High-Solids Content Waterborne Polymer-Clay Nanocomposites

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Summary: Waterborne polymer clay nanocomposites (WPCN) were prepared by emulsion and miniemulsion copolymerization of butyl acrylate and methyl methacrylate with enhanced mechanical, thermal and barrier properties for coating applications. Emulsion polymerization was used to synthesize WPCN using pristine Na-MMT (sodium montmorillonite) and miniemulsion polymerization to prepare the WPCNs when the pristine clay was organically modified and hence its incorporation into the polymerization loci was not guaranteed by the conventional emulsion polymerization technique. Both techniques allowed preparing stable nanocomposite latexes of BA/MMA copolymers with partially exfoliated morphologies as demonstrated by wide X-ray difraction (WAXD) and transmission electron microscope (TEM) measurements. Furthermore, latexes with solids contents up to 45 wt% and manageable viscosities were prepared for the first time using seeded semibatch emulsion polymerization.

Keywords: BA/MMA copolymer; (mini)emulsion polymerization; high-solids content; Na-MMT; polymer/clay nanocomposite

Introduction

Polymer clay nanocomposites have attracted a great deal of interest in both academia[1–3] and industry[4–7] because of the improved mechanical, thermal and barrier properties (among others) that the nanocomposite materials have shown in comparison to pure polymers or microcomposites. The techniques reported for the production of these nanocomposites can be summarized as polymer/pre-polymer intercalation from solution, melt intercalation, and in-situ polymerization, which includes bulk, solution, and any type of dispersion polymerization. In the last years, the latter method that mainly includes emulsion polymerization, has gained a lot of interest because of the simplicity of the polymerization and the advantages that emulsion polymerization offers. Thus, the vast majority of articles related with the production of waterborne polymer/clay nanocomposites have been published in the period 2003–2007 (>75%) according to the ISI Web of Science.

Natural montmorillonite, Na-MMT, is formed of stacks of four or five platelets 1 nm thick each, and 200 to 300 nm wide, being composed of two silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either magnesium or aluminium hydroxide, with a spacing between platelets of 1 nm approximately. Due to isomorphic substitution the platelets are negatively charged, the cations that reside in the interlayer space being the charge counterbalance that keeps the layers together.

For a given concentration of montmorillonite, the properties of the polymer/clay nanocomposites are best when the clay platelets are completely exfoliated in the polymer matrix.[2,3] Polymer/clay nanocomposites in which the clay is partially exfoliated or a modest amount of polymer

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is intercalated between the clay layers showed lower performance. Therefore, the goal is to completely exfoliate the clay in the polymer matrix.

Due to its hydrophilic character, Na-MMT is fully hydrated in an aqueous solution and hence the ordered structure of the stacks is broken and the platelets are individually and randomly (exfoliated) dispersed in the aqueous solution. Therefore, emulsion polymerization in the presence of exfoliated clay may lead to a polymer/clay nanocomposite upon film formation. Lee et al.[8–11] were the first exploiting this feature and carried out emulsion polymerizations with several monomers including styrene, MMA and acrylonitrile-styrene, producing in most of the cases intercalated nanocomposites upon film formation. Other authors have also followed this method but using other surfactants and initiator systems (e.g. 2-acrylamido-2-methyl-1-propanesulfonic acid, AMPS[12–14]) to help compatibilizing clay and polymer matrix and hence better dispersing the clay platelets in the polymer matrix in order to render nanocomposites with exfoliated structures.[15–17] Nevertheless, this feature has been ignored by plenty of the works in which the organically modified clay, O-MMT, has been directly used in emulsion polymerization processes; namely, by dispersing the hydrophobic clay in the aqueous phase.[9,18–21] First, the clay is rendered hydrophobic by exchanging the naturally occurring Na^+ and Ca^{2+} of the interlayer with long alkyl ammonium or phosphonium cations. In some cases clay aggregation (when dispersed in water) was avoided by a post-treatment as it was shown by Negrete-Herrera et al.[20,22] for laponite modified with 2,2′-azo-bis(2-amidinopropane) dihydrochloride, AIBA. In a related process, the modified clays were dispersed in the monomer, which was polymerized in a conventional emulsion polymerization procedure.[23–26] In this case, the organophilic clay cannot be incorporated into the polymer particles because diffusion through the water phase is not favoured, as it occurred with highly hydrophobic monomers that hardly polymerize in emulsion polymerization.[27]

A promising approach for synthesizing polymer/clay nanocomposite particles (in the submicron range) using organically modified clays is miniemulsion polymerization, where the monomer droplets might contain the hydrophobic clay stacks that upon polymerization (the nucleation and polymerization occurs in the miniemulsion droplets) might lead to exfoliated nanostructures. There are very few examples in the literature where miniemulsion polymerization has been used to prepare waterborne polymer/clay nanocomposites.[28–31] All of them presented styrene polymerizations (or copolymerization with butyl acrylate[31]), in the presence of modified laponite,[28,29] saponite[30] or montmorillonite.[31] The solids contents of the reported stable latexes ranged from 5 to 17%, needing high amounts of emulsifier to stabilize the recipe in some cases (17% of TX-405[30]).

In most of these works, formulations with low solids content (<20 wt%) and batch operation were used to produce the nanocomposites. These solids contents are far from what is required for commercial applications (>45 wt%). In addition, if successful procedures for achieving high solids contents were developed, they should be semicontinuous to allow reactor temperature control.

There are few works in the open literature where a semibatch operation has been adopted to produce the nanocomposites,[12,13,15,16] and only the work of Yang and Yu[15] achieved a solids content of 33 wt%. In the patent literature there are examples of both semibatch operation and higher solids content to produce waterborne polymer clay nanocomposites (see for instance Chou et al. from Rhom&Haas[5]), but little information about the process and the morphology of the nanocomposites produced is provided, although the product showed improved mechanical and dielectrical properties.

In this work emulsion and miniemulsion polymerization processes were used to

produce waterborne (MMA-BA)/MMT nanocomposite latexes. Pristine Na-MMT and organically modified montmorillonite (both commercial and modified in-house) were used in emulsion and miniemulsion polymerization processes, respectively. Stable latexes with 30 wt% solids content were synthesized by both methods in batch and semibatch operation. Furthermore, for the first time in the open literature, nanocomposite copolymer latexes with solids contents around 45 wt% were prepared by seeded semibatch emulsion polymerization with partially exfoliated structure.

Experimental Part

Materials

Na-Montmorillonite, Na-MMT, and an organically modified clay, Cloisite 30B, were obtained from Southern Clay Products Inc. (Texas/USA). Na-MMT has a cationic exchange capacity (CEC) of 92.6 meq/100 g clay. Cloisite 30B (C30B) is a natural montmorillonite modified with a quaternary ammonium salt: methyl tallow bis-2-hydroxyethyl quaternary ammonium and has a cationic exchange capacity of 90 meq/100 g clay. Interlayer spaces as measured by X-ray Diffraction (XRD) were 1.15 and 1.85 nm, respectively.

Na-MMT was also modified with two reactive cationic species synthesized in our lab. One of the species was 2-methacryloyloxy ethyl hexadyldimethyl ammonium bromide, MA16, which was synthesized as reported by Zeng and Lee.[32] The second reagent was a living oligomer synthesized in aqueous phase by polymerizing methyl methacrylate and styrene (90/10 molar ratio) in the presence of AIBA (2,2′-azo-bis(2-amidinopropane) dihydrochloride) and SG1, N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (kindly supplied ARKEMA) at a molar ratio SG1: AIBA = 1.1 at 90 °C. The number average molecular weight of the oligomer measured by GPC was 2660 g/mol. The cationic exchange was carried out under the following conditions: Na-MMT (10.0 g) was dispersed in water (200 g) and the reactive species (20 meq) were added to the clay solution and kept for 3 hours under mechanical stirring (700 rpm) at 0–5 °C (MA16, 2-methacryloyloxy ethyl hexadyldimethyl ammonium bromide) or room temperature (reactive oligomer). The dispersion was precipitated and washed several times with water and a powder was recovered and used in miniemulsion polymerizations as explained below. The interlayer space of the clay upon cationic exchange with these reactive species was 3.32 and 1.56 nm, respectively, which demonstrated that the reactive cations were successfully intercalated in the interlayer space of the clay. Sodium lauryl sulfate (SLS, Aldrich) was used as emulsifier both in emulsion and miniemulsion polymerization. Stearyl acrylate (SA, Aldrich) was used as co-stabilizer (in the miniemulsion polymerizations), ascorbic acid (AsAc, Aldrich) and t-butyl hydroxyperoxide (TBHP, Panreac) were used as redox initiators and potassium persulfate (KPS, Aldrich) and 2-2′-azo-bis-isobutyronitrile (AIBN, Aldrich) as thermal initiators. The redox system was employed in miniemulsion polymerizations and KPS and AIBN in emulsion polymerizations. The monomers: methyl methacrylate, MMA, butyl acrylate, BA, and styrene, S, all from Quimidroga (Spain) were used as received, without further purification.

Characterization

Polymer particle size and monomer droplet size were measured by dynamic light scattering using a Coulter N4 Plus in unimodal analysis. For this analysis, a fraction of the latex (or miniemulsion) was diluted with deionized water (saturated with monomers in the case of miniemulsion droplet size measurement). The reported particle size (droplet size) values represent an average of 3 repeated measurements. Conversion was measured by gravimetry.

Wide-angle X-ray Diffraction (WAXD) analyses were performed on a Philips PW 1729 Generator connected to a PW 1820 (Cu K_α radiation with $\lambda = 0.154056$ nm) at

room temperature. The range of the diffraction angle was $2\theta = 1$–12° with a scanning rate of 0.02°/3 sec. The (001) basal spacing of the clay (d) was calculated using the Bragg equation: $n\lambda = 2d\sin\theta$. To perform the WAXD analysis, the films cast from the latex were rinsed to get rid of the SLS and to avoid its peaks at 7°, 5° and 2.5° in the WAXD patterns. The morphology of the nanocomposite films was studied by means of a transmission electron microscope, TEM, (Hitachi 7000FA at 75 kV). The samples were cryosectioned with a LEICA ULTRACUT FCS cryoultramicrotome using a DIATOME 35 degrees diamond knife. The ultra-thin sections were placed on a 300 mesh formvar coated copper grid and observed with the transmission electron microscope.

Dynamic mechanical thermal analysis (DMTA) was used to analyze the thermomechanical behavior of the polymer/clay nanocomposites. To perform the DMTA analysis a latex film 1 mm thick was heated from $-50\,^\circ$C to $100\,^\circ$C with a heating rate of $0.3\,^\circ$C /min. The thermal stability of the nanocomposites was studied by thermogravimetric analysis (TGA). To perform the TGA analysis the sample was heated from $20\,^\circ$C to $600\,^\circ$C with a heating rate of $10\,^\circ$C/min using Q500 V6.5 build 196 TGA instrument. The mechanical properties of the nanocomposites were analyzed by an universal testing machine INSTRON 4301. The measurements were carried out at controlled temperature and humidity conditions ($T = 23 \pm 2\,^\circ$C and relative humidity $= 50 \pm 5\%$) applying a stretch force of 1.5N at 20 mm/min to the latex film. Heat release rate measurements under sample combustion were carried out in a Cone Calorimeter (FTT).

Synthesis of Waterborne (MMA-BA)/MMT Nanocomposites by Emulsion Polymerization

All the reactions were carried out in a 1 L glass jacketed reactor fitted with a reflux condenser, sampling device, N_2 inlet, two feeding inlets and a stainless steel anchor stirrer equipped with two blade impellers rotating at 250 rpm. Reactor temperature and monomer feed flow rates were controlled by an automatic control system (Camile TG, Argonaut). The nanocomposite latexes were produced by seeded semibatch emulsion polymerization reactions. A typical procedure was as follows: the seed was prepared by loading the reactor with Na-MMT (8.1 g), SLS (5.4 g) and distilled water (550 g) and mixed at 250 rpm at room temperature for 30 minutes under a gentle nitrogen flow (15 ml/min). Monomer (MMA/BA = 50/50 by weight, 135 g) was added and the temperature raised to $75\,^\circ$C. Once the reaction temperature was reached, 0.675 g of 2.5 wt% aqueous solution of initiator, KPS (50% of the total amount in the formulation) was added to the reactor to start the polymerization. After one hour in batch in which monomer conversion reached >99%, the remaining amount of monomers (135 g) and initiator (0.675 g dissolved in 50 g of deionized water) were fed in two separate streams for 3 hours. Afterwards, the reactor content was allowed to polymerize for one more hour at $75\,^\circ$C. The final solids content of the latex was 30 wt% and the content of MMT was 3 wt% based on monomer.

For the formulation with higher solids content (45 wt%) a similar procedure was adopted, but in this case the solids content of the seed was 25 wt% and not all the clay was loaded during the seed stage. A preemulsion of the monomers and clay (3 wt% based on monomer) and the initiator solution were fed for 3 hours. The final solids content of the nanocomposite latex was 45 % and the content of clay was again 3 wt% based on monomers.

Synthesis of Waterborne (MMA-BA)/MMT Nanocomposites by Miniemulsion Polymerization

Miniemulsions were prepared as follows: the oil phase was prepared by dissolving the costabilizer (stearyl acrylate) and the organically modified clay in the monomers (MMA and BA; 50/50 wt %). This mixture was stirred for 15 min at 1000 rpm with a magnetic stirrer. The aqueous phase was

Table 1.
Formulation used to prepare the miniemulsions for synthesizing the (MMA-BA)/O-MMT nanocomposite latexes by miniemulsion polymerization.[a)]

Ingredient	Amount (g)	Wt% monomer
MMA	135	–
BA	135	–
SA	8.1	3
O-MMT clay[b)]	0 or 8.1	0 or 3
SLS	10.8	4
Water	480	–

[a)] The polymerizations with MA16-MMT and AIBA-$(S/MMA)_n$-SG1-MMT were carried out at a lower scale (1/4). In addition the polymerization temperature for experiment with AIBA-$(S/MMA)_n$-SG1-MMT was 90 °C.

[b)] O-MMT clay: Cloisite 30 B, MA16-MMT and AIBA-$(S/MMA)_n$-SG1-MMT.

prepared by dissolving the emulsifier in water. Both phases (aqueous and oil phase) were brought together and mixed for 15 min at 1000 rpm. The dispersion was sonified using a Branson Sonifier 450 (operating at 8-output control and 80% duty cycle for 15 min in ice bath and under magnetic stirring). The pH of the miniemulsion was adjusted to 10 by using an aqueous solution of boric acid. Note that if the pH of the dispersion was acidic, unstable latexes and coagulum was formed upon polymerization. A typical formulation used to prepare the miniemulsions is presented in Table 1.

The latexes with solids content of 30 wt% were synthesized batchwise. For the higher solids content, seeded semibatch operation was used where the seed was prepared by polymerizing a miniemulsion. For the batch operation, the miniemulsion prepared as above was charged in the reactor (the setup described for the emulsion polymerizations was also used here) and the temperature raised to 70 °C under nitrogen flow. Upon reaching the reaction temperature, aqueous solutions of the redox components (TBHP/AsAc = 2:1 mol ratio) were fed to the reactor in two separate streams (0.675 and 1.25 g in 75 g of water each, respectively) for 3 hours. For the seeded semibatch operation, the seed (30 wt% solids content) was prepared by miniemulsion polymerization at 70 °C with all the clay in the miniemulsion as in the above batch miniemulsion polymerization for 150 min. Then, neat monomers and an oil-soluble initiator (AIBN, azobisisobutyronitrile) were fed to the reactor. The final nanocomposite latex has 42 wt% solids content and 1.8 wt% Cloisite 30B based on monomer.

Table 2 presents a summary of all the experiments carried out with indication of the solids content, type of process employed, and the percentage and type of clay used in the experiments. For comparison purposes, nanocomposite latex EP3 was prepared by blending a previously synthesized latex (EP1) with a Na-MMT clay aqueous dispersion.

Results and Discussion

Figure 1 presents the evolution of the instantaneous conversion and average particle size for the seeded semibatch emulsion

Table 2.
Summary of the nanocomposite latexes synthesized by means of emulsion and miniemulsion polymerization.

Latex	Solids Content (wt %)	Process	wt% clay[a)]	Type of clay
EP1	30	Emulsion/Semibatch	–	–
EP2	30	Emulsion/Semibatch	3	Na-MMT
EP3	30	Emulsion/Blend[b)]	3	Na-MMT
EP4	45	Emulsion/Semibatch	3	Na-MMT
MP1	30	Miniemulsion/Batch	–	–
MP2	30	Miniemulsion/Batch	3	Cloisite 30B
MP3	30	Miniemulsion/Batch	3	MA16-MMT
MP4	30	Miniemulsion/Batch	4	Living_oligomer-MMT
MP5	42	Miniemulsion/Semibatch	1.8	Cloisite 30B

[a)] Based on the total amount of monomer in the recipe.

[b)] This nanocomposite latex was prepared by blending latex EP1(blank) with an aqueous solution of Na-MMT by magnetic stirring (700 rpm) during 3 hours at room temperature.

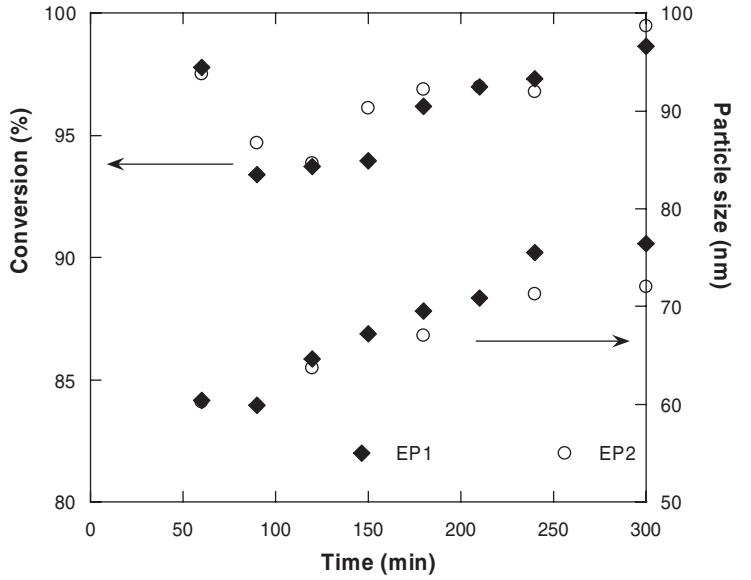

Figure 1.
Time evolution of the instantaneous conversion and average particle size for the seeded semibatch emulsion copolymerizations of MMA/BA carried out without (EP1) and with (EP2) Na-MMT.

polymerizations labelled as EP1 and EP2 in Table 2. The evolution of the instantaneous conversion was not affected by the presence of the clay and full conversions were achieved in both cases. The particle size of the seed was 60 nm in both cases and the final particle sizes were 76 and 72 nm, for EP1 and EP2, respectively. This indicates that no secondary nucleation occurred during the monomer addition period and that the clay did not significantly affect the kinetic and particle growth.

The polymerization of acrylic monomers might yield gel polymer due to the chain transfer to polymer reactions coupled with termination by combination.[33,34] However, Elizalde et al.[35] and Gonzalez et al.[36] have shown that when BA is copolymerized with MMA, and for the monomer ratio employed in this work, the amount of gel is usually below 5%. This was also observed in latexes EP1 and EP2, where the amount of insoluble polymer after soxhlet extraction in THF was negligible in both cases. The polymer obtained after extraction in THF for 24 hours was analyzed by GPC. The GPC traces of the blank (EP1) and nanocomposite latex (EP2) were similar and both showed a shoulder at high molecular weights indicating that chain transfer to polymer took place during the polymerization due to the high polymer concentration in the polymer particles (see Figure 1). For the sake of brevity the GPC traces are not included in this case. These results can hardly be compared with other literature results, since there are few works in the literature regarding the effect of the presence of Na-MMT on the kinetic of semibatch emulsion polymerization.[12,13,15,16] Only the first one reports the final conversion, which is not affected by the clay, as it happens in our case. There is, however, an interesting kinetic study carried out for *ab-initio* emulsion polymerization of styrene in the presence of Na-MMT.[37] This work reported that the polymerization rate was faster in the presence of Na-MMT because of the higher number of micelles produced when Na-MMT is added into the formulation. They also found that the particle size was smaller when Na-MMT was added in the formulation. The molecular weights

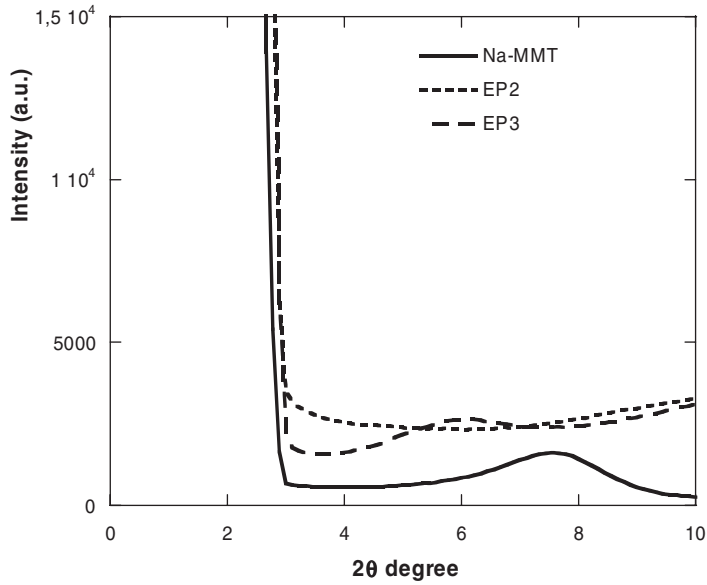

Figure 2.
XRD patterns of the nanocomposite latex films and the pristine clay.

were only slightly higher when Na-MMT was used. In our experiments, we have not found any effect of the clay on kinetics and particle size neither in the presence of micelles (seed formation) nor in its absence (semibatch period).

Figure 2 shows the XRD diffraction patterns of films prepared with both nanocomposites EP2 (prepared by emulsion polymerization), EP3 (blend) and that of the Na-MMT clay. Nanocomposite EP2 shows no peaks indicating that the basal spacing of the pristine montmorillonite ($2\theta = 7.63°$; d(001) = 1.15 nm) have been extended beyond the separation that can be detected by WAXD (3.5 nm), namely that the ordered structure of the clay have been lost during the polymerization. Latex EP3 still shows a broad peak at lower angles ($2\theta = 6.0°$; d(001) = 1.47 nm), which can

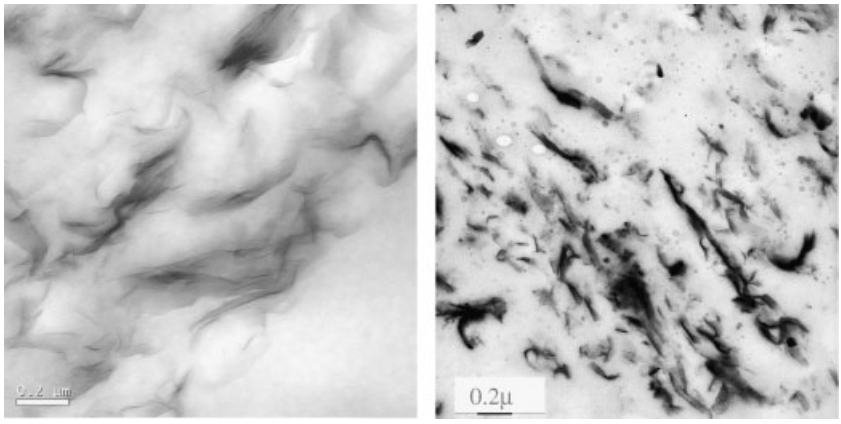

Figure 3.
TEM micrographs of the film of nanocomposite latexes: (left) EP2; (right) EP3.

Table 3.
Properties of nanocomposite latexes prepared by miniemulsion polymerization.

Run	Final Conversion (%)	Miniemulsion droplet size (nm)	Particle size(nm)
MP1	>99	108	93
MP2	>99	194	119
MP3	>99	202	112
MP4	>98	220	136

indicate that upon film formation a certain clay arrangement with intercalation of oligomeric species could have taken place.

Figure 3 presents the TEM micrographs of the films cast with EP2 and EP3. It can be seen that in nanocomposite EP2 a mixed exfoliated/intercalated structure is obtained, which is in agreement with the XRD pattern. For EP3 the situation is different, the clay is not well dispersed in the matrix and tactoids and aggregates of clay platelets, as well as some intercalated structures, can be observed.

Table 3 presents a summary of the nanocomposites prepared by miniemulsion polymerization using different organically modified clays. The idea was to incorporate the hydrophobic clay platelets (200–300 nm wide) in the monomer droplets, and delaminate the clay by polymerization in the interlayer. However, the surfactant concentration adequate to produce droplet sizes above 300 nm (as to fully engulf 2–3% of clay in the droplets) yielded unstable miniemulsions. The minimum amount of surfactant required to produce stable nanocomposite latex with negligible amount of coagulum was 4 wt% based on monomer. This led to sizes in the lower part of 200–300 nm range, namely the clay was just engulfed by the monomer. In addition, the stability of the latexes was greatly improved when high pH was used in the reaction medium, likely because the edges-to-face agglomeration was avoided.

The miniemulsion polymerizations were fast and full conversion was achieved in 60 minutes in all the cases. The droplets size of the miniemulsion containing clay was larger than those without clay and the final particle sizes of the nanocomposites were smaller than those of the droplets, showing that particles were produced through mechanisms other than droplet nucleation. This in agreement with the results presented by Sun et al.[29] and Moraes et al.[31] Furthermore, the particle size decreased along the reaction (see Figure 4a).

Using a parking area of 131 $Å^2$/molecule for SLS on MMA/BA copolymers, simple calculations showed that under the conditions used for miniemulsions MP1-MP4, micelles were present in the medium. Therefore, it is likely that micellar nucleation occurred during the polymerizations.

Figure 5 presents the XRD patterns of the nanocomposite latexes prepared by miniemulsion polymerization. The XRD patterns show that for the O-MMT clays prepared in this work, the basal space increased from the d(001) = 1.15 nm of the pristine clay to d(001) = 3.32 nm for the MA16-MMT modified clay and d(001) = 1.56 nm for cationic reactive oligomer, indicating that the reactive species were successfully intercalated in the interlaminar space of the clay platelets. Upon polymerization no diffraction peaks were observed for the nanocomposites MP2, MP3 and MP4 (apart from those characteristic of SLS) which indicated that the platelets were separated at least 3.5 nm. The TEM micrographs of the nanocomposites (which are not shown for brevity) show partially exfoliated structures.

Table 4 displays mechanical, thermal, barrier and heat release properties of the nanocomposite latexes synthesized by emulsion and miniemulsion polymerization processes.

For the nanocomposite latexes synthesized in emulsion polymerization tensile strength and storage modulus increased for nanocomposites EP2 and EP3 at the

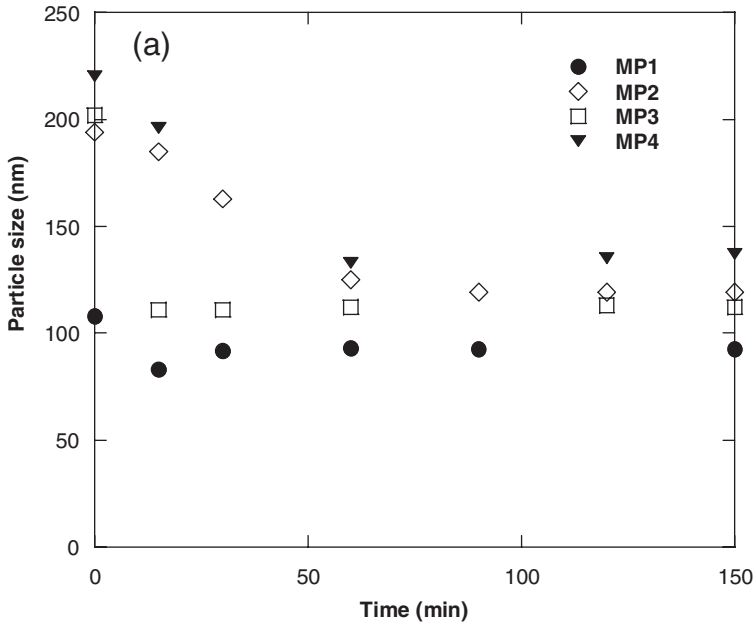

Figure 4.
Evolution of the particle size along the miniemulsion polymerizations carried out with organically modified clays.

expense of a reduction in the elongation at break, which was significantly more affected in the blend. This is in agreement with the morphology of the nanocomposite observed in both XRD and TEM analysis, where more tactoids and a worse dispersion of the clay was observed for latex EP3; that was produced by a blending procedure. In this sense, Beall et al.[38] concluded that unexfoliated platelets can act as stress concentrators, contributing to loss in impact.

The glass transition temperature, Tg, also increased for the latexes EP2 and EP3, but the increase was modest (less than 4 °C) and specially for EP2 where the increase was roughly only one degree. This is

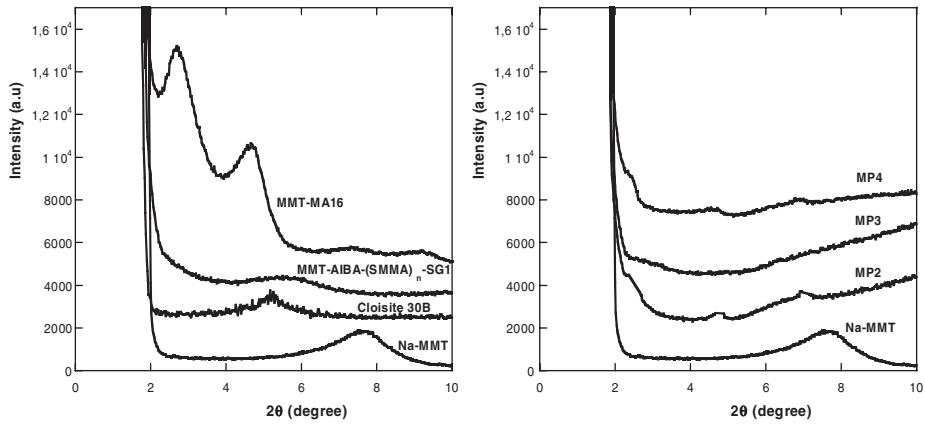

Figure 5.
XRD diffraction patterns of pristine clay and the organically modified clays as well as nanocomposite latex films prepared by miniemulsion polymerization.

Table 4.
Properties of the waterborne nanocomposite latexes prepared by emulsion and miniemulsion processes.

Entry	Tensile strength[a] (MPa)	Storage Modulus* (MPa)	Elongation at break* (%)	Tg (°C) DMTA	Td (°C) At 50% loss	WVTR® (g mm/cm² days)	O_2 Permeation (bar)	Heat Release Rate (kW/m²)
EP1	9 ± 1	78	327 ± 10	38.3	387	21.0 ± 0.3	–	–
EP2	13.1 ± 1	162	270 ± 8	39.5	401	11.8 ± 0.2	–	–
EP3	16 ± 1	405	153 ± 5	42.0	398	12.3 ± 0.7	–	–
MP1	7 ± 1	26	455 ± 17	37.0	413	19.0 ± 1.5	4.34 ± 0.2	234.2
MP2	7.5 ± 0.2	82	277 ± 12	48.5	419	12.2 ± 1.1	3.40 ± 0.1	125.3
MP3	5.6 ± 1	4.6	265.3 ± 6	–	417	15.7 ± 0.7	–	–
MP4	–	–	–	–	410	–	–	–

[a] Measured in strain/stress measurements in an INSTRON equipment.
® Water vapour transmission rate. The permeability analysis was performed by the film-air side of the washed films. The value displayed on the table corresponds to an average of three measurements.

important for latexes in coating applications because an increase in the Tg will affect the film formation temperature in a deleterious way.

On the other hand, the decomposition temperature of nanocomposite films at 50% loss of weight increased significantly for both nanocomposites. Water vapour permeability, WVTR, was also studied for the pure copolymer and the two nanocomposites EP2 and EP3. The data shown in the table corresponds to the film-air interface. The film-substrate interface was hardly affected by the presence of clay. The films were rinsed to avoid the effect of the SLS migrated to the interface during film formation on water vapour permeability.[39] It can be seen that the presence of the clay in the polymer matrix reduced the permeability of the films significantly, although no much difference can be observed between nanocomposite EP2 and EP3. The decrease of the permeability is attributed to a more tortuous diffusion path through the polymer film.

For the nanocomposites synthesized by miniemulsion polymerization similar results were obtained. Thus, the mechanical properties of nanocomposite MP2 were better than those of the reference polymer, MP1. However, for nanocomposite MP3 lower tensile strength and very low storage modulus were obtained. This is likely due to the low molecular weight of the copolymer produced in this nanocomposite (ca. 80,000 g/mol).

The Tg of the nanocomposite MP2 was 11 °C higher than the counterpart without clay, MP1. Admittedly, we cannot offer an explanation for such an increase and further characterization is needed to shed light on this difference, that was not observed in the nanocomposites synthesized in emulsion polymerization. The decomposition temperatures are also higher than for the nanocomposites prepared by emulsion polymerization, but in this case the copolymers without clay also show noticeable differences. It has to be pointed out that these differences are not produced by the average composition of the copolymers, as

complete conversion was achieved in all the cases.

WVTR and oxygen permeability decreased for the nanocomposites MP2 and MP3 in a similar way as for the nanocomposite latexes produced in emulsion.

Finally, the heat release rate was measured for the nanocomposite MP2 and the pristine polymer latex MP1. A significant reduction on the heat release rate was observed for nanocomposite MP2.

High Solids Content Latexes

In most of the literature works polymer/clay nanocomposite latexes were synthesized by means of batch processes and polymer dispersions with solids content well below 20 wt% were obtained. These solids contents are far from what is required in commercial practice. There are two main difficulties to increase the solids content of a polymeric nanocomposite dispersion containing clay: i) increasing the solids content, while maintaining the ratio clay/monomer, means increasing significantly the clay/water ratio, and this implies a significant increase in the viscosity of the aqueous phase; ii) maintaining the stability of the latex during the polymerization is also more difficult because platelet to platelet interaction is enhanced (which increases the effective volume fraction of the particles in the dispersion) and hence coagulation risk is higher. In this work, stable latexes with solids content around 45 wt% were produced by seeded emulsion polymerization carried out in semibatch operation.

Figure 6 displays the evolution of the instantaneous overall conversion and particle size as well as the XRD patterns of the high solids nanocomposite latex prepared by emulsion polymerization. Na-MMT was added in both the initial charge and in the monomer pre-emulsion fed to the reactor. The instantaneous conversion was high (>92%), i.e., the polymerization proceeded under rather starved conditions. The final particle size was 123 nm and the viscosity of the latex was 2525 cp. The XRD shows intercalated structure with a broad shoulder at low angles corresponding to a basal distance of 2.76 nm.

Latex MP5, with 42 wt% solids content was also synthesized by seeded emulsion polymerization. The seed was prepared by miniemulsion polymerization at 70 °C and with all the clay (Cloisite 30B) in the miniemulsion as in the batch miniemulsion experiments above. Then, two separate streams were fed to the reactor: one with neat monomer and the other one with an initiator solution (AIBN). The final solids content of the latex was 42 wt% with 1.8 wt% of clay based on the monomer and the final latex viscosity was 170cp. The

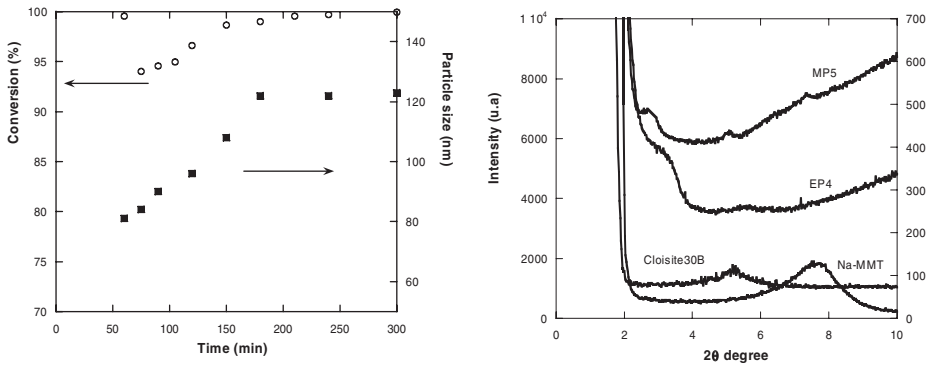

Figure 6.
Time evolution of the instantaneous conversion and particle size for the production of nanocomposite latex EP4 (left) and XRD patterns of nanocomposite films from latexes EP4 and MP5(right).

XRD shows no peak (apart from the three little peaks corresponding to the SLS surfactant) indicating at least intercalated or partially exfoliated structure.

Conclusions

Waterborne (MMA-BA)/MMT nanocomposites with partially exfoliated structure and improved mechanical and barrier properties were prepared by emulsion and miniemulsion polymerization. In the emulsion process pristine sodium montmorillonite was used because it readily exfoliates in aqueous phase. On the other hand for the miniemulsion process organically modified montmorillonites were used in order to incorporate the clay to miniemulsion monomer droplets. These nanocomposites can be used as binders for coating applications. The nanocomposite dispersions were synthesized at solids content ca. 45 wt% and using a seeded semibatch operation, as it is typically used in industry.

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