

Influence of the Type of Quaternary Ammonium Salt Used in the Organic Treatment of Montmorillonite on the Properties of Poly(Styrene-co-Butyl Acrylate)/Layered Silicate Nanocomposites Prepared by *In Situ* Miniemulsion Polymerization

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Received 8 December 2009; accepted 15 July 2010

DOI 10.1002/app.33067

Published online 30 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Hybrid latices of poly(styrene-co-butyl acrylate) were synthesized via *in situ* miniemulsion polymerization in the presence of 3 and 6 wt % organically modified montmorillonite (OMMT). Three different ammonium salts: cetyl trimethyl ammonium chloride (CTAC), alkyl dimethyl benzyl ammonium chloride (Dodigen), and distearyl dimethyl ammonium chloride (Praepagen), were investigated as organic modifiers. Increased affinity for organic liquids was observed after organic modification of the MMT. Stable hybrid latices were obtained even though miniemulsion stability was disturbed to some extent by the presence of the OMMTs during the synthesis. Highly intercalated and exfoliated polymer-MMT nanocomposites films were produced with good MMT dispersion throughout the polymeric matrix. Materials containing MMT modified with the 16 carbons alkyl chain salt (CTAC)

resulted in the largest increments of storage modulus, indicating that single chain quaternary salts provide higher increments on mechanical properties. Films presenting exfoliated structure resulted in the largest increments in the onset temperature of decomposition. For the range of OMMT loading studied, the nanocomposite structure influenced more significantly the thermal stability properties of the hybrid material than did the OMMT loading. The film containing 3 wt % MMT modified with the two 18 carbons alkyl chains salt (Praepagen) provided the highest increment of onset temperature of decomposition. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3658–3669, 2011

Key words: colloids; hybrid latices; miniemulsion polymerization; nanocomposites; organoclay

INTRODUCTION

In recent decades, significant effort has been devoted to the development of polymer-clay or polymer-layered silicate nanocomposites (PLSN) because of improvements in the properties of the materials that can be achieved, such as thermal, mechanical, dimensional, electrical, and barrier properties, even at low filler loading (i.e., <5 wt %).^{1,2} The properties of this new class of material allow applications in a wide range of products, from barrier packaging³ to transportation industries,⁴ extending polymer appli-

cation to areas which were dominated by metal and glass.

The concept of nanocomposites implies that at least one dimension of the filler is in the range of 1–100 nm. These nanocomposites can be obtained by dispersing montmorillonite (MMT), which consists of stacks of 1-nm-thick nanoplatelets of varying widths, in a polymer matrix. When intercalation of the polymer chains within the MMT platelets or exfoliation of these platelets within the polymer matrix takes place, a nanocomposite is formed, and the material benefits from the remarkable increase in the matrix/filler interaction. Within such conditions, materials with less than 5% filling may present remarkable improvements in their properties.¹

Polymer-clay nanocomposites can be obtained using emulsion,⁵ or miniemulsion⁶ polymerization. The final product of an emulsion or a miniemulsion polymerization is called latex and consists of waterborne colloidal dispersions of polymer particles.

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Contract grant sponsors: FAPESP, CAPES, CNPq.

TABLE I
Quaternary Ammonium Salts Used in this Work

Salts	Chemical formula	Trade name	Structure
Distearyl dimethyl ammonium chloride	$[(\text{CH}_3)_2\text{R}_2 \text{N}^+] \text{Cl}^-$; R = mainly C18	Praepagen WB	
Alkyl dimethyl benzyl ammonium chloride	$[(\text{CH}_3)_2(\text{CH}_2\text{C}_6\text{H}_5)\text{R} \text{N}^+] \text{Cl}^-$; R = mainly C18	Dodigen 226	
Cetyl trimethyl ammonium chloride	$[(\text{CH}_3)_3(\text{C}_{16}\text{H}_{33})\text{N}^+] \text{Cl}^-$; R = mainly C16	CTAC-50	

These products are used in several industrial applications, including synthetic rubbers, adhesives, binders, and paints.⁷ Several studies have reported the production of hybrid latices synthesized via emulsion or miniemulsion polymerization using smectite clays such as saponite⁸ and montmorillonite.⁹ The inorganic filler can be organically modified or not, depending on the specific synthesis approach; (i) *in situ* intercalative polymerization^{8,10} or (ii) exfoliation-adsorption, respectively.^{11–13} Materials originated from these hybrid latices present enhanced gas and liquid barrier,¹⁴ mechanical and thermal properties¹⁵ and fire retardancy,¹⁶ among other improved properties¹ which are interesting for different applications, for instance as binders for food packaging¹⁷ and coatings in general.¹⁸

While in emulsion polymerization micellar and homogeneous nucleation are the two main types of particle formation,⁵ in miniemulsion polymerization droplet nucleation is responsible for the most part, and ideally for all, particles' nucleation.⁶ This is achieved by using a source of high shear to reduce the size of the droplets, increasing their surface area, and therefore eliminating big monomer droplets and free micelles. A hydrophobic agent, such as hexadecane, is often used to help stabilize the droplets against Ostwald ripening.^{6,19} Thus, in miniemulsion polymerization, all monomer droplets are ideally transformed into polymer particles upon their polymerization by free radicals. In this way, the necessity of monomer transfer from monomer droplets to growing polymer particles is avoided, a fact that differentiates miniemulsion from emulsion polymerization. Because of this difference in particle nucleation mechanism, miniemulsion proved to be a powerful approach for the encapsulation of organic and inorganic materials in the production of hybrid particles.¹⁹

In the specific case of clay containing miniemulsions, one can increase the affinity between the monomer droplets and the clays by organically modifying the clay surface. Because of its organophilic character, the clay swells to a larger extent in the

presence of monomers, increasing the distance between the clay stacks. This change increases the chances of intercalation or exfoliation by the polymer during the monomers (*in situ*) polymerization. Moreover, the organic treatment also results in improved dispersion of the clay within the polymeric matrix in the final nanocomposite.²⁰

In principle, two different organic modifications can be applied to the layered silicate to promote *in situ* polymerization: grafting of silane coupling agents at the broken edges²¹ or cation exchange with cationic surfactants.^{8,22} In previous works by our group, we organically modified the MMT with cetyl trimethyl ammonium chloride (CTAC) by cation exchange and analyzed the influence of different factors, such as the organic modification parameters,¹⁰ MMT granulometry and the effect of using Na-MMT versus OMMT²⁰ on the properties of poly(styrene-*co*-butyl acrylate)/MMT hybrid materials.

In this work, we report results comparing the use of three different ammonium salts as organic modifiers: CTAC, alkyl dimethyl benzyl ammonium chloride (Dodigen) and distearyl dimethyl ammonium chloride (Praepagen). The influence of these organic modifier agents on the nanocomposite material synthesis, structure and properties was evaluated and discussed as a function of their different molecular structures.

EXPERIMENTAL

Materials

Brasgel PBS-50, natural sodium montmorillonite (Na-MMT) with cation exchange capacity (CEC) of 69 meq/100 g, was supplied by Bentonit União Nordeste (Paraíba, Brazil). Aqueous solution of CTAC, Dodigen, and Praepagen, with 50, 50, and 75 wt % actives, respectively, were obtained from Clariant. The salts are detailed in Table I. Styrene (Sty, 99.8%) and butyl acrylate (BuA, 99.7%) were supplied by IQT S.A. (Taubaté, SP) and Tekno S.A. (Guaratinguetá, SP), respectively. Ammonium persulfate (APS, ≥98%) and

n-hexadecane ($\geq 99\%$) were obtained from Sigma-Aldrich. Sodium bicarbonate (NaHCO_3 , $\geq 99\%$) was obtained from Fluka. Sodium dodecyl sulfate (SDS) in water solution (29.7 wt % actives) was obtained from Cognis. Toluene ($\geq 99.5\%$) was obtained from Labsynth. The monomers were further purified through distillation under reduced pressure. All other chemicals were used as received. Deionized water was used throughout the work.

Preparation of OMMT

Colloidal size MMT particles were obtained by sedimentation. A diluted Na-MMT/water suspension was vigorously stirred. Then, the colloidal stable suspension was collected after 72 h, according to Stokes law. The collected MMT had average particle size of 1.4 microns.²⁰

The organophilic MMT were prepared as follows: the colloidal MMT suspension (4 wt % of MMT) was stirred for about 30 min. A water solution of ammonium quaternary salt, at a concentration equivalent to 1.3 CEC of the Na-MMT, was slowly added to the suspension. After stirring for 30 min at room temperature, the suspension was filtered and washed with deionized water until free of chlorine ions. The MMT was further dried at room temperature. More details can be found in Moraes et al.'s article.²⁰

Hybrid latices synthesis

Sty (18 g) and BuA (22 g) were placed in a container with 2 g of hexadecane and OMMT (3 or 6 wt % based on monomers) and stirred for 20 h (swelling time). The organic phase was poured under strong agitation into another flask containing 2.7 g of SDS solution (29.7 wt % actives), 0.08 g of NaHCO_3 , and 188 g of deionized water. The dispersion was later sonicated for 72 s, at an output of 90% (Sonics VCX 750, probe $3/4''$). To avoid polymerization by heating and monomer loss by evaporation, the dispersion was placed in an ice-bath during sonication. Immediately after sonication, the miniemulsion was transferred to a 250-mL jacketed glass reactor equipped with nitrogen purging tube, condenser, temperature controller, and stirrer. To start the polymerization, the temperature was raised 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 for 6 h. Samples of 5–6 g were removed periodically from the reactor with a syringe for conversion and particle size analyses.

Characterizations

All MMT samples and hybrid films were analyzed by X-ray diffraction (XRD) using a Philips X'Pert

MPD diffractometer with Cu $k\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) and scanning rate of $1^\circ (2\theta)/\text{min}$. Films of hybrid polymers were prepared for XRD by depositing 6 mL of latex on a $80 \times 35 \text{ mm}^2$ glass surface and dried at room temperature.

The swelling degree of OMMTs in toluene was applied as a method to obtain the degree of affinity of the organoclays to organic compounds.²³ The experimental procedure was based on Foster's work.²⁴ About 1 g of MMT was added to a graduated cylinder containing 50 mL of organic solvent. The sedimentation of the MMT particles occurred after 1 h. Then, the suspension was mixed, and the volume of swelled sediment (swelled MMT) was measured after 48 h. The values are reported in mL/g. The swelling degree of MMT can be classified as²⁵: (1) Non-swelling: values $< 2 \text{ mL/g}$, (2) Low-swelling: values between 3 and 5 mL/g, (3) Medium-swelling: values between 6 and 8 mL/g, and (4) High-swelling: values $> 8 \text{ mL/g}$.

Average latex particle sizes from 20 runs 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 critical micelle concentration was used as diluent.²⁶ Conversions were determined by gravimetric analysis by drying the samples in an air-circulating oven at 100°C for 8 h. Dried coagulum contents were determined in terms of the theoretical total mass of solids by filtering the latices in an ASTM No. 270 sieve and drying them in the same conditions as the gravimetric samples. Latex samples were examined by transmission electron microscopy (TEM) operating at an accelerating voltage of 80 kV (Philips CM 120, Centre Technologique des Microstructures (CT μ), Claude Bernard University, Lyon, France). The films for dynamic mechanical analysis (DMA) and thermogravimetric analysis (TG) were prepared by evaporating the latices, placed in silicon molds ($125 \times 80 \times 5 \text{ mm}^3$), at room temperature. DMA were carried out using a DMA-2980 TA-Instruments equipment, using the tension mode, from -50 to 130°C , with a heating rate of $3^\circ\text{C}/\text{min}$, at a frequency of 1 Hz. TG analysis coupled with differential thermal analysis (TG-DTA) curves of the MMT before and after modification were obtained in a simultaneous TG-DTA, model SDT Q600, from TA Instruments. Samples from 6 to 10 mg in open platinum crucibles were heated from 25 to 800°C , at a heating rate of $10^\circ\text{C}/\text{min}$. The purge gas was nitrogen, at a flow rate of 100 mL/min. TG analysis of the films were carried out in a Shimadzu TGA-50, from ambient temperature to 800°C , in flowing nitrogen, at $10^\circ\text{C}/\text{min}$ heating rates. Prior to analyses, all TG samples were dried under vacuum at a temperature of 90°C , for 48 h.

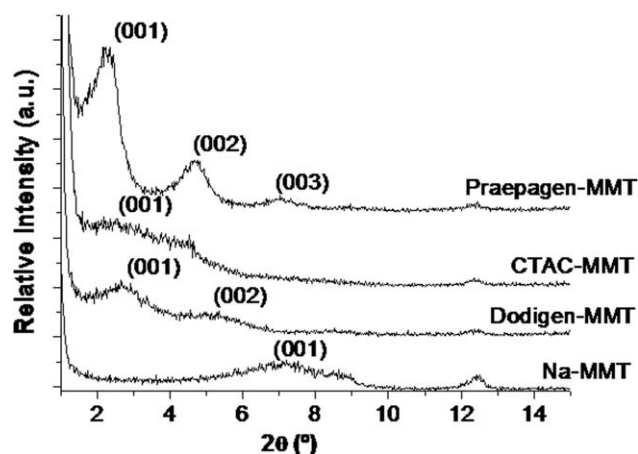


Figure 1 XRD patterns of sodium and organophilic MMTs.

RESULTS AND DISCUSSION

Clay characterization

XRD patterns of montmorillonite before and after organic modification are shown in Figure 1. After modification of the Na-MMT with quaternary ammonium salts, the diffraction peaks shifted to smaller angle values, which is an evidence of the intercalation of the organic cations between the silicate layers. Table II presents the basal spacing ($d_{(001)}$) values of sodium and OMMTs. The $d_{(001)}$ value of Na-MMT was 1.24 nm, which is characteristic of hydrated MMT containing one water layer in the interlayer space.²⁷ The Praepagen-MMT presented higher basal spacing value than CTAC-MMT and Dodigen-MMT. In Figure 1, the small peaks presented in Dodigen-MMT and Praepagen-MMT XRD patterns correspond to (002) and (003) planes of MMT. These higher order peaks suggest that these organoclays presented a well-ordered layered structure. The CTAC-MMT XRD pattern exhibited a broad and weak (001) diffraction peak, possibly because of layer disorder. The OMMT presented $d_{(001)}$ values between 3.3 and 3.9 nm, characteristic of paraffin-type arrangements of the alkylammonium ions in the interlayer space of the MMT.²³

Table III presents the Foster swelling degree of MMTs in toluene. The degree of affinity of all OMMTs for organic compounds was increased when compared with that of Na-MMT. Praepagen-MMT presented higher degree of swelling in toluene than the OMMT treated with CTAC and Dodigen.

TABLE II
Basal Spacing Values of Samples Presented in Figure 1

Clay	d_{001} (nm)
Na-MMT	1.24
CTAC-MMT	3.48
Dodigen-MMT	3.29
Praepagen-MMT	3.88

TABLE III
Foster Swelling Degree of the Different MMT in Toluene

Sample	Foster swelling degree (mL)
Na-MMT	no swelling
CTAC-MMT	10
Dodigen-MMT	9
Praepagen-MMT	13

To explain the swelling behavior and the XRD patterns, the MMTs were submitted to TG analysis.

The mass loss, the derivative mass loss (DTG) and the DTA curves of the sodium and organophilic MMTs studied are shown in Figure 2 (a–c), respectively. The percentages of mass loss of the organic

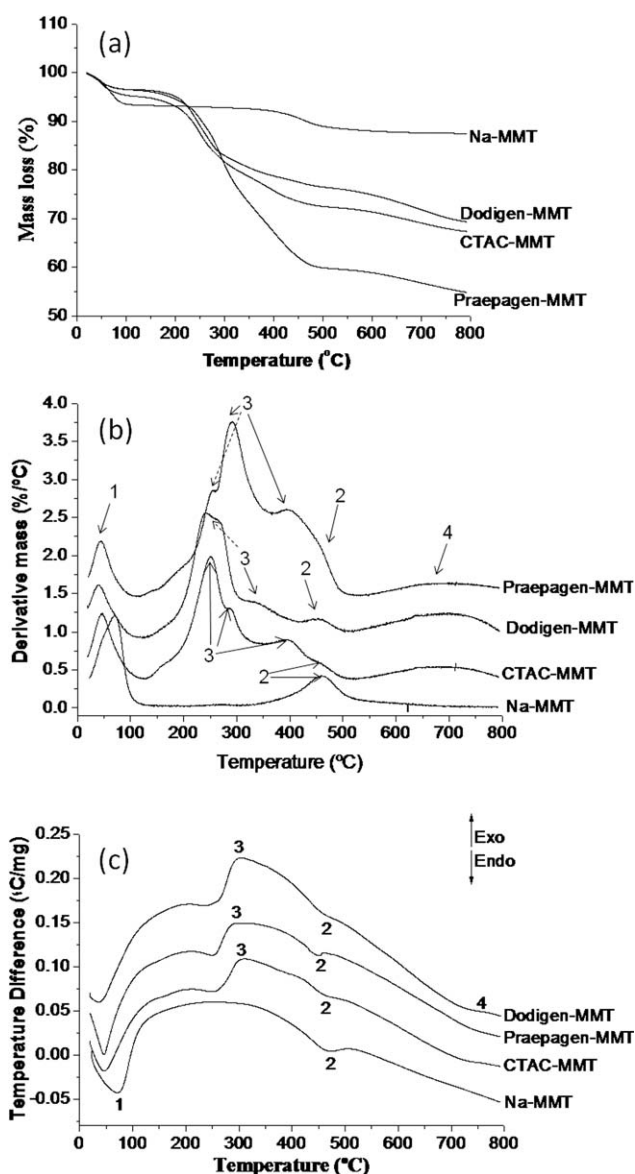


Figure 2 Thermal analyses of MMTs: (a) mass loss curves, (b) derivative mass loss curves, and (c) differential thermal analysis of sodium and organophilic MMTs.

TABLE IV
Results of Thermogravimetric Analysis of MMTs and of Ammonium Quaternary Salts

Sample	Organic cations mass loss (%)	Onset temperature (°C)	Multi Peak 3 Peak temperature (°C)		Total mass loss (%)
			3a	3b	
Na-MMT	–	–	–	–	12.4
CTAC-MMT	25.7	125	250	286/394	32.6
Dodigen-MMT	23.1	124	–	245/260/334	30.7
Praepagen-MMT	37.6	120	257/290	395	45.1
CTAC			266 ^a		–
Dodigen			200/220 ^a		–
Praepagen			204/353 ^a		–

^a These values had been reported in another work.³³

cations present in the OMMTs were estimated by subtracting the mass loss of Na-MMT, due to dehydroxylation, from the total mass loss of the OMMTs, in the range of temperature from 120 to 800°C. The onset temperature was determined by the deviation of DTG curves from the baseline (a deviation of less than 1% was considered).²⁸ The DTG curves were used to determine the temperature at maximum mass loss rate (peak in DTG curves). Araujo et al.²⁹ showed that the thermal decomposition of pure salts occurred in steps: the Dodigen and Praepagen salts presented two endothermic peak temperatures, while the CTAC salt presented one peak temperature.

The DTA curves of sodium and organophilic MMTs [Fig. 2(b)] showed:

- Two endothermic peaks, labeled 1 and 2, (peaks 1 and 2 in the DTG curves; Figure 2(b)) which correspond to: (a) loss of gaseous species and dehydration^{30–32} of the MMT (between 25 and 120°C) and (b) dehydroxylation of the smectite layers between about 330 and 550°C for Na-MMT, and between about 420 and 510°C for OMMTs.
- The two exothermic peaks, labeled 3 and 4, (multi peak 3 and broad peak 4, in DTG curves) which correspond to decomposition of the quaternary ammonium salts (only values for peak temperatures 3b in Table IV) and decomposition of residual organic carbonaceous residues of salts (between 520 and 690°C),^{30–32} respectively.

The results also indicate that the MMT treated with Dodigen presented only interlayer salts (only values for peak temperatures 3b in Table IV), whereas the MMT treated with CTAC and Praepagen contained salts within the MMT platelets and weakly attached to the surface of the MMT particles (values for peak temperatures 3a and 3b in Table IV). More details can be found in Valera et al.³³

The MMT treated with Praepagen salt presented higher basal spacing value and swelling degree value than MMTs treated with Dodigen and CTAC. Low interlayer salt concentration associated with high basal spacing value result in high accessible volume (empty spaces between the alkylammonium ions) within the MMT galleries; therefore, the molecules of organic solvent can enter more easily in the interlayer space of Praepagen-MMT, when compared with CTAC-MMT and Dodigen-MMT. Similar results were obtained when MMT clays treated with different alkyl ammonium salts were used.³²

Latex synthesis

The evolutions of miniemulsion droplet/particle diameter with reaction time for experiments with (a) 3 and (b) 6 wt % of OMMT are shown in Figure 3. An experiment with no clay addition was carried out as reference. The addition of the OMMT appeared to disturb the miniemulsion stability during the course of polymerization, especially in the first 50 min of reaction, as can be seen by the change in particle diameter. The experiment performed with no clay addition presented a good stability and, in this case, droplet nucleation was predominant over any secondary nucleation. The hybrid miniemulsions with 3 wt % of OMMT presented larger initial droplet sizes followed by a decrease in particle size shortly after the beginning of the polymerization. This is an indication that secondary nucleation occurred. Among the latices with 3 wt % OMMT, the system with Dodigen-MMT presented the most expressive change in particle size and Praepagen-MMT latex presented the least variation. After this unstable period, larger particles were observed for hybrid latices when compared with the latex with no clay addition. For experiments with 6 wt % OMMT, the system with CTAC-MMT presented larger initial droplet size when compared with the experiment with no clay addition. Independent of the initial droplet

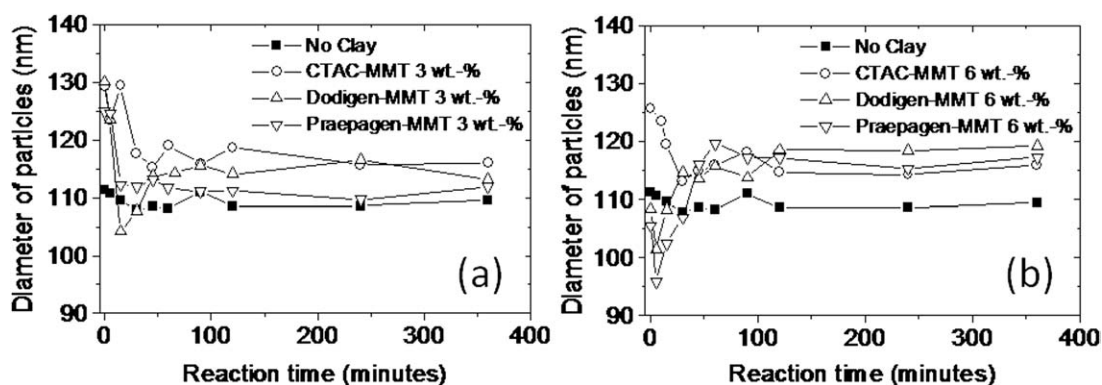


Figure 3 Evolution of average diameter of droplets/particles during the course of polymerizations performed with different modified MMTs: (a) OMMT = 3 wt %, and (b) OMMT = 6 wt %.

size, all hybrid latices showed a tendency of droplet/particle size reduction in the first minutes of polymerization, followed by an increase and stabilization. Among the latices with 6 wt % OMMT, the systems with Dodigen and Praepagen-MMT showed the most significant changes in particle size before stabilization.

The destabilization of the miniemulsion polymerization by the addition of OMMT was also observed by Diaconu et al.⁹ during the miniemulsion copolymerization of methyl methacrylate and BuA in presence of OMMT. The destabilization of the miniemulsion in presence of OMMT is due to significant secondary nucleation mechanisms as opposed to droplet nucleation. The secondary nucleation can be either micellar, caused by the existence of free micelles in the system,³⁴ or homogeneous nucleation, due to the slightly enhanced hydrophilicity of the BuA present in the monomers composition.⁷ This perturbation phenomenon can be related to the large size of the MMT, which may influence the sonication process and the particles' stabilization. In addition, the droplet/particle size determinations at low conversions were sensitive to the sample preparation (concentration, time, etc), which could be a source of

imprecision, due to variability of results that can be obtained at this stage.

The evolutions of miniemulsion monomers conversion with reaction time for experiments with (a) 3 and (b) 6 wt % of OMMT are shown in Figure 4. The addition of Praepagen-MMT resulted in rates of polymerization that were higher than the miniemulsion polymerizations performed with no clay addition. The addition of Dodigen-MMT resulted in reaction rates that are close to the reaction rate of the copolymerization with no clay addition, and the addition of CTAC-MMT results in rates of polymerization that are slightly lower than the experiment with no clay addition.

The reaction rate (R_p) (mol/L s) in emulsion polymerization depends on several parameters,⁷ such as the propagation rate constant (k_p) (L/mol s), the concentration of monomer within the particle M_p (mol/L), the average number of radicals per particle (\bar{n}), and the concentration of particles (N_p) (L^{-1}), as follows:

$$R_p = k_p M_p \frac{\bar{n} N_p}{N_A} \quad (1)$$

where N_A corresponds to Avogadro's number and is a constant.

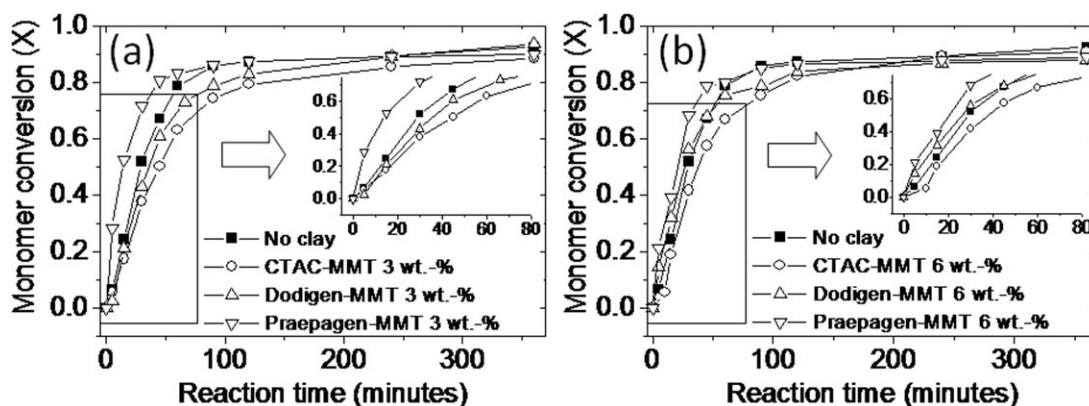


Figure 4 Evolution of conversion of monomers with polymerization time for the different modified clay experiments: (a) OMMT = 3 wt % and (b) OMMT = 6 wt %.

Assuming that k_p is the same for all experiments, since there is no significant change in either reaction temperature or monomer composition among the experiments, the differences in reaction rates observed in this work may be related to different parameters such as M_p , \bar{n} , and N_p for the different conditions studied.

Kinetics differences as an effect of differences in N_p

From Figure 3, it is observed that the sizes of the particles of the latex for the different organoclays ranked as follows: Praepagen-MMT < Dodigen-MMT < CTAC-MMT. The size of the particles affects N_p within the latex, which in turn exerts a significant influence on the rate of polymerization. According to eq. (1), the number of mols of monomer converted into polymer per volume-second is directly proportional to N_p , which in turns is inversely proportional to the average diameter of particle to the power 3. Therefore, the small difference in diameter of particles of the hybrid latices observed in Figure 3 could be affecting the reaction kinetics. This effect was especially relevant in the first hour of reaction, when the maximum rate was achieved and a large part of the monomers conversion was observed.

Among the hybrid latices, the performed experiment using Praepagen-MMT in 3 wt % resulted in smaller particle sizes during most part of the synthesis, as observed during the first 50 min of synthesis (same for 6 wt %). This effect may be due to the fact that Praepagen has more hydrophobic characteristics, compared with CTAC and Dodigen, because of its molecular structure: two alkyl chains of, in average, about 18 carbons linked to the ammonium ion compared with one alkyl chain of about 16 carbons from CTAC and one alkyl chain of about 18 carbons plus one benzyl group from Dodigen. In addition, due to its molecular structure, Praepagen-MMT showed higher organic mass fraction when compared with the others OMMTs as shown in Table IV. Possibly, the superior hydrophobic character of Praepagen-MMT provided a higher osmotic pressure in the droplets, in addition to the stabilization against Ostwald ripening provided by the hydrophobic agent. These results are in agreement with results reported by Tong and Deng,⁸ who verified a decrease in minimum emulsion particle diameter with an increase in hydrophobe concentration.

Another factor that should be considered is that the smaller particles sizes of the latices containing Praepagen-MMT at the beginning of the polymerization could originate from an eventual excess of free Praepagen molecules in the system. As discussed before, this OMMT presented salt molecules on the external surfaces of the silicate that were weakly attached to it (Table IV, peak temperature 3a). When

dissolved in water, Praepagen may result in the spontaneous formation of vesicles,^{35,36} which could act as polymerization sites, increasing the reaction kinetics observed in the experiments conducted in the presence of Praepagen-MMT. Thus, the increased initial N_p would boost the rate of polymerization even though the particles seem to coalesce one over the other after reaching about 70% conversion.

Kinetics differences as an effect of change in M_p

In addition to the effects in rate of polymerization originated from changes in N_p , the higher reaction rates observed in the presence of Praepagen-MMT can also originate from the larger basal spacing and the higher affinity between the monomers and the two alkyl chains of, in average, about 18 carbons.^{23,37} The results of Foster swelling presented in Table III showed that the swelling degree was greater for Praepagen-MMT than for CTAC-MMT and Dodigen-MMT, which suggests that the longer carbonic chains of Praepagen promote higher affinity of the OMMT to organic liquids, such as Sty and BuA. When Praepagen-MMT was used, the monomer concentration was likely to be higher, if not in the entire polymer particle, at least within the MMT galleries and probably contributed to the higher reaction rates observed with this modifying agent. This hypothesis could be applied independently of the MMT location: buried inside the particles, adsorbed at the particles' surfaces or even in dispersed MMT aggregates. In addition, the results obtained from TGA and XRD suggest that the MMT modified with Praepagen presents more empty space (or accessible volume) within the galleries, probably the reason why a higher degree of swelling in toluene was observed (Table III),^{23,37} which in turn also facilitates the accessibility of radicals to the interlayer space.

Kinetics differences as an effect of change in \bar{n}

It is accepted that the \bar{n} depends on several parameters, such as particle size, rate of absorption and desorption of radicals, coefficient of radical transfer to monomer, etc.³⁸ Nonetheless, when it comes to polymer/clay hybrid latices, the discussion goes further. Depending on the hybrid particle morphology, the MMT platelets could work as a shield and lower the entry rate of radicals into the particles, as was proposed by Tong and Deng.⁸ These authors synthesized hybrid latices of polystyrene/octadecyl trimethyl ammonium (OTAB)-modified MMT and observed a lower R_p and final conversions for a 2 wt % MMT loading. However, more recently, Tong and Deng³⁹ reported a detailed study of the kinetics of miniemulsion polymerization in the presence of MMT and verified that, theoretically, \bar{n} increased

TABLE V
Physical Properties of the Hybrid Latexes Obtained After 6 h of Polymerization

Sample	Dp ^a (nm)	PdI ^b	N _d /N _p ^c	X ^d (%)	Coag. ^e (%)
No clay	110	0.091	0.95	89.2	0
CTAC-MMT 3 wt %	116	0.248	0.72	88.4	0.5
Dodigen-MMT 3 wt %	113	0.081	0.66	93.7	0
Praepagen-MMT 3 wt %	112	0.331	0.72	90.0	0.2
CTAC-MMT 6 wt %	116	0.323	0.78	91.0	0.1
Dodigen-MMT 6 wt %	119	0.189	1.33	87.7	0.2
Praepagen-MMT 6 wt %	117	0.246	1.37	89.1	0.2

^a Average diameter of particles.

^b Polydispersity index.

^c Ratio of number of droplets to number of particles.

^d Monomer conversion.

^e Coagulum contents (wt % based on the mass of monomers).

significantly with MMT content. The authors suggested that, in addition to the larger value of particle size, the other factor that could be related to the increased \bar{n} was the enhanced viscosity inside the particles due to the MMT swelling, which reduces radical mobility. One could also think of MMT platelets working as dividers, allowing, therefore, further segregation of radicals inside the particles. This is an issue that still requires further investigation.

Table V presents the physical properties of the latexes obtained at the end of each polymerization. The final particle sizes were slightly larger for the hybrid latexes when compared with the reference latex with no clay addition, and the difference increased with MMT loading. The addition of OMMT increased the organic phase content of the miniemulsion, which should increase the droplet/particle size for the same mass of SDS.

In addition, higher polydispersity index (PdI) was observed for the hybrid latexes when compared with the reference no clay experiment. PdI is used to describe the width of the particle size distribution around the average. This parameter is calculated from the Cumulants analysis of the autocorrelation function derived from the measured intensity of dynamic light scattering.⁴⁰ High PdI values are an indication that the particles were significantly different in sizes and possibly in particle morphologies, as suggested recently by Moraes et al.²⁰

From Figure 3, the experiment with no clay addition showed good stability throughout the synthesis and the ratio of number of droplets to number of particles (N_d/N_p) was 0.95 (Table V). For all experiments with 3 wt % OMMT, the N_d/N_p ratio was about 0.7, indicating that more particles than the original number of droplets in the miniemulsions were produced. As discussed previously, this was probably due to the occurrence of secondary (micellar and/or homogeneous) nucleation. Similarly, the N_d/N_p ratio for CTAC-MMT latex with 6 wt % OMMT was 0.78. However, the experiments with

Dodigen and Praepagen-MMT at 6 wt % presented an N_d/N_p ratio of about 1.3, indicating that fewer particles were nucleated than the original number of droplets, which does not accurately describe the entire process, as shown in Figure 3(b).

Final conversions for all experiments were very similar, as shown in Table V. The conversion values are in the range of 90%. In addition, an acceptable degree of coagulation was observed for all hybrid latexes syntheses.

Films characterization

The XRD patterns of the hybrid films are shown in Figure 5 and the respective basal spacing values are shown in Table VI. No diffraction peak corresponding to the plane (001) of smectitic clay was observed for all samples with 3 wt % MMT and the sample containing 6 wt % CTAC-MMT. The absence of an

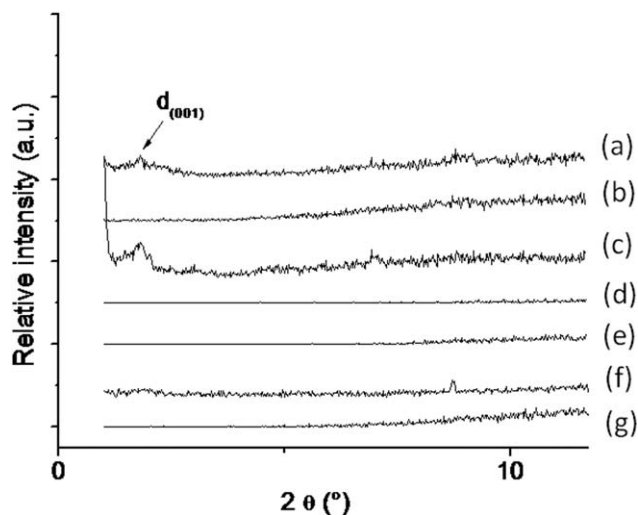


Figure 5 XRD patterns of pure and hybrid films: (a) Dodigen-MMT (6 wt %), (b) Dodigen-MMT (3 wt %), (c) Praepagen-MMT (6 wt %); (d) Praepagen-MMT (3 wt %), (e) CTAC-MMT (6 wt %), (f) CTAC-MMT (3 wt %), and (g) No clay.

TABLE VI
Basal Spacing Values of Samples Presented in Figure 5

Films	d_{001} (nm)
Pure (no clay)	–
CTAC-MMT (3 wt %)	Exfoliated
CTAC-MMT (6 wt %)	Exfoliated
Dodigen-MMT (3 wt %)	Exfoliated
Dodigen-MMT (6 wt %)	4.78
Praepagen-MMT (3 wt %)	Exfoliated
Praepagen-MMT (6 wt %)	4.84

XRD peak indicates that the MMT can present an exfoliated structure within the film. The samples containing 6 wt % Dodigen-MMT and Praepagen-MMT led to an increase in the interlayer spacing from 3.29 to 4.78 nm and from 3.88 to 4.84 nm, respectively, in comparison with the OMMT clay prior to polymerization. This is an indication that intercalation of the silicate platelets by the polymer occurred.

The storage modulus (E') and $\tan \delta$ as a function of temperature from DMA is presented in Figure 6. All materials presented only one transition, showing that in spite of the difference in reactivity ratios of the comonomers Sty and BuA,⁴¹ the composition drift of the copolymer did not compromise the homogeneity of the matrix. Numerical values of E' at -40 and 80°C and the values of $\tan \delta$ peaks are presented in Table VII for comparison purposes.

As expected, the addition of OMMT resulted in increments on E' . Below T_g , the most significant increment occurred for 6 wt % CTAC-MMT, while, above T_g , larger increments were observed for all 6 wt % OMMT nanocomposites, when compared with the 3 wt %. This increase in E' could be due to a stress transfer to the MMT monolayers when the material is submitted to deformation,⁴² or to a reduced degree of freedom of the polymer inserted within the silicate layers.⁴³

For both MMT loadings, the E' versus temperature profiles could be classified in the following descending order: CTAC-MMT hybrid films > Dodigen-MMT hybrid films \approx Praepagen-MMT hybrid films > No clay. These results can be explained as a function of the materials' microstructure. It is known that the modulus of a polymer-clay composite material increases with clay content and the clay aspect ratio. Nonetheless, above T_g the increase will also depend on interactions between the clay and the matrix, interaction of the type clay-to-clay and the clay dispersion within the polymer.^{44,45} According to the results of basal spacing after polymerization in Table VI, the materials synthesized in presence of CTAC-MMT (both 3 or 6 wt %) resulted in exfoliated materials. The exfoliation of the silicate platelets was a factor that contributed to the appreciable increments of E' observed in the DMA analysis. The microstructure of the CTAC-MMT in the material can be visualized in Figure 7(a). The syntheses in presence of Dodigen-MMT produced exfoliated and intercalated materials for 3 and 6 wt % OMMT contents, respectively, according to the results of XRD. The same was observed for materials synthesized in presence of Praepagen-MMT. DMA results are very similar for Dodigen-MMT and Praepagen-MMT materials, as can be seen in Table VII. From the same table, materials containing 3 wt % OMMT, all with exfoliated structure, presented similar E' at both temperatures; around 1000 Mpa at -40°C and 0.7 Mpa at 80°C . Both Dodigen-MMT and Praepagen-MMT materials presented intercalated structure with 6 wt % OMMT and their E' were around 1200 MPa at -40°C and ~ 1.8 MPa at 80°C . The effect of the exfoliated versus intercalated structure on the mechanical properties can be clearly observed by comparing the results of the exfoliated 6 wt % CTAC-MMT material with the two intercalated materials with same OMMT content, Dodigen-MMT, and Praepagen-MMT. At -40°C , the exfoliated

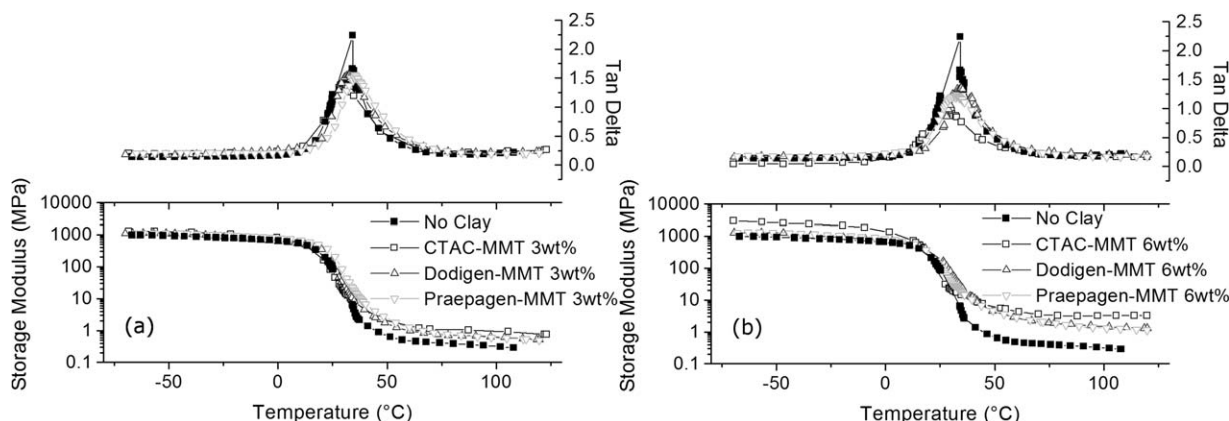


Figure 6 Storage modulus and $\tan \delta$ as a function of temperature for materials synthesized in presence of the different modified MMTs: (a) OMMT = 3 wt %, and (b) OMMT = 6 wt %.

TABLE VII
Values of Storage Modulus and Tan δ Peaks for
Materials Synthesized in Presence of Different Modified
Clays at Both 3 and 6 wt % Clay Loading

Material	E' at -40°C (MPa)	E' at 80°C (MPa)	Tan δ peaks (°C)
No clay	867	0.4	34.3
CTAC-MMT 3 wt %	1197	1	30.3
CTAC-MMT 6 wt %	2436	3.2	27.4
Dodigen-MMT 3 wt %	1033	0.7	32.1
Dodigen-MMT 6 wt %	1147	1.8	34.6
Praepagen-MMT 3 wt %	1064	0.7	35.4
Praepagen-MMT 6 wt %	1204	1.7	32.8

material presented E' about 2 times higher than the intercalated materials and at 80°C the exfoliated material presented E' of about 1.8 times higher than the intercalated materials.

From the peaks of tan δ as a function of temperature, which corresponds to the ratio of dissipated energy to the stored energy, one can estimate the glass transition temperature (T_g) of the materials. Relative to the material with no clay addition, the hybrid material films presented peaks with lower intensity, obviously due to the increment in the hybrid materials' resistance. The value of T_g of the hybrids was not significantly affected by the presence of MMT, as can be seen from the peaks of tan δ in Figure 6. Several authors reported different effects of the addition of OMMT on the T_g of the hybrid material. Either decrease,⁴⁶⁻⁴⁸ increase,^{14,49,50} slight increments^{51,52} and no significant effect^{18,53,54} on the T_g were observed for different polymers and OMMTs.

The reason that the T_g was not significantly affected in this work is probably the miniemulsification step. During sonication, the amount of energy released in the form of shear can probably exfoliate a considerable fraction of the OMMT clays before polymerization, considering that these are extremely swollen by monomers. Thus, the MMT should exert

no significant effect in the mechanism of polymerization or in the molecular weight or mobility of the polymers obtained, therefore not affecting T_g to a significant extent.

TEM images of hybrid materials are presented in Figure 7. It is possible to see that the silicate layers were well dispersed and distributed within the matrix for the nanocomposite prepared with 6 wt % CTAC-MMT [Fig. 7(a)]. The fact that this morphology was observed throughout other regions of the sample justifies the observation that the XRD did not detect any basal planes for this sample (Table VI; CTAC-MMT 6 wt %). On the contrary, from Figure 7(b), it is possible to see larger tactoids (MMT aggregates), which concurs with the results from XRD, suggesting a predominantly intercalated structure for the material prepared with 6 wt % Dodigen-MMT.

TG results of the hybrid and pure films obtained in this work are presented in Figure 8. The onset temperatures of decomposition of these films are presented in Table VIII. The onset temperatures of decomposition of hybrid films were higher when compared with that of the pure film, indicating that the thermal stability of hybrid films was improved in every case. Studies on the thermal decomposition of polymer/MMT nanocomposites showed that the presence of MMT can significantly improve the thermal resistance of polymers. The enhancement of thermal resistance was more expressive when a greatly intercalated or exfoliated structure was obtained, due to the barrier to mass transport created by the silicate platelets and the insulation provided to the polymer by the silicate layers.^{1,55,56}

Comparing the results of onset temperature of TG from Table VIII with the basal spacing values of the final materials presented in Table VI, for MMTs modified with the same quaternary ammonium salt, the materials which presented higher improvements in thermal stability are the same that presented exfoliation of the OMMT. The highest increment in

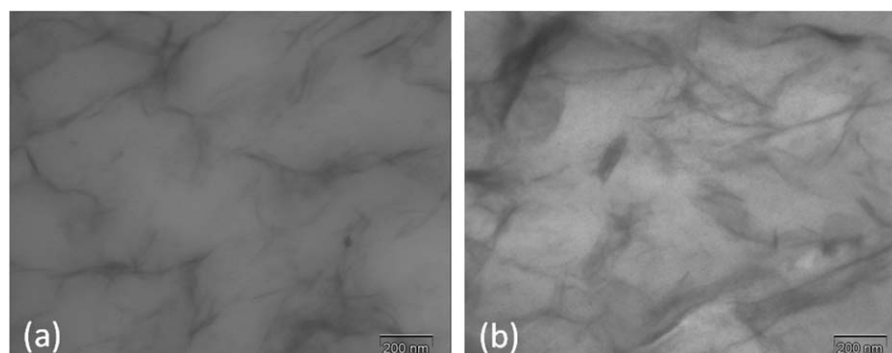


Figure 7 Transmission electron microscopy of composite materials with 6 wt % loading (a) CTAC-MMT and (b) Dodigen-MMT.

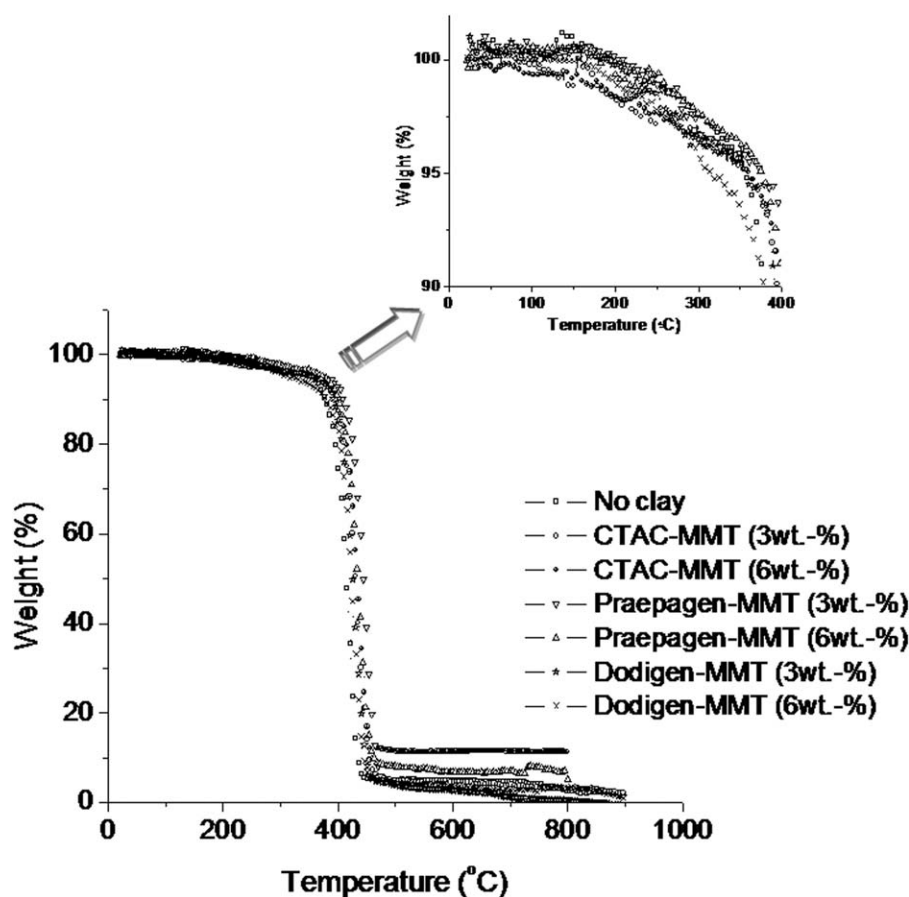


Figure 8 Thermogravimetric curves of pure and hybrid films.

thermal stability (62°C) was observed for the material prepared with 3 wt % Praepagen-MMT. According to these results, the MMT loading (3 or 6 wt %) played a less significant role in the thermal stability of the nanocomposite than did the structure of the material obtained.

CONCLUSION

In this work, poly(styrene-*co*-butyl acrylate)/OMMT nanocomposites were produced successfully from hybrid latices synthesized via *in situ* polymerization. Three different structures of quaternary ammonium salts (CTAC, Dodigen, and Praepagen) were studied

as organic modification agents. Stable hybrid latices were produced, but miniemulsion stability was disturbed by the presence of the OMMT. The use of two alkyl chains of about 18 carbons salt (Praepagen) resulted in the largest basal spacing of the modified MMT. In addition, this salt resulted in higher rates of polymerization, which were correlated to the highest affinity of this OMMT to the monomers.

Highly intercalated and exfoliated polymer-MMT nanocomposites were obtained, and the silicates were shown to be well-dispersed. The storage moduli of the films increased upon addition of the OMMT. The largest increments were observed for the MMT modified with the single (16 carbons) alkyl chain salt (CTAC) at the level of 6 wt %. The addition of OMMT also increased the thermal stability of the material. The largest increase in the onset temperature of decomposition resulted from the material containing 3 wt % of the MMT modified with Praepagen. For the range of MMT content studied, it was observed that the increments in thermal stability of the composite materials were more strongly related to the degree of exfoliation of the silicate layers than to the MMT loading.

TABLE VIII

TG Data (Onset Temperature) for Pure and Hybrid Films

Films	Onset temperature (°C)
No clay	321
CTAC-MMT 3 wt %	359
CTAC-MMT 6 wt %	370
Dodigen-MMT 3 wt %	349
Dodigen-MMT 6 wt %	339
Praepagen-MMT 3 wt %	383
Praepagen-MMT 6 wt %	353

The authors thank Pierre-Yves Dugas for the TEM analysis and Luan Scheid da Silva for the TG analysis.

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