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Polymer-clay nanocomposites prepared via in situ emulsion polymerization

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Abstract A series of novel polystyrene and poly(butyl methacrylate) montmorillonites (MMT-Na) nanocomposite latexes have been successfully prepared by emulsion polymerization. First of all, chemical modification of MMT-Na with a reactive coupling agent (MMT-QS) has been employed for the synthesis of hybrids. Subsequently, in situ seeded emulsion polymerization of hydrophobic vinyl monomers, such as butyl methacrylate and styrene, using sodium dodecyl sulfate (SDS) and ammonium persulfate (APS) as surfactant and initiator, respectively, were used for nanocomposite preparation. This technique allowed preparing of stable nanocomposite latexes with high (30–45 wt.%) solids contents and with loading of inorganic particles up to 5 wt.%. The prepared wet dispersions were subsequently characterized by light scattering method. In order to characterize the microstructure of the clay layers, and that of the organoclay in polystyrene and poly(butyl methacrylate) nanocomposites, wide and small angle X-ray analyses (WAXS, SAXS) and transmission electron microscopy (TEM) techniques were used.

Keywords Organic-inorganic hybrid · Organoclay · Emulsion polymerization · Polymer nanocomposite · Montmorillonite · Butyl methacrylate · Styrene

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Introduction

Organic–inorganic hybrids with well-defined morphology and structure at the nanometric scale represent a very interesting class of materials with unique properties. These materials represent a new class of polymeric materials which combine the properties of the inorganic particles (mechanical strength, modulus, thermal stability) with processability and the flexibility of the organic polymer matrix. In order to prepare such materials either organic molecules can be embedded into inorganic materials (or vice versa) or inorganic particles can be encapsulated by polymers. The latter approach allows to achieve a good dispersion of the inorganic compound and to increase interfacial adhesion between the polymer and the mineral. Nanocomposites, where the organic and inorganic grouping can be linked by stable chemical bond, have been a research hot point in recent years because of these composite particles offer potential advantages in many application fields such as cosmetics, inks, paints, adhesives, textiles, optics, controlled release and electronics from the improved compatibility between the filler and the binder [1–4].

There has been a great number of reports on the synthesis of nanocomposite by in situ intercalative polymerization. However, these approaches mainly produce polymeric solutions of exfoliated clay sheets and do not give rise to particles. Thus, attempts to synthesize polymer-layered clays nanocomposites latexes through emulsion polymerization have been recently described in the open literature. This heterogeneous polymerization provides an effective way of synthesizing nanoparticles with various architectures and forms. This polymerization process offers many advantages compared to solution or bulk polymerization such as a low viscosity of the suspension medium, high molecular weights, and the possibility to control reaction rate, particle size and morphology effectively [5, 6].

Seeded emulsion polymerization is commonly used technology in production of emulsion, that is, the seeded emulsion polymerization occurs beforehand in the presence of water, emulsifier, water-borne initiator and small amount of monomer, in which the emulsion has a large number of particles with very small size. Then the polymerization reaction continues in the presence of the seeded emulsion, water, emulsifier, initiator and monomer.

In recent literature, emulsion polymerization is more and more popular as a new polymer-encapsulating technology. Latex-encapsulating technology has been developed for coating of the fine inorganic powders (submicrometer in size) in aqueous systems by emulsion polymerization. Fillers, such as titanium dioxide, talc, mica, calcium carbonate, china, clays, several oxides and metal powders were covered by means of conventional emulsion polymerization [7–11].

When the hydrophobic coat layer is simply adsorbed on the hydrophilic inorganic particle surface, the poor chemical interaction between inorganic and polymer can result in desorption of the polymer. Therefore, the modification of the particle surface has been often employed for the synthesis of hybrids. Chemical modification of silica particles surface with a reactive coupling agent, anchoring of the monomer by adsorption have been employed for the synthesis of hybrids by subsequent emulsion polymerization of hydrophobic vinyl monomers, such as acrylates and styrene (St) [11–15].

The tremendous surface area of the clays can significantly influence properties at much lower weight loadings than traditional fillers, therefore the majority of research activities has been shifted from traditional fillers to clays. In layered clay–polymer composites with nanometer dimensions, the compatibility between clay and a polymer matrix is the key factor that determines the structure of the composite as a conventional microcomposite or nanocomposite. However, it is extremely difficult to achieve complete exfoliation of the layers due to strong electrostatic interaction between silicate layers and intragallery cations. A successful attempt to avoid this difficulty is carried by replacing inorganic cations by some quarternized ammonium or phosphonium salts, preferably with long alkyl chain. Such alkylammonium or alkylphosphonium cations reduce the surface polarity of the silicate layers and enhance the affinity between the silicate and the polymer matrix. Commercially available montmorillonite clays, hydrophobically modified, are too hydrophobic to transport through water and often result in batch coagulation when introduced to an emulsion polymerization therefore in some processes, the modified clays were dissolved in the monomer, which was polymerized in a conventional emulsion polymerization procedure [16–20].

The goal of this work was to prepare high solids content waterborne polymer/clay nanocomposites by in situ emulsion polymerization. First, the modification of two types of montmorillonites (MMT-Na) (Cloisite-Na and Nanocor-Na) with a modifier containing a cationic head with a reactive tail is described. Second, in situ emulsion polymerization of St and butyl methacrylate (BMA) in the presence of organoclay is presented. The cationic head formed an ionic bond with a clay platelet and the reactive vinylic group can allow anchoring of polymer onto MMT-Na and formation of polymer/clay nanocomposites. Third, the effect of the platelets content on the particle size of prepared nanocomposite latexes and morphological properties of the nanocomposite films are presented and compared with neat polymer and polymer composites containing clay in sodium form prepared under the same conditions.

Experimental

Materials

Styrene and BMA from Fluka were freshly distilled under reduced pressure before polymerization. Ammonium persulfate (APS), sodium dodecyl sulfate (SDS) were purchased from Fluka and used as received. MMT-Na: Nanocor-Na which contains exchangeable cations of primarily Na^+ was provided by Nanocor Inc.; its cation exchange capacity (CEC) was 145 meq/100 g (average dry particle size 16–22 μm). Cloisite-Na with CEC 92.6 meq/100 g (typical dry particle sizes 10% less than 2 μm, 50% less than 6 μm and 90% less than 13 μm) was obtained from Southern Clay Products. MMT-Na were used without further purification. Modification cationic agent [2-(acryloyloxy)ethyl]trimethylammonium chloride (QS) was purchased from Fluka. Solvents (chloroform, ethanol) were purchased from Fluka.

Preparation of organoclay by cationic exchange process

The natural forms of clays including montmorillonite are hydrophilic and not miscible at a molecular level with polymers. In order to make these layered inorganics compatible with polymer systems, a counterion, usually Na^+, inside the gallery space must be exchanged for a molecule that makes the surface of the platelet organophilic. The exchange of this ion is said to create an "organoclay" more compatible with the polymer matrix. The organoclays in this paper were prepared by cation exchange reaction of MMT-Na (Nanocor, Cloisite) with the monomer containing quaternary ammonium group, in particular with [2-(acryloyloxy)ethyl]trimethylammonium chloride.

The formation of intercalated vinyl monomers into clay interlayer proceeded as follows: sodium montmorillonite (10 g) was dispersed in distilled water (60 mL) and swelled under stirring at ambient temperature for 24 h. Then the temperature was increased to 70 °C and suspension was heated under stirring for 1 h. After cooling down, a calculated amount of modifying organic monomer corresponding to multiples of the CEC of the clay (1, 1.5, 2 and 3) were added to the dispersions. The monomer addition was done at once or stepwise. In case of the stepwise addition, in the beginning an equivalent of monomer in form of quaternary ammonium salt was added. Then the mixture was stirred for 4–6 h at room temperature followed by the next portion of monomer addition. The overall time of ion-exchange reaction was 12 h. Subsequently, the suspension was filtered off, followed by repeated washing with distilled water until the excess of unadsorbed cations was removed. The degree of ion-exchange reaction was evaluated from the elemental analysis.

Preparation of organically modified MMT/polymer nanocomposites by emulsion polymerization

Nanocomposite polystyrene/MMT latexes were prepared using seeded in situ emulsion polymerization of organic monomer in the presence of organically modified clay (MMT-QS). The polymerization was carried out in a glass reactor fitted with a nitrogen inlet, a thermometer and an anchor-type agitator. In a typical synthesis, the reactor was charged with solution of deionized water (56.8 mL) and surfactant (SDS) (0.138 g). The initial charge was stirred at 500 rpm and heated up to 85 °C under nitrogen for 10 min. Emulsion mixture containing 38.5 mL of water, 0.921 g of organoclay, 1 g of SDS and 92.1 g of monomer was prepared in a separate flask by following procedure: the organoclay was dispersed in distilled water and the suspension was kept for 30 min under vigorous stirring. Then the surfactant and monomer were added to the clay suspension in water under stirring. Stirring of prepared emulsion mixture was continued under nitrogen for another 30 min. Then 5 g of emulsion mixture was placed into the reactor and a solution of initiator, prepared by dissolving of 0.25 g of APS in 0.8 g of deionized water, was added. The charge was stirred for 10 min. Afterward, the reactor was fed with the remaining emulsion mixture under nitrogen and constant flow rate slow enough to reach monomer starved conditions and the reactor was simultaneously fed with a solution of initiator (0.11 g of APS in 7.5 mL of water). The monomer emulsion

Table 1 Formulation used for the encapsulation of inorganic particles through the seeded emulsion polymerization of styrene and butyl methacrylate

Sample	Monomer		Clay (g)			APS (g)	SDS (g)	Deionized water (g)
	(wt.%)	(g)	1[a]	3[a]	5[a]			
SA1, B1, BA1	46.7	92.10	0.921	2.763	4.605	0.36	1.138	105.1
SA2, B2, BA2	39.7	69.08	0.691	2.0722	3.454	0.36	1.138	105.1
SA3, B3, BA3	30.5	46.05	0.461	1.3815	2.303	0.36	1.138	105.1

Clay represents MMT-Na or organically modified clay (MMT-QS)

[a] wt.% of MMT-Na or MMT-QS related to monomer

feed was stirred and continuously purged with nitrogen during the addition period. The time period of feeding was 300 min, then the solution of 0.25 g of APS in 1.5 mL of water was added. Afterward, the polymerization mixture was allowed to polymerize for another 30 min at 85 °C. The system was cooled to room temperature and the final latex was obtained without any post preparative treatments. A detailed recipe for both the basic latex (46.7 wt.% of monomer relative to water) and that with the amounts of monomer lowered to 39.7 or 30.5 wt.% is given in Table 1.

For comparison purposes, a blank emulsion polymerization and nanocomposite latexes with MMT-Na were prepared following the above described procedure, without inorganic particles or with MMT-Na, respectively.

The instantaneous and overall conversions for blank polymerizations were determined from gravimetric measurement of solids content. Samples (ca 3 cm^3) were prepared using procedure described by Britton [30–32] (quenching in a ice/water bath with hydroquinone, dialysis, coagulation by freeze-thaw cycling, washing with deionized water and drying to constant weight at higher temperature under lower pressure).

Preparation of organic-inorganic composite films

Prepared latexes were precipitated by pouring under vigorous stirring into tenfold excess of ethanol. The white precipitate was filtered off, repeatedly washed with ethanol and purified by repeated re-precipitation from chloroform solution to ethanol. X-ray and TEM analysis were performed on nanocomposite clear films prepared by casting from chloroform solution.

Characterization

The mean polymer particle sizes were measured by dynamic light scattering (DLS) technique using a Coulter Nano-Sizer (Coulter, UK) in unimodal analysis. For analysis, a fraction of the latex was diluted with deionized water. The reported mean particle size values represent an average of four repeated measurements.

Characterization of nanocomposite morphology

An important issue is to relate the performance of nanocomposites to their morphological structure. Wide angle X-ray scattering (WAXS) is frequently used because such analysis is relatively simple. WAXS patterns of clays, organoclays, polystyrene and poly(butyl methacrylate) nanocomposites were obtained by X-ray diffraction, using powder diffractometer HZG/4A (Freiberger Praezisionsmechanik GmbH, Freiberg) with Cu Kα radiation ($\lambda = 0.1542$ nm, 40 kV, 45 mA, Ni-filter) in the 2θ range of 4–60°, step size 0.25°.

Small angle X-ray scattering (SAXS) can be more informative and somewhat quantitative explained by numerous authors [2, 21–23], therefore SAXS experiments were performed using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocused X-ray beam generator (Osmic MicroMax 002) operating at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector with an active area diameter of 20 cm (Gabriel design). Two experimental setups were used to cover the q range of 0.005–1.1 Å^{-1} ($q = (4\pi/\lambda)\sin\Theta$, where λ is the wavelength and 2Θ is the scattering angle).

A far more direct way of visualizing nanocomposite morphology is via transmission electron microscopy (TEM). The morphology of nanocomposite films was studied by means of a transmission electron microscope, TEM (Tecnai G2 Spirit Twin 12). The 50 nm thick specimens for TEM were prepared by ultramicrotomy (an ultramicrotome Leica Ultracut UCT), transferred to standard TEM copper grids with carbon film, covered with thin carbon layer to eliminate sample damage under electron beam and observed at 120 kV in bright field.

Results and discussion

The ion-exchange reaction of polymerizable cation into the clay interlayer leads to the vinyl monomer anchored-MMT. The modified organic derivatives of clays were characterized using elemental analysis (C, H, N) and the efficiency of ion-exchange reaction was evaluated. Comparing of carbon and nitrogen contents in modified clay related to the ion-exchange capacity of MMT, declared by manufacturer, gave the efficiency of ion-exchange reaction. The contents of carbon and nitrogen after total ion-exchange reaction of sodium cation to [2-(acryloyloxy)ethyl] trimethylammonium cation (QS) corresponded to 7.9 wt.% of C and 1.15 wt.% of N for Cloisite and 11.65 wt.% of C and 1.697 wt.% of N for Nanocor. The average values of carbon and nitrogen contents of modified MMTs and calculated degree of modification are reported in Table 2.

Table 2 presents the results of overall efficiency of ion-exchange reaction for MMT-Na. It was found that with the increasing amount of QS used (the increasing ratio QS/Na), the extent of ion-exchange increased. It could be pointed out that under conditions of stepwise addition of QS to clay suspension, an increase of ion-exchange reaction efficiency was observed. With the increasing number of steps the higher degree of modification was reached. The lower degrees of modification for Nanocor than for Cloisite were found for all samples. Results shown in Table 2

Table 2 Degree of Na-MMT modification by organic cation

QS	Cloisite				Nanocor			
	C_D (wt.%)	Modif. (%)	N_D (wt.%)	Modif. (%)	C_D (wt.%)	Modif. (%)	N_D (wt.%)	Modif. (%)
1	6.620	83.80	0.915	79.43	8.415	72.23	1.150	67.76
1.5	7.100	89.87	0.980	85.07	7.625	65.45	1.025	60.39
2	7.315	92.59	0.93	80.70	8.715	74.81	1.215	61.61
3	7.495	94.87	0.925	80.30	8.790	75.45	1.215	71.59
2[a]	7.265	91.96	0.955	82.90	8.535	73.26	1.220	71.83
3[a]	7.380	93.42	0.970	84.80	8.420	72.27	1.225	72.17
3[b]	7.440	94.18	1.045	90.70	8.800	75.53	1.205	71.00

QS: equivalent of [2-(acryloyloxy)ethyl]trimethylammonium chloride used for ion-exchange reaction; C_D, N_D: average values calculated from three elemental analysis determination; Modif.: overall ion-exchange reaction correlated to CEC of clay in Na form

[a] Addition in two steps

[b] Addition in three steps

confirmed that the modifying monomer, [2-(acryloyloxy)ethyl] trimethylammonium chloride, added into the clays aqueous dispersions can be stably adsorbed onto the clay platelets with a great absorption efficiency via the electrostatic interaction. Organoclays prepared by treatment with a threefold excess of the QS equvivalent by stepwise additon in three steps (yielding the highest degrees of modification) were used for the nanocomposite preparation.

Modification of nanoclay

XRD is a common technique used for examining of intercalation and expansion of clay interlayer spacing after cation exchange. The WAXS patterns of Nanocor-Na, Cloisite-Na and organically modified MMTs-QS with polymerizable [2-(acryloyloxy)ethyl]trimethylammonium cation (C-QS, N-QS) are shown in Fig. 1.

The clays Cloisite-Na, Nanocor-Na, Cloisite-QS and Nanocor-QS were used to prepare PSt/MMT and PBMA/MMT nanocomposites. The interlayer spacings d_{001} of MMT-Na as received, 11.9 Å for Cloisite-Na and 12.7 Å for Nanocor-Na, were determined in the WAXS pattern. After cation exchange reaction the organic cations penetrate into the layer space, replacing the inorganic Na cations and interlayer spacing increases. A slight shift of the interlayer spacing to 14.3 Å for Cloisite-QS and 14.7 Å for Nanocor-QS confirming ion-exchange was found. These data also indicated that the reactive species were successfully intercalated in the interlaminar space of the clay platelets.

Preparation of inorganic-organic particles via emulsion polymerization

In most of the published papers, the low solid content (<20 wt.%) in stable nanocomposite latexes is reported. The first paper in the open literature dealing with

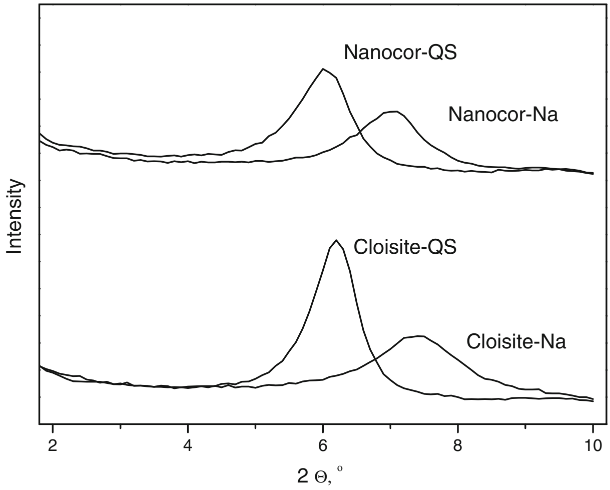

Fig. 1 XRD diffraction patterns of Cloisite-Na, Nanocor-Na and the organically modified clays Cloisite-QS and Nanocor-QS

preparation of latexes with high solid content (around 40 wt.%) was reported last year by Diaconu et al. [24, 25].

To prepare series of nanocomposite latexes, in this study, MMTs-Na and organically modified inorganic particles (MMTs-QS) were synthesized via in situ seeded emulsion polymerization. For clay modification a surface modifier containing a cationic head with a reactive tail was employed. The cationic head formed an ionic bond with a clay platelet and the reactive vinylic group can form a covalent bond with the monomer during polymerization and can allow anchoring of polymer onto MMT-Na and formation of polymer/MMT nanocomposites.

The latex stability was achieved by using an anionic surfactant, such as SDS, which can provide a heterogeneous reaction system with a potential energy barrier against coagulation. The potential energy barrier is attributed to the repulsive force between the negatively charged electric double layers of the disperse particles. The role of this surfactant and the relation between latex particle size and SDS concentration for emulsion polymerization of BMA was explained by Naderi et al. [26]. Polymerization was carried out under starved–feed condition. The effect of monomer concentration on the morphology of poly(methyl methacrylate)/silica nanocomposite latex via emulsion polymerization has been reported by Luna-Xavier et al. [27]. When the amount of MMA is increased, the polymer content increases, which means that more polymer is built up at the inorganic surface although the efficiency decreases. This effect is not very important for low MMA content where the most of monomer is solubilized in the water phase. For concentration above its limit of solubility, the formation of free polymer is promoted by the presence of free micelles and the efficiency dramatically decreases. This could be avoided and coating efficiency could be improved by addition of monomer under starved–feed conditions.

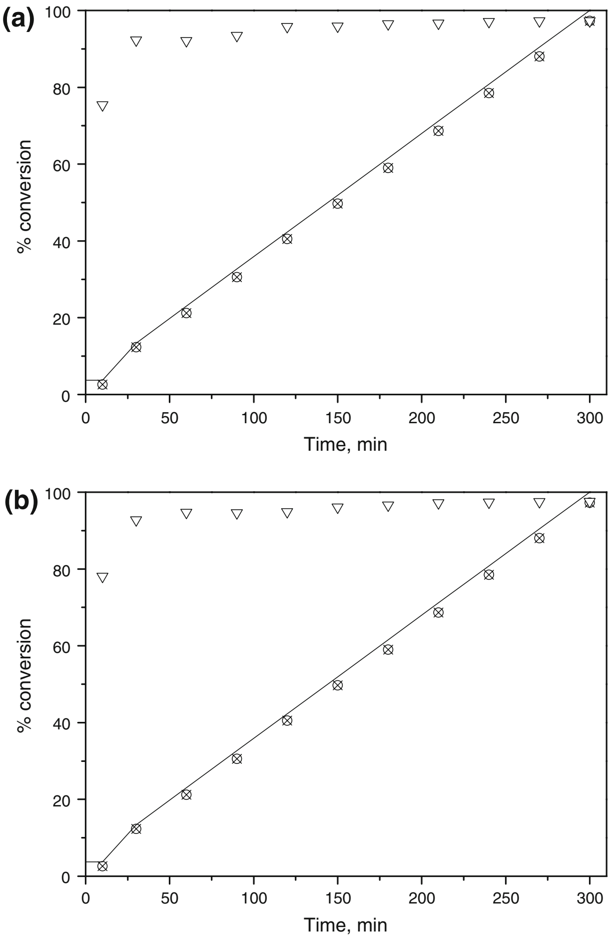

Fig. 2 Instantaneous conversion (*inverted triangles*) and overall conversion (*crossed circles*) with reaction time of emulsion polymerization carried at 85 °C. The *solid lines* show the monomer feed profile for 46.7 wt. % of final solids reaction: **a** styrene, **b** butyl methacrylate

Usually, monomer-starved conditions are defined in the terms of the instantaneous monomer conversion. The instantaneous conversion is the percentage conversion of the monomer added up to that point (including the monomer used in the seed stage), whereas the overall conversion is the percentage conversion of the total amount of monomer in the formulation. The normalized growth-stage monomer feed rates (given in % min^{-1}) were calculated as the ratio of the monomer mass feed rate to the total mass of monomer in formulation [30–32].

Figure 2a and b shows plots of time evolution of instantaneous and overall conversions for emulsion polymerization of St and BMA (latex with 46.7 wt.% of solids content). The results showed that polymerizations only proceeded under monomer-flooded conditions during the seed stage, in which only 3.75% of the total monomer is polymerized. From the beginning of growth stage the instantaneous

Table 3 Summary of the nanocomposite latexes synthesized by means of emulsion polymerization

Latex	Solids content (wt.%)	wt.% of clay[a]	Type of clay
S0, B0	46.7	–	–
B1	46.7	1 or 3 or 5	MMT-Na
SA1, BA1	46.7	1 or 3 or 5	MMT-QS
B2	39.7	1 or 3 or 5	MMT-Na
SA2, BA2	39.7	1 or 3 or 5	MMT-QS
B3	30.5	1 or 3 or 5	MMT-Na
SA3, BA3	30.5	1 or 3 or 5	MMT-QS

S0, B0: blank polystyrene, poly(butyl methacrylate) latexes; B: poly(butyl methacrylate) latexes with MMT-Na; SA, BA: polystyrene, poly(butyl methacrylate) latexes with organically modified clay (MMT-QS)

[a] Related to the total amount of monomer in the recipe

conversion is in range 92–96%. for each polymerization. Hence, the majority (96.25%) of the polymers were formed under monomer-starved conditions. The variation of instantaneous conversion with reaction time being similar for both of the used monomers.

The composition of hybrid organic–inorganic materials was varied from 0 to 5 wt.% of MMT clay to the PSt (PBMA) content as summarized in Table 3. The solids content was varied from 30.5 to 46.7 wt.%. The neat PSt, neat PBMA and PBMA/MMT-Na latexes were also prepared simultaneously as control experiments for comparative studies.

Particle size of nanocomposite latexes

Tables 4a and b summarize the mean particle size of PSt and PBMA hybrid latexes determined by DLS method. It was found that the nanocomposite latexes have higher particle size than neat latex, by around 20%, depending upon the amount and type of MMT used.

The neat latex (SO) containing only PSt had the mean particle size at 68 nm. By insertion of organically modified inorganic particles, the obtained polymeric nanocomposite hybrids revealed the growth of particle size in the case of both used clays as shown in Table 4a. The mean particle size of nanocomposite latexes was slightly dependent on the solids content of latexes. With increasing concentration of solids content, the particle size of nanocomposite latexes were slightly higher than that of the neat latex. The mean particles size was strongly influenced by concentration of organoclay. Increasing concentration of inorganic particles led to the growth of the mean particle size of prepared nanocomposite latex and occurrence of the aggregates was observed for some high loading of organoclays and solids. The loading of 5 wt.% of Nanocor-QS caused the aggregation of latex with the solids contents 46.7 wt.% and it was not possible to prepare homogeneous latex under given conditions. For latex prepared in the presence of Cloisite-QS in content 3 and or 5 wt.%, the partial aggregation of latex was observed.

Table 4 The mean particle size of latexes

Latex	wt.% of PSt	The mean particle size (nm)					
		wt.% Nanocor-QS			wt.% Cloisite-QS		
		1	3	5	1	3	5
a Polystyrene/clay nanocomposite latexes							
SA1	46.7	118	141	–	105	–	–
SA2	39.7	96	125	170	101	100	96
SA3	30.5	72	81	70	76	82	83

Latex	wt.% of PBMA	The mean particle size (nm)					
		wt.% Nanocor			wt.% Cloisite		
		1	3	5	1	3	5
b Poly(butyl methacrylate)/clay nanocomposite latexes							
BA1	46.7	99	105	108	107	–	–
BA2	39.7	88	103	106	88	95	–
BA3	30.5	66	78	99	66	67	61
B1	46.7	121	92	103	87	90	92
B2	39.7	67	70	86	88	82	83
B3	30.5	69	71	73	69	70	–

The compatibility of the monomer with the organophilic clay is also an important factor. The polarity and hydrophobicity of monomer greatly affect dispersion of the clay. It has been shown that media that posses both polar and non polar characteristics had excellent ability to swell and disperse ammonium modified organophilic MMT. BMA contains both low polar (butyl group) and high polar (ester group) parts. Zeng [28] and Blumstein [29] showed that MMA has stronger compatibility with the polar clay surface than St. Similarly, for BMA, it could be achieved the organic cation intercalation due to more favorable interaction between BMA and clay surface in comparison with St. Therefore, BMA was used as monomer for nanocomposite preparation.

The neat latex (BO) containing only PBMA had the maximum particle size at 69 nm. The values of the mean particle size of nanocomposite latexes containing both organically modified and sodium form of MMTs are summarized in Table 4b. The data shown in this Table indicated that the mean particle size was slightly dependent on the solids content of latexes. For latexes prepared using MMTs-Na, a slight decrease in particle growth was found and prepared nanocomposite latexes were homogeneous except that with loading of 5 wt.% of Nanocor-Na. Introduction of organoclays caused the growth of latex particles in dependence on organoclays loading. As shown in Table 4b, similarly to results for PSt latexes, for PBMA nanocomposite latexes containing 3 and 5 wt.% of Cloisite-QS (with the highest solid content) and 3 wt.% of Cloisite-QS (39.7 wt.%), aggregation occurred during polymerization. The finding that the nanocomposite latex mean particle size is often smaller than the often assumed length of MMT platelets was explained by Paul and Robeson [2], who pointed out that while thickness of MMT platelets is a well-defined crystallographic dimension, the lateral dimensions of the platelets are not. In dependence on the growing of particles from solutions during preparation, the particles are not all of the same length and the lateral dimensions of particles varied in a very broad range. Authors showed a more realistic picture of clay tactoids and explained the fact that the particles became shorter after processing without any breakage.

Characterization of nanocomposite morphology

In order to characterize the microstructure of the clay layers in PSt and PBMA nanocomposite latexes and to confirm inner structure of the hybrid films prepared from nanocomposite latexes, SAXS, WAXS, and TEM techniques were used. Figure 3 summarizes the WAXS patterns taken from PSt/MMT-QS films. Upon polymerization no diffraction peaks were observed for the film prepared from latex containing 1 and 5 wt.% of organically modified clays and 39.6 wt.% of polymer content which indicate that the platelets were separated in the PSt matrix. Small amounts of some larger tactoids of neat or organically modified MMTs were identified in samples with 1 and 5 wt.% of Cloisite-QS.

Both scattering methods, SAXS and WAXS, were used for PBMA/MMT nanocomposites characterization.

The presence of a scattering maximum at $q \sim 5\ \mathrm{nm}^{-1}$ is usually taken as an evidence for lamellar structure of the clay component of nanocomposites, while its absence is believed to indicate exfoliated state of the clay [23]. Our SAXS study of the PBMA nanocomposites demonstrates that these arguments are not always valid.

The SAXS curves of the PBMA nanocomposites (Fig. 4) exhibit distinct maximum at $q = 5.2\ \mathrm{nm}^{-1}$ $(2\theta = 7.3°)$ suggesting an ordered multilamellar

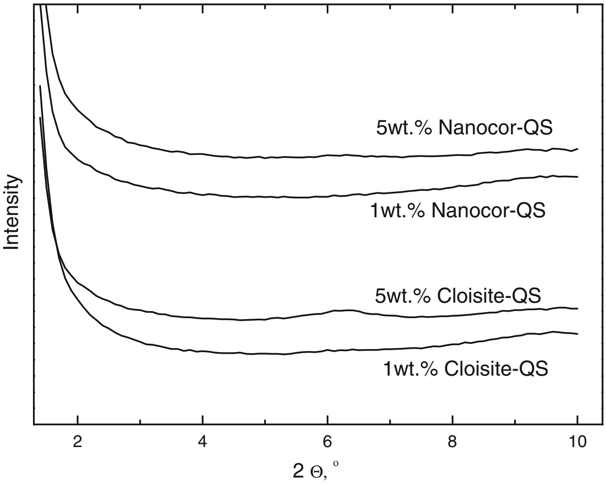

Fig. 3 WAXS patterns of polystyrene/MMT-QS nanocomposites with 39.7 wt.% of solids content

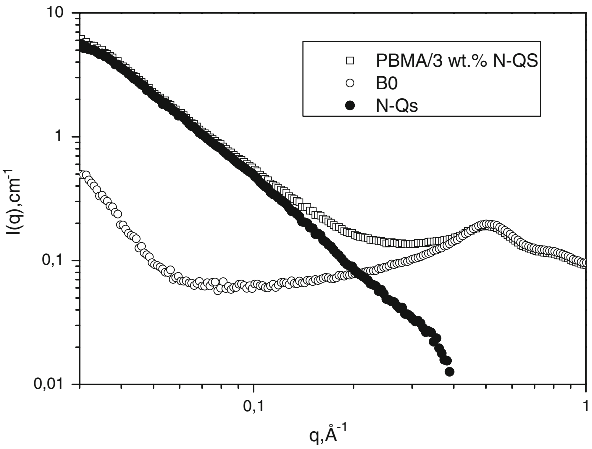

Fig. 4 SAXS curves of the neat PBMA latex (B0), nanocomposite latex PBMA with 3 wt.% Nanocor-QS (PBMA/3wt.%N-QS) and their difference, Nanocor-QS (N-QS)

structure of the clay. However, similar maximum is also observed for the PBMA latexes without clay. In addition, a closer inspection of the SAXS data for the latex with 1.1 g N-QS/100 mL (PBMA/3 wt.%N-QS) reveals that this clay is exfoliated in the latex. The Guinier analysis of the PBMA/Nanocor-QS SAXS data after subtraction of the scattering contribution PBMA suggests that the clay forms platelike particles with thickness of ca 1.3 nm. It is in a reasonable agreement with the value expected for single sheets. This result has been obtained from both slope of the ln $I(q)q^2$ versus q^2 plot (Fig. 5), and from absolute intensities $I(q)q^2$ extrapolated to zero scattering vector. This plot provides the radius of gyration of the plate thickness, R_{gt}, and the mass per unit area, M_A, using following formula:

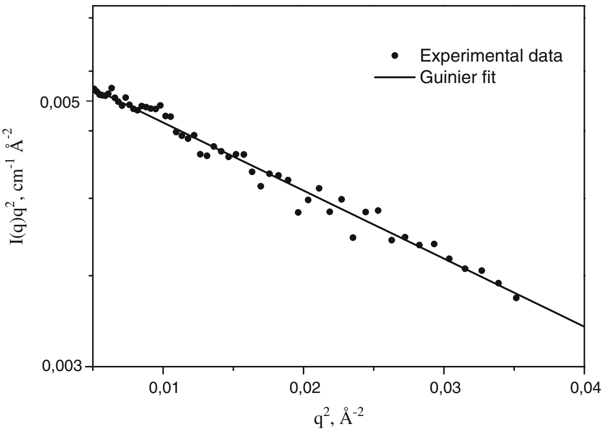

Fig. 5 Guinier plot of the thickness factor of the PBMA/3wt. % Nanocor-QS latex with the scattering from the PBMA matrix being subtracted

$$I(q) \times q^2 = \frac{2\pi c(\Delta b)^2 M_A e^{-R_{gt}^2 q^2}}{N_A}$$

where the excess scattering length per 1 g of solute, $\Delta b = b - \overline{V}\rho_0$, with b and $\overline{V}$ being the scattering length and partial volume, respectively, and ρ_0 is the scattering length density of the solvent. Using the value $\Delta b = 5.0 \times 10^{10}$ cm/g, based on the mass density of the clay of 2.85 g/cm^3, the mass of the clay per unit area of 18 g/mol/Å^2 was obtained. This value is close to that for the fully exfoliated clay (22 g/mol/Å^2).

One of the reasons for the choice of PBMA as a polymeric component of the nanocomposite was that its scattering length density, 9.50×10^{10} cm^{-2}, is very close to that of water (9.42×10^{10} cm^{-2}). This reduces the scattering from the latex particles in aqueous media and makes it possible to observe clay particles at relatively low concentrations. Regardless of low contrast, due to high solid content and high molar mass, very high scattering intensities were observed for the neat PBMA latex (Fig. 6). Fitting of the SAXS curve to scattering function of spherical particles with Schultz–Zimm size distribution resulted in the following characteristics of the latex particles: mean diameter = 79 nm, relative standard deviation = 0.16, weight average of molar mass = 0.22×10^9 g/mol, specific surface (interface area per unit volume) = 26 m^2/cm^3.

Scattering from the film prepared from the PBMA latex shown in Fig. 6 is even stronger compared to that from the latex. Source of this scattering is not yet clear (nano- or micropores?).

Using SAXS technique, three types of nanocomposites were studied: latex as aqueous dispersion, and after transferring to solid state via lyophilization (powders) or casting (films). No qualitative changes connected with variation of the clay type or concentration have been found for the solid samples. Representative SAXS data of all three types of nanocomposites containing two different concentrations of MMT-Na and organoclay at fixed latex solid loading are displayed in Fig. 7. It

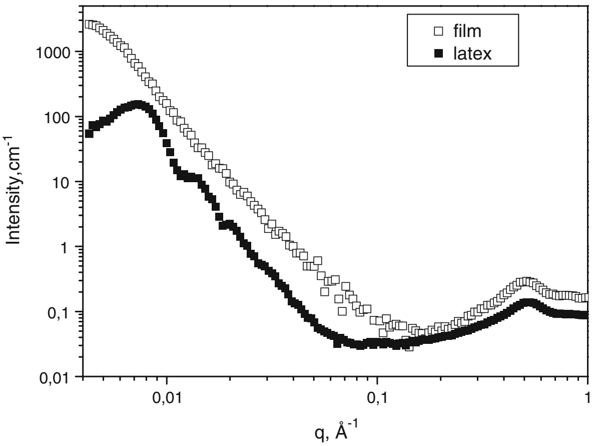

Fig. 6 The SAXS curves of the neat poly (butyl methacrylate) (B0) in latex and as a film

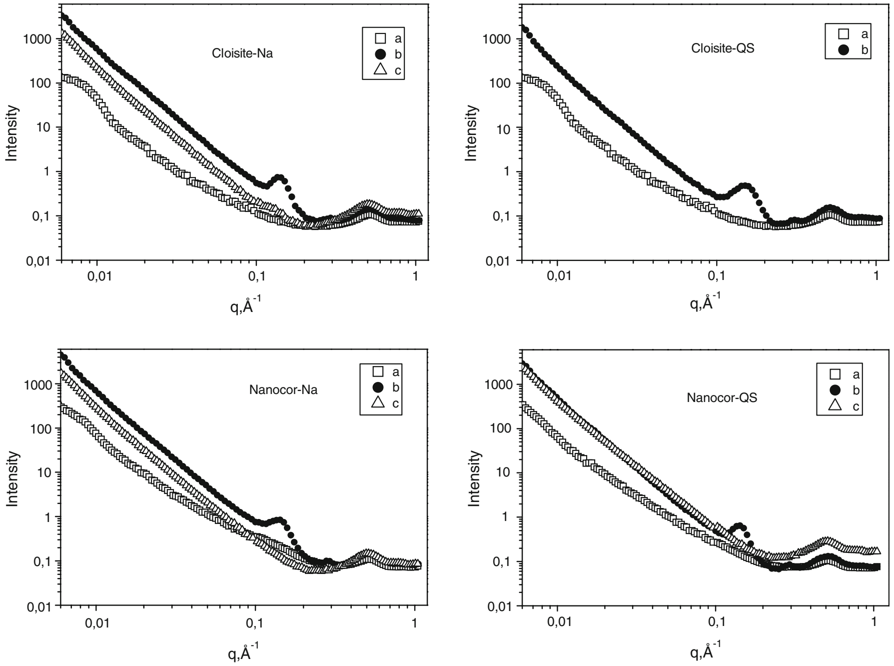

Fig. 7 Examples of the SAXS curves of PBMA/MMT nanocomposites with 30.5 wt.% solids content and 3 wt.% of clay loading for various types of samples: latex (**a**), lyophilised powder (**b**), film (**c**)]

should be noted that the SAXS curves of the powders exhibit two maxima, at $q = 1.5\ \text{nm}^{-1}$ ($2\theta = 2.1°$) and $q = 3\ \text{nm}^{-1}$ ($2\theta = 4.2°$). These maxima can be ascribed to the SDS used as a surfactant during emulsion polymerization and not removed during lyophilization. Therefore, they cannot serve as an evidence of clay intercalation.

Analysis of the SAXS curves of the latexes reveals the power law behavior with a slope close to -2. This is a signature of an exfoliated clay. The different scattering behavior at the smallest q's reflects the particulate character of the latex structure. The SAXS curves of the powders and films exhibit a power law behaviour with an exponent of about -3. This could correspond to crumpled clay sheets with large mass fractal dimension (approaching 3) or to globular nonfractal clusters (exponent smaller than -3).

Figure 8 shows a series of thin films WAXS patterns obtained from Cloisite-Na, Cloisite-QS, Nanocor-Na and Nanocor-QS poly(butyl methacrylate) nanocomposites of different clay content and fixed polymer loading during emulsion polymerization (39.6 wt.%). All poly(butyl methacrylate) nanocomposites show a diffraction peaks with an identical interlayer spacing corresponding to PBMA. The obtained results suggest partial exfoliation of the clays in polymer matrix. It was proved that the maxima found in the case of PBMA/Cloisite-Na correspond to crystalline SDS which was not completely removed from measured samples.

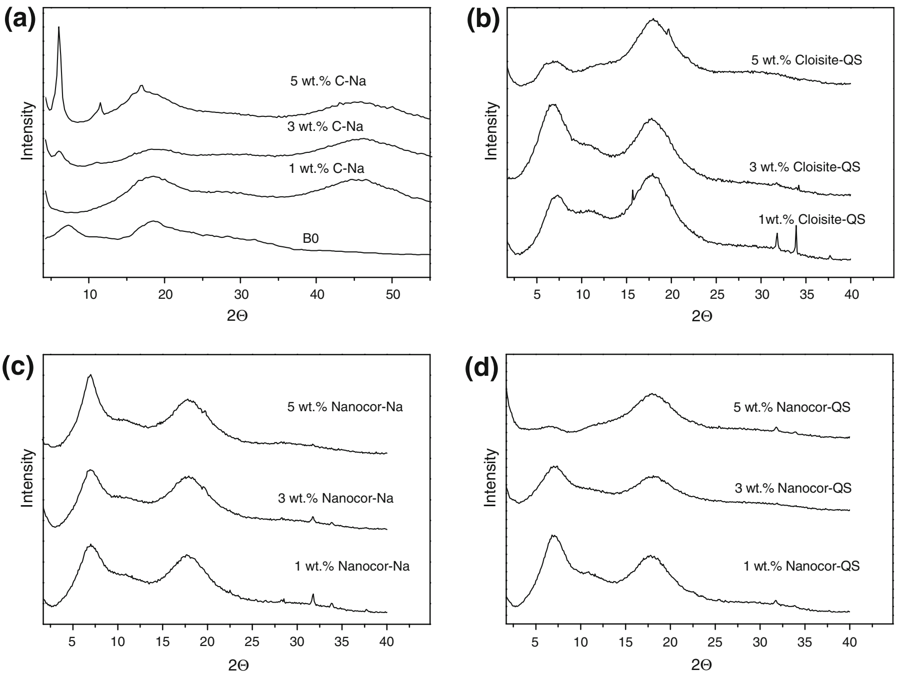

Fig. 8 The WAXS patterns of blank poly(butyl methacrylate) (B0), nanocomposites with Cloisite-Na (**a**), Cloisite-QS (**b**), Nanocor-Na (**c**) and Nanocor-QS (**d**) latexes with 39.7 wt.% of solids content

In order to compare the exfoliation of MMT-Na and organoclays in polymer matrix in more detail, thin films from nanocomposite PBMA latexes containing 3 wt.% of inorganic particles and 39.6 wt.% of polymer loading were prepared. The films were cut into ultrathin sections and studied by TEM using bright field (BF) mode at 120 kV. Typical TEM micrographs of Cloisite (C–Na, C-QS; Figs. 9a, b and 10a, b) and Nanocor (N–Na, N-QS; Figs. 9c, d and 10c, d) show light areas of PBMA matrix with darker clay sheets, larger tactoids and/or agglomerates. It might be worth noting that the contrast in TEM/BF micrographs is mostly due to diffraction on clay particles and, as a result, some clay single sheets are hardly observable, especially if they are perpendicular to electron beam.

As supposed, TEM micrographs MMT-Na composites (Figs. 9a, c and 10a, c) showed worse dispersion of clay platelets in polymer matrix in comparison with the organoclay composites (Figs. 9b, d and 10b, d). TEM micrographs also confirmed that Cloisite-Na systems (Figs. 9a, 10a) contained larger agglomerates than Nanocor-Na systems (Figs. 9c, 10c). Moreover, the overall dispersion of particles in organoclay systems (Figs. 9b, d and 10b, d) was more homogeneous, especially in case of organically modified Nanocor (Figs. 9d, 10d). Within organoclay composites (Figs. 9b, 10b versus Figs. 9d, 10d), the extent of exfoliation in both Cloisite-based systems and Nanocor-based systems looked very similar, which corresponded to WAXS results (cf. Figs. 8, 9b, d and 10b, d). According to both TEM and WAXS results, the best dispersion was achieved for systems with

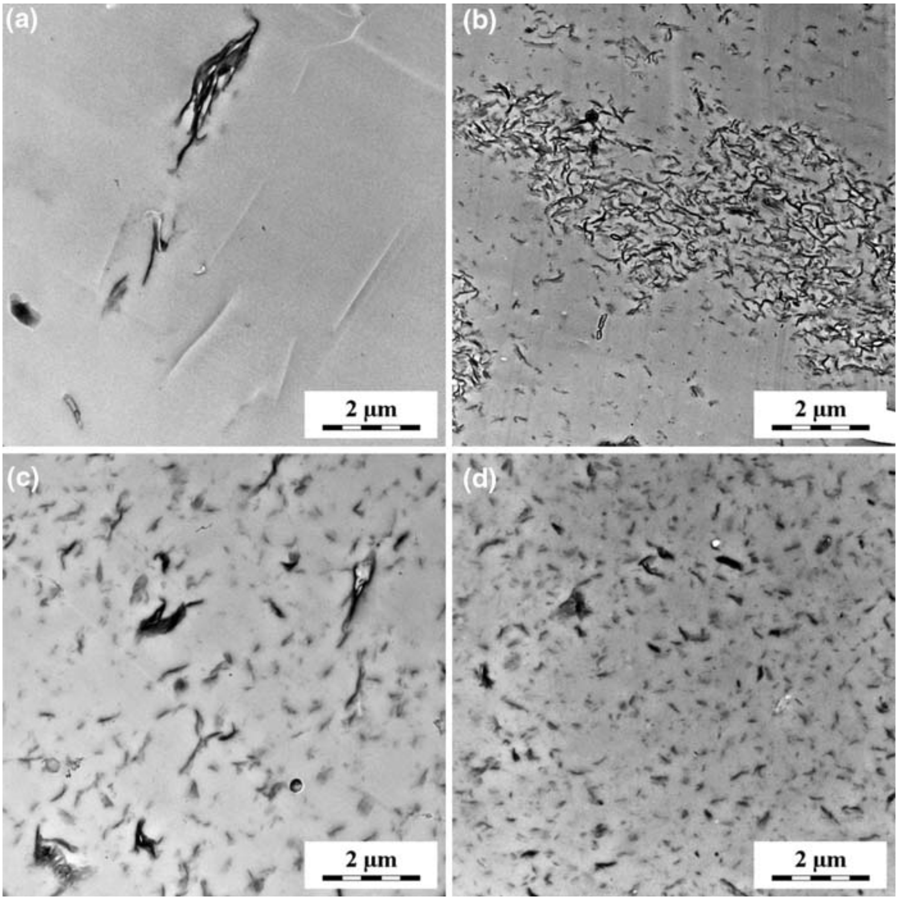

Fig. 9 TEM micrographs of the films prepared from nanocomposite PBMA/MMT latexes with solids content 39.7 wt.% and 3 wt.% of inorganic particles: **a** Cloisite-Na, **b** Cloisite-QS, **c** Nanocor-Na, **d** Nanocor-QS

organically modified Nanocor (Figs. 8, 9d, 10d). All TEM micrographs of nanocomposite with organically modified Nanocor displayed partially exfoliated morphology of MMT and corresponding WAXS patterns showed the lowest clay diffractions. Chemical modification of clay resulted in better polymer-clay affinity, which resulted in partial exfoliation and quite well dispersion of organoclay in the polymer matrix.

Conclusions

New polymer–clay high solids content hybrid emulsions, have been synthesized by in situ seeded emulsion polymerization of St and BMA using a vinyl MMT-monomer. The preparation was carried out by modification of Cloisite and Nanocor

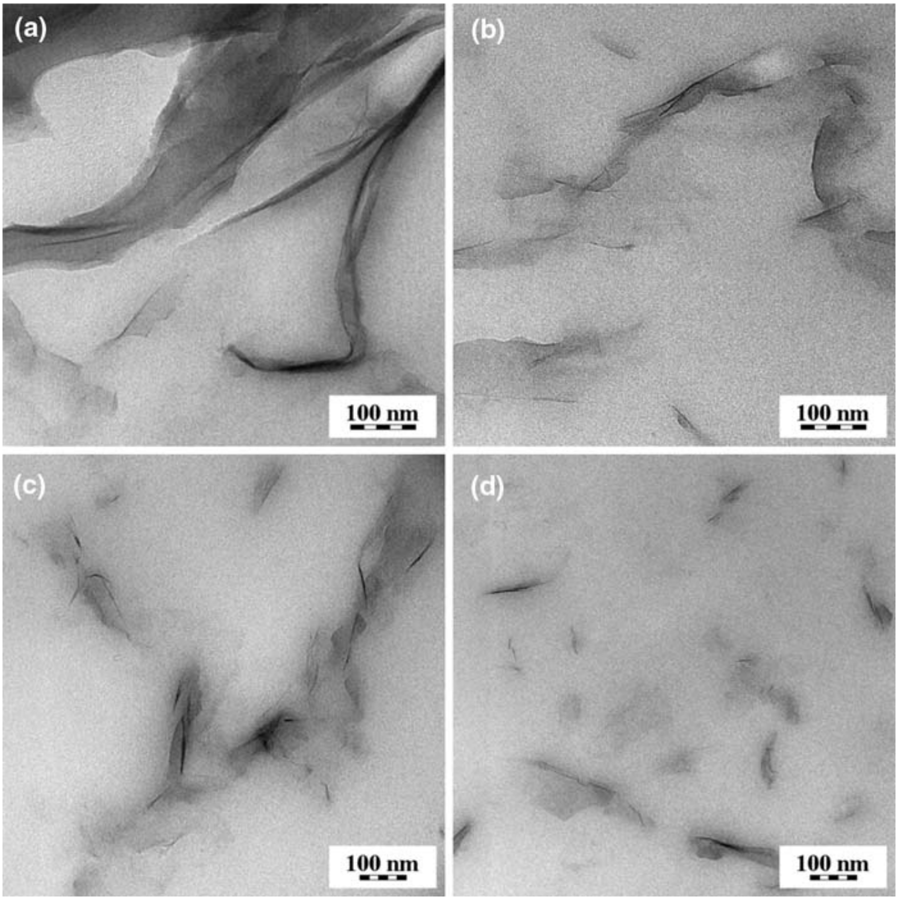

Fig. 10 TEM micrographs of the films prepared from nanocomposite PBMA/MMT latexes with solids content 39.7 wt.% and 3 wt.% of inorganic particles: **a** Cloisite-Na, **b** Cloisite-QS, **c** Nanocor-Na, **d** Nanocor-QS

with vinyl monomer [2-(acryloyloxy)ethyl]trimethylammonium chloride; in situ emulsion polymerization of the St and BMA monomers with different clay loading and different solid content was then carried out. The obtained high solids content hybrid emulsions (a milky dispersion with no evidence of macroscopic precipitation) were stable at room temperature for several months. The mean particles size of all types of the prepared hybrid latexes was influenced by solids content and concentration of clay. Increasing concentration of inorganic particles led to the growth of the mean particle size of prepared nanocomposite latex. Verification of the intercalation of the vinyl monomer-cation within the clay interlayers was achieved by WAXS and SAXS analyses. WAXS patterns taken from PSt/organically modified MMTs reveal exfoliated structure for both of used clays. It has been shown that the PBMA/MMT-QS nanocomposites exhibit a better dispersion of disordered clay platelets in polymer matrix films than that of hydrophilic MMT-Na for both of used clays.

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