing SDS, at the same concentration as the one used in all recipes, was used as eluent.[23–25] Conversions were determined by gravimetric analysis. Dried coagulum contents were determined in terms of the theoretical solids total mass of each synthesis by filtering the latexes in an ASTM #270 sieve. Some latex samples were examined by transmission electron microscopy (TEM) operating at an accelerating voltage of 80 kV [Philips CM 120, Centre Technologique des Microstructures (CTμ), Claude Bernard University, Lyon, France]. The films for dynamic mechanical analyses (DMA), thermogravimetry analyses (TG), and small amplitude oscillatory shear analyses were prepared by evaporating the latexes, placed in silicon molds ($125 \times 80 \times 5$ mm^3), at room temperature. DMAs were carried out using a DMA-2980 TA-Instruments equipment, using the tension mode, from -50 to $150°C$, with a heating rate of $3°C/min$, at a frequency of 1 Hz. TG analyses were performed using a Shimadzu TGA-50. The samples were heated until $900°C$ at a $20°C/min$ rate, under nitrogen atmosphere. The rheological tests of the films were carried out using a Rheometric Scientific SR-5000 rheometer. A parallel-plate configuration was used with a gap size of 0.8 mm and a plate diameter of 25 mm at a temperature $170°C$, under a nitrogen atmosphere. Stress sweep tests were performed to define the linear viscoelasticity region. Dynamic frequency sweeps were performed for the hybrid and pure films.

RESULTS AND DISCUSSIONS

Clay characterization

Table I presents the clay's average particle size obtained using a Malvern Mastersizer E instrument and the SSA of clay particles. It can be seen from Table I that the disaggregation process resulted in a reduction of the amount of large particles. The SSA presented in Table I confirms the average particle size

TABLE I
Average Particle Size and the SSA of Clay Particles

Sample	SSA (m^2/g)	Average particle size (μm)	PDI
Na#200	66.9	5.8	3.9
Na#270	72.9	4.2	2.3
Na#325	76.7	4.0	2.0
Na#400	86.9	3.7	1.9
Na (colloidal size clay particle)	104.4	1.4	2.9

TABLE II
Basal Spacing of Clays and Composite Materials: Effect of the Clay Granulometry

	Basal spacing (Å)			
	d-Na[a]	d-org[b]	d-Na final[c]	d-org final[d]
#200	14.2	30.5	38.7	–
#270	14.1	30.5	42.0	45.0
#325	12.0	27.8	38.7	42.8
#400	12.9	39.2	53.8	Exfoliated
Colloidal	12.9	45.0	39.2	Exfoliated

[a] Basal spacing of Na-MMT.
[b] Basal spacing of OMMT.
[c and d] Basal spacings of Na-MMT and OMMT composite materials, respectively.

results since the surface area increases when the particle size decreases.

Table II presents the basal spacing for the Na-MMT (d-Na), OMMT (d-org) clays, and composites obtained. "d-Na final" corresponds to the spacing for the composites obtained using Na-MMT and "d-org final" corresponds to the spacing for the composites obtained using the organophilic clay. It can be seen from Table II that the granulometry does not affect the basal spacing of the clay before treatment with CTAC. It can also be seen that the basal spacing of the clay after treatment with CTAC increases with decreasing clay granulometry. Decreasing the size of the agglomerates increases the surface area and makes it easier for the CTAC molecules to penetrate the interlayer spacing. The values of the basal spacing for the composites will be discussed further in the article.

Nanocomposite latexes

Figures 1–6 show conversion versus time plots (Figs. 1 and 2), evolution of droplet/particle size with conversion (Figs. 3 and 4), evolution of pH of polymerization medium versus time (Figs. 5 and 6) for the
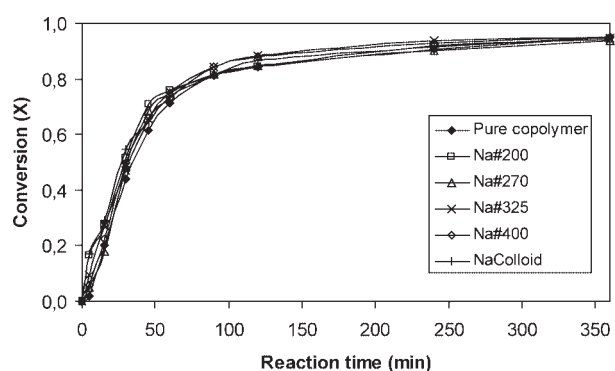

Figure 1 Conversion versus time plot: syntheses carried out with sodium montmorillonites.
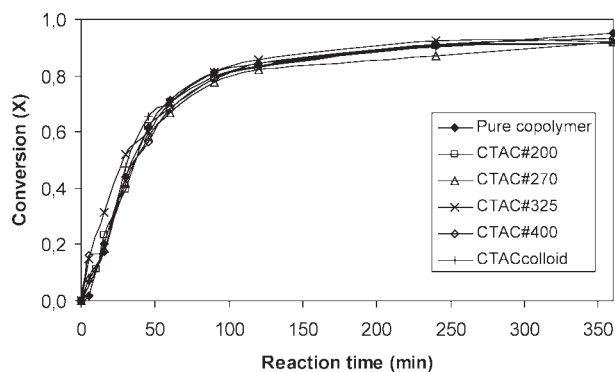
Figure 2 Conversion versus time plot: syntheses carried out with organically modified montmorillonites.

Figure 4 Evolution of droplet/particle size: syntheses carried out with organically modified montmorillonites.

synthesis of nanocomposites using different clay granulometries of Na-MMT and OMMT, respectively. Table III presents a summary of those characterizations.

By analyzing the results presented in Figures 1–6 and Table III, the following observations can be done:

1. No significant effect in conversion can be observed when the granulometry of the clays is changed.
2. The particle size tends to increase slightly with increasing clay granulometry for both types of clay (pristine Na-clay and organophilic clay). However, it is important to point out that the light scattering results may be biased by the presence of clay particles and not representative of the size of the latex droplets and particles.
3. In the case of polymerization without clay addition, the pH is reduced instantaneously at the beginning of the reaction. This behavior is well known and can be explained by the formation of sulfuric acid as a subproduct of the initiator (APS) decomposition.[26] When clays are present in the reacting medium, it takes longer times for the pH to decrease (buffer effect).[27,28] The extent
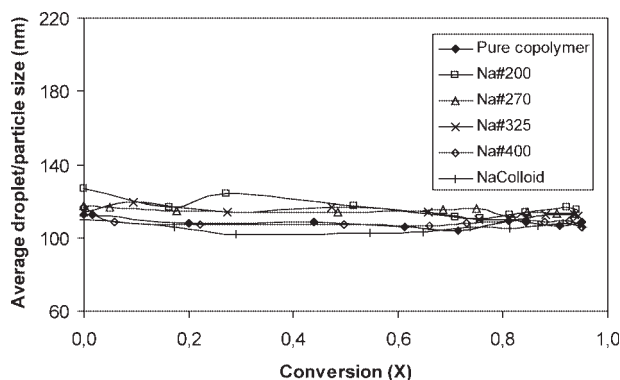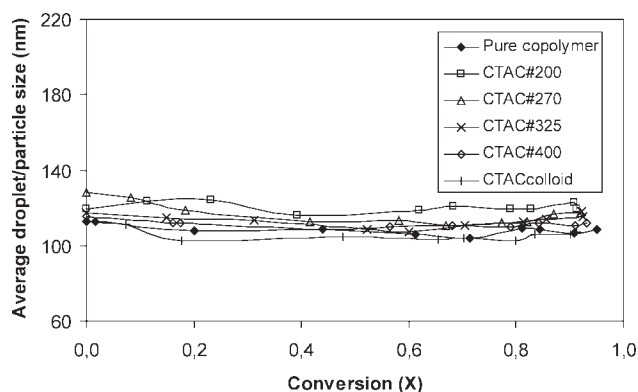
of this buffer effect is not affected by the clay granulometry.

4. There is a difference between the buffer effect for sodium and organically modified clays. All the Na-MMT promotes longer pH stability than OMMT. This effect may be attributed to the treatment of natural MMT with Na_2CO_3, which is one of the steps in the transformation of polycationic clay into Na-MMT. Na_2CO_3 may be considered as the responsible for the increment in buffer effect because of its alkaline characteristics.
5. No important coagulum content was observed in these sets of experiments. The highest content of coagulum was obtained for CTAC#200 clay (1.37%). This higher instability could be attributed to clay interactions (face-to-edge) at lower pH.[29]

Figure 7 presents the different possible morphologies of latex that have been suggested in the literature for hybrid particles polymer/clay. Figure 7(a) presents the case when the organoclays are encapsulated inside the monomer droplets. This is usually observed for very small clay layers that are typical of synthetic clays such as Laponites[11] or when larger
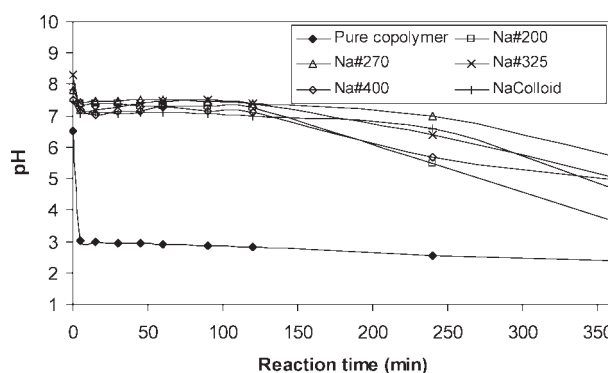

Figure 3 Evolution of droplet/particle size: syntheses carried out with sodium montmorillonites.

Figure 5 Evolution of pH versus time: syntheses carried out with sodium montmorillonites.
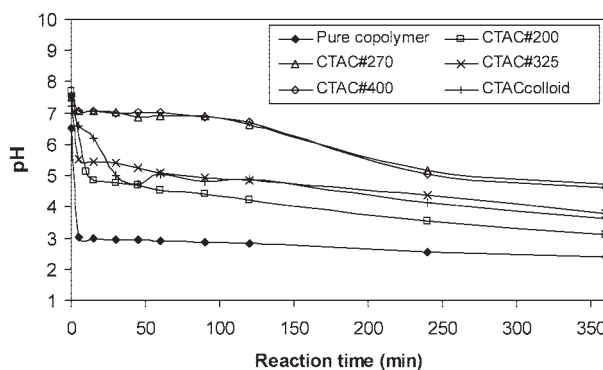
Figure 6 Evolution of pH versus time: syntheses carried out with organically modified montmorillonites.

layers are broken into smaller pieces. Figure 7(b) presents the case when the clay layers are adsorbed at the surface of polymer droplets. This can be obtained using clays presenting very small layer size (ex laponite) and when the clay surface is modified to enhance physico-chemical interaction between the clay and polymer. This type of morphology has been observed by Negrete-Herrera et al.[14] in the emulsion polymerization, of styrene with butyl acrylate, in presence of silylated and cation exchanged Laponite. When the clay layer size is small, but for different chemical treatment, morphologies such as the ones schematically presented in Figure 7(c) may be obtained. This morphology is very similar to the one reported by Voorn et al.,[20] for PMMA/silylated Laponite system, obtained by emulsion polymerization, and named by the authors as dumbbell-like or snowman-like morphology. When the size of the layer increases, more than two polymer particles (which is the case of the snowman morphology) can be adsorbed at the layer surface as shown in Figure 7(d,e). As the number of polymer particles adsorbed at the layer surface increases, coalescence between those will occur to turn the system more thermodynamically stable. Figure 8 presents a typical morphology of the latex obtained in this work. In this
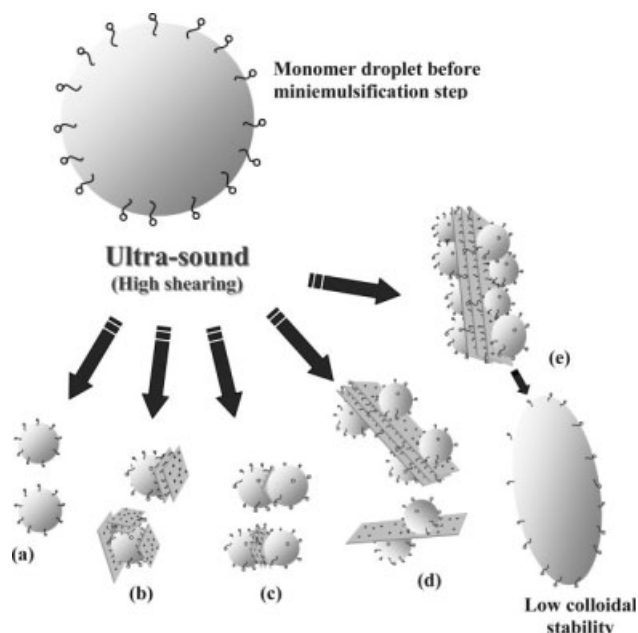

Figure 7 Schematic illustration of the diverse possible morphologies of polymer/organophilic MMT during the miniemulsification step and miniemulsion polymerization: (a) small clay particles encapsulation, (b) clay particles acting at the surfaces of droplets/particles, (c) dumbbell-like or snowman-like morphology, (d) dispersed silicate platelets with miniemulsion droplets or polymer particles adsorbed to its surface, and (e) encapsulation of a large clay particle and probable colloidal instability.

case, the morphology of the latex obtained with the addition of colloidal Na-MMT [Fig. 8(a)] and of colloidal OMMT [Fig. 8(b)] is shown. It can be seen that a morphology intermediate to the ones shown schematically in Figure 7(b,c) was obtained. When colloidal Na-MMT was added to the latex the clay particles locate themselves at the surface of the latex particles preventing coalescence of the particles [Fig. 8(a)]. When colloidal OMMT was added to the latex, the coverage of the latex particles is smaller and some coalescence can be observed [Fig. 8(b)]. This coalescence is expected to occur during the grid preparation for the TEM analysis because the glass transition temperature (T_g) of the copolymer is around room temperature (24–28°C),[12] causing the polymer particles to stick to each other during evaporation of the water. Nevertheless, it is possible to visualize that the O-MMT are well dispersed into the polymeric matrix, what can be attributed to a better compatibility offered by the organic treatment.

Composites properties

It can be seen from Table II that the composite materials obtained using Na-MMT present an increase of basal spacing from around 12 Å to around 40 Å independently of the granulometry of the clay

TABLE III
Hybrid Latexes Characterizations[a]

	DP (nm)	PDI	pH	Coag. (%)	Conv. (%)
Pure copolymer	108	0.067	2.4	0.05	95.0
Na#200	115	0.050	3.7	0.14	93.7
Na#270	113	0.103	5.7	0.05	94.0
Na#325	112	0.050	5.7	0.06	94.4
Na#400	106	0.059	5.0	0.07	95.0
Na-Colloid	106	0.045	4.7	0.07	95.2
CTAC#200	120	0.031	3.1	1.37	91.3
CTAC#270	117	0.230	4.7	0.08	92.0
CTAC#325	118	0.186	3.8	0.17	92.1
CTAC#400	112	0.150	4.6	0.05	93.2
CTAC-colloid	108	0.256	3.6	0.16	91.3

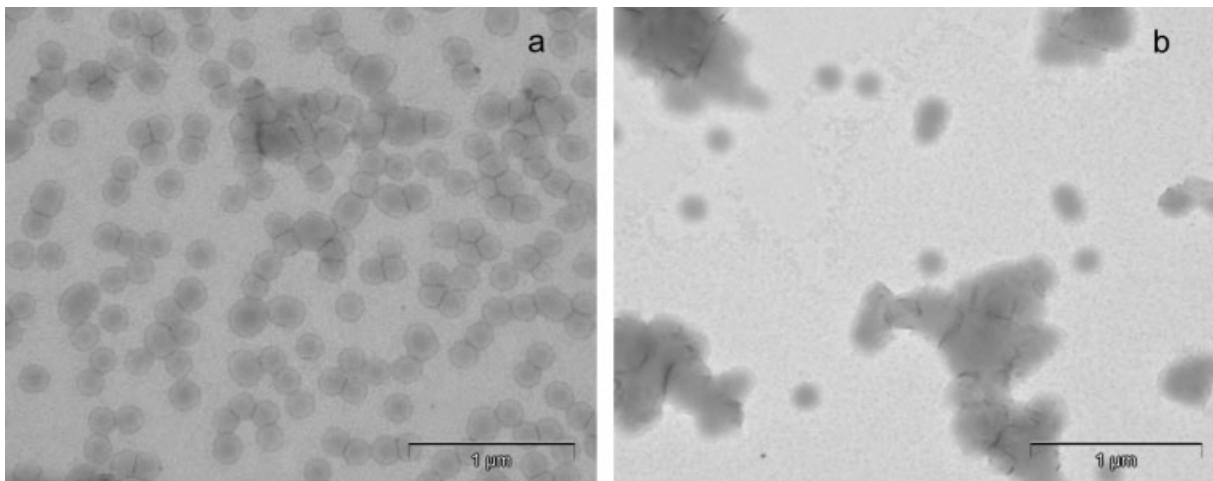[a] Data obtained after 6 h of polymerization.

Figure 8 TEM images of hybrid latexes with (a) Na-MMT colloidal and (b) OMMT colloidal.

(a slightly higher value is found for #400), indicating that intercalated morphologies might have been obtained. A different behavior can be observed for the composites materials obtained using the organophilic clays. In this case, smaller granulometries resulted in larger basal spacing and probably in exfoliation, mainly for CTAC#400 and CTAC-colloidal clay particles. This is probably due to the increase of surface area originated from the reduction of the granulometry: this increase of area facilitated the organic treatment and therefore an increase of the level of intercalation/exfoliation can be observed.

Dynamic-mechanical properties

Figures 9 and 10 present the results of DMA in terms of storage modulus (E') as a function of temperature for the pure copolymer and for the nanocomposites produced with different granulometries of Na-MMT and OMMT, respectively. Table IV presents, for all the materials, the values of E' at temperatures of −40 and 80°C.
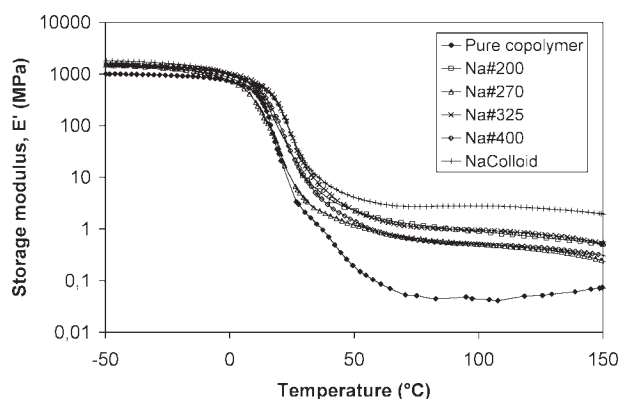
It can be seen from Figures 9 and 10 that only one principal transition is observed for the copolymer indicating that no composition drift occurred during the polymerization.

It can be also seen from Figures 9 and 10 and Table IV that the addition of inorganic material resulted in larger values of storage modulus in comparison with the ones of the pure copolymer for all granulometries, independently if the clays were organically modified or not, most likely due to the fact that nanocomposites were obtained.[4,6] Larger increases were obtained for CTAC#400 and CTAC-colloidal for which exfoliated morphologies must have been obtained as evidenced by the XRD results discussed earlier. Large increases of E' were also obtained for temperatures above T_g. This behavior may be associated with a sort of percolation phenomena, that is, the formation of a silicate platelet tridimensional network.[30]

It can be seen from Table IV that the decrease of granulometry does not influence the values of the modulus of the composites obtained using Na-MMT (with the exception of Na-Colloid), but has a large

Figure 9 Storage modulus as a function of the temperature: materials synthesized in presence of sodium montmorillonites.
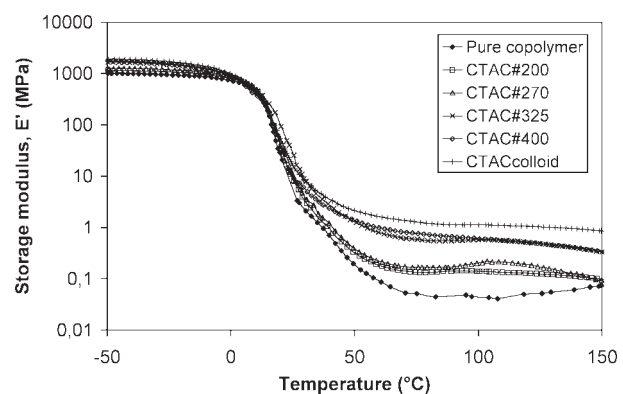

Figure 10 Storage modulus as a function of the temperature: materials synthesized in presence of organically modified montmorillonites.

TABLE IV
DMA Data for the Materials Produced Using the Different Granulometries of Na-MMT and OMMT

	E' at $-40°C$ (MPa)	E' at $80°C$ (MPa)
Pure copolymer	990	0.04
Na#200	1400	1.11
Na#270	1550	0.61
Na#325	1180	1.04
Na#400	1460	0.56
Na-Colloid	1750	2.72
CTAC#200	1130	0.13
CTAC#270	1250	0.17
CTAC#325	1630	0.55
CTAC#400	1720	0.72
CTAC-colloid	1820	1.20

effect on the values of the modulus of the composites obtained using organophilic clays. These results show that the increase of mechanical properties is not only due to an increase of interface area between the organic and inorganic material which increases the reinforcement effect[31] but also from a better silicate dispersion within the matrix as shown by the XRD results in Table I. When using Na-MMT, there is a lack of compatibility between the polymer and the inorganic material, promoting agglomeration and heterogeneity.[5]

Comparing the results from Table IV, it is possible to verify that at 80°C, for each specific granulometry, except for CTAC#400, all materials obtained using Na-MMT present superior storage modulus. Thus, the dual role played by organoclays, (a) as nanofiller leading to the increase of storage modulus and (b) as plasticizer leading to the decrease of storage modulus, as was suggested by Xie et al.,[32] seems to have been confirmed by these results. The plasticizing effect could be explained by different types of polymer/clay interactions. Shi et al.[33] verified that the matrix direct interaction with the clay basal plane

leads to higher increment of storage modulus than interactions between the matrix and the organic chains from the quaternary ammonium salts tethered to the clay basal planes.

It can be also seen from Table IV that at $-40°C$, for large granulometries (#200 and #270) the moduli of the hybrids materials obtained using Na-MMT are larger than the ones of the hybrid materials obtained using OMMT. A reverse trend is observed for the materials obtained with the clays with smaller granulometries. These results can be explained if we remember that the basal spacing of the clay after treatment with CTAC increases with decreasing clay granulometry.

Rheological properties

Figure 11(a,b) show, respectively, the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ for pure film and hybrid films containing sodium and organophilic clay. It can be seen from Figure 11 that the storage and loss moduli at low frequencies for the hybrid materials are larger than the ones of the pure films, except in the case of the material prepared using organically modified clay with particle size <45 μm (ASTM #325 sieve). For most of the materials studied in this work, G'' is greater than G' at low frequencies and a crossover point occurs at higher frequencies as is normally observed for most viscoelastic materials. It was observed that the crossover point occurs at lower frequency and higher modulus values with decreasing MMT particle size. In particular, in the case of CTAC#400 and CTAC-colloidal hybrid films no crossover point was observed. For CTAC#400 films, at lower frequencies, the G' and G'' curves overlap and at higher frequency, G' is higher than G'', whereas for CTAC-colloidal films, G' is always higher than G''. This increase of elasticity at small
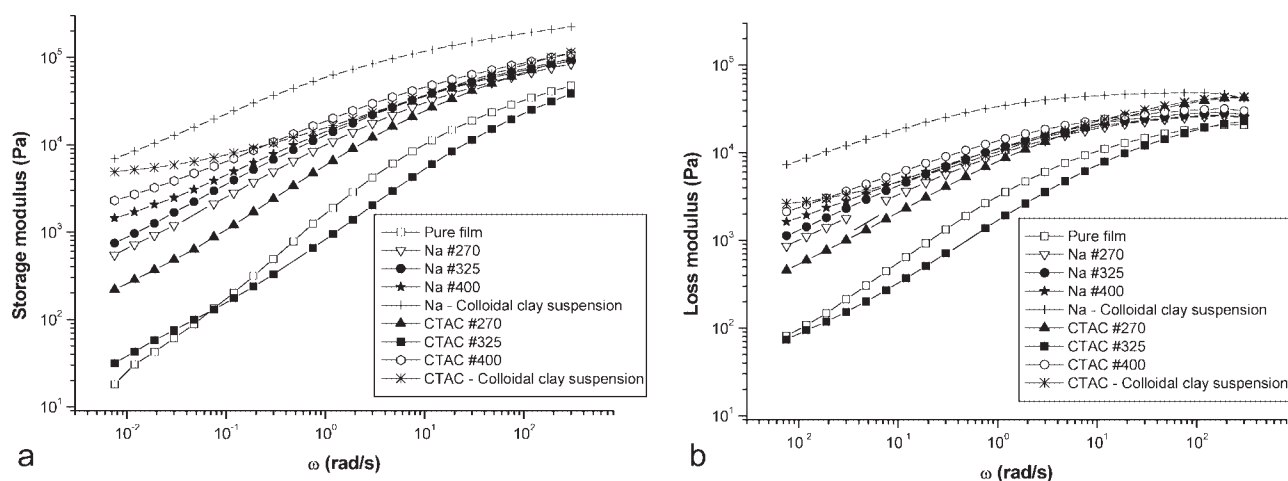
Figure 11 (a) Storage modulus and (b) loss modulus for pure and hybrid films containing sodium and organophilic MMT.
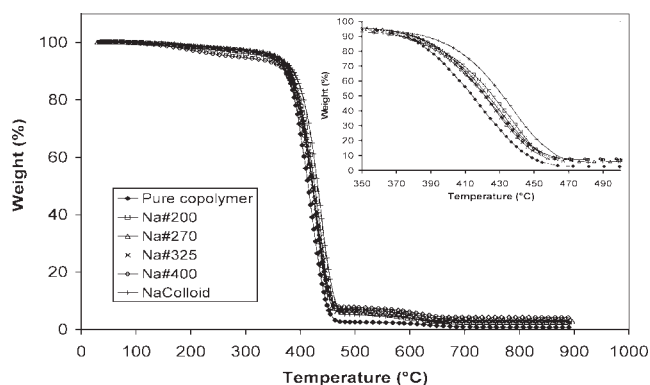
Figure 12 TG curves: materials synthesized in the presence of sodium clays; inset the region of higher weight loss in 1st event.

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.[34] In the case of intercalated samples, this deviation is usually not observed. Therefore, the results presented here indicate that the hybrid films might present regions with exfoliated structure. In particular, the hybrid films containing organoclays with the finest granulometries (<38 μm and the colloidal clay dispersion) presented more expressive deviations from terminal behavior, indicating that the amount of exfoliated regions increased, altering the hybrid material structure.

Thermal properties

Figures 12 and 13 present TG curves for the materials synthesized in this work.

Table V summarizes the data of TG analysis, in terms of temperature intervals (ΔT), weight loss percentage (wt %), and temperature of higher weight
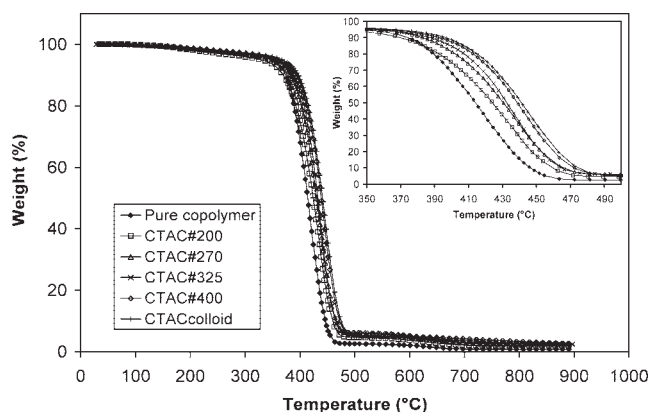

Figure 13 TG curves: materials synthesized in the presence of organically modified montmorillonites; inset the region of higher weight loss in 1st event.

TABLE V
TG Analysis Data from the Composite Materials Produced Using Na-MMT and OMMT at Different Granulometries and from the "Pure Copolymer" and "Na#200 Clay" as References

	ΔT (°C)	wt %	dm (°C)
Na#200—Clay	T_{room}, 250	7.4	79
	250–800	5.7	502
		Σ 13.1	
Pure copolymer	T_{room}, 800	99.3	420
Na#200	T_{room}, 500	93.5	437
	500–800	4.0	600
		Σ 97.5	
Na#270	T_{room}, 550	94.4	428
	550–800	3.1	620
		Σ 97.5	
Na#325	T_{room}, 500	93.2	429
	500–800	3.6	645
		Σ 96.8	
Na#400	T_{room}, 500	93.0	429
	500–800	3.5	624
		Σ 96.5	
Na-Colloid	T_{room}, 550	94.8	438
	550–800	3.5	645
		Σ 98.3	
CTAC#200	T_{room}, 550	96.4	434
	550–800	2.3	–
		Σ 98.7	
CTAC#270	T_{room}, 550	94.7	437
	550–800	3.2	–
		Σ 97.9	
CTAC#325	T_{room}, 550	95.0	437
	550–800	3.2	–
		Σ 98.2	
CTAC#400	T_{room}, 800	97.1	444
CTAC-colloid	T_{room}, 800	97.3	447

ΔT, temperature interval; wt %, weigh loss percentage; dm, temperature of higher weight loss for each interval.

loss for each interval (dm) for the composite materials obtained using sodium and organically modified clays of different granulometries, pure copolymer and Na#200—Clay.

Figures 12 and 13 and Table V show that the presence of inorganic material results in an increase of thermal decomposition temperature, indicating higher thermal stability for the composite materials. In the case of composites obtained using Na-MMT no effect of clay granulometry can be observed: the addition of ASTM #200 and colloidal granulometries clay results in an increase in thermal stability of about 17–18°C, whereas the addition of ASTM #270, #325, and #400 granulometries clay results in smaller increases of about 8–9°C. In the case of composites obtained using organically modified clays, the decomposition temperatures increased with decreasing clay granulometries. The dm temperatures observed for the materials produced in presence of organoclays of larger granulometries (CTAC#200, CTAC#270, and CTAC#325) presented 14–17°C increments with respect to the pure copolymer, whereas for smaller

granulometries such as ASTM #400 and colloidal clays, the increments were in the order of 24–27°C. These increments in the material thermal properties seem to be related to the nanocomposite structure, because superior increments are found for materials that presented higher basal spacing (Table II). The increase of thermal decomposition temperature on clay addition is well known for nanocomposites and results from a homogeneous distribution of the layered silicates. The silicate layers hinder the diffusion of volatile decomposition products, causing increase in thermal stability.[35] The results obtained in this work are in good agreement with the study presented by Mohanty and Nayak[36] who observed 7°C increase in thermal stability for the material PS/Na-MMT, 20°C for the PS melt blended with MMT modified with stearyltrimethyl ammonium chloride, and 47°C for the commercial OMMT, Cloisite 20A, at the same clay loading (3%).

Furthermore, the first event of weight loss is verified in the interval from room temperature to 550°C, corresponding to the thermal decomposition of the polymer and the quaternary ammonium salt for the cases where organophylic clays were used. A second event (550–800°C) is observed for the materials produced with Na-MMT and #200, #270, and #325 OMMT, what is attributed to structural dehydroxylation of the MMT[37] and is observed for the Na#200-Clay on the 250–800°C interval. In addition, the first event for the Na#200-Clay is visualized between room temperature and 250°C, referent to dehydration of water molecules adsorbed by interlamellar metallic cations.[37] The composite materials obtained using #400 and colloidal organically modified clays did not present the second event regarding the MMT structural dehydroxylation. This could be attributed to a possible tethering of the quaternary ammonium cation at the clay edges, exactly where structural octahedral hydroxyls are exposed during the cation exchanging treatment. It is believed that with the reduction of the clay size, these reactive sites would be highly available and the alkaline pH in the clay treatment would turn those sites negatively charged,[27] providing the possibility of interaction with the quaternary ammonium cations. This quaternary ammonium salts tethering at the clay edges would increase the clays thermal stability. It is interesting to note that for these same materials (experiments with CTAC#400 and CTAC-colloid clays), the residues presented are ∼ 3%. This is in agreement with the system clay loading, indicating that clay did not suffer significant degradation. The composite materials synthesized with sodium clays presented variation of residue values ranging from 1.7 to 3.5%, what may be related to some microheterogeneity of the material due to the lack of compatibility between the polymer and the sodium clay.

CONCLUSIONS

In this work, poly(styrene-*co-n*-butyl acrylate)/Brazilian MMT hybrid latexes with good colloidal stability were successfully obtained via miniemulsion polymerization. The influence of the MMT granulometry and organic modification on hybrid latexes and nanocomposites properties was evaluated. XRD analysis showed no significant variation on Na-MMT basal spacing with decrease of clay granulometry. After organic modification, an increase in basal spacing was observed for all clay granulometries and smaller the clay size, the greater the basal spacing increment. The presence of clays during the polymer synthesis neither plays significant influence on the kinetics of polymerization nor on miniemulsion stability. Slightly slower polymerization rates were observed resulting from the difference in particle sizes. Slightly larger average particle sizes were observed when organically modified clays were used because of the increase in organic phase content. DMAs showed that improvements in material mechanical properties are observed as the clay size is reduced, probably due to an increase in the interface area between the inorganic filler and the polymeric matrix. The XRD analysis of the composites indicated that intercalated morphologies were obtained for larger clay granulometries and that exfoliated morphologies seem to have been obtained in the case of treated clay with very small granulometries. TG analysis showed that increments in thermal properties of the composite materials seem to be related to the degree of the layered silicate dispersion. The highest increments in thermal stability were obtained for the materials synthesized using smaller organically modified clays. The miniemulsion polymerization technique demonstrated to be an alternative process for the production of hybrid latexes using organically modified MMT and it was shown that lower granulometries resulted in more exfoliated morphologies, what apparently leads to optimization of nanocomposites properties.

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