The effect of clay on the morphology of multiphase latex particles

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Abstract The effect of montmorrilonite clay (MMT) platelets on the morphology of polystyrene/poly(methyl methacrylate) (PMMA) composite latex particles prepared via PMMA-seeded (semi-) batch emulsion polymerization of styrene was studied. It was found that the particle morphology obtained greatly depended on the ability of the clay platelets to diffuse through the polymer particle. Indeed, when the reactions were strictly under kinetic control, i.e., where the clay platelets were unable to diffuse during polymerization, anisotropic core-shell-like morphologies with split core were observed. A better mobility of the clay platelets could more or less restrict the diffusion of the second-stage polymers within the host polymer, leading to original kinetically controlled morphologies. In the case of a full migration of the clay platelets to the particle surface, the penetration of the second-stage polymer species in the seed latex was found to be more limited, enhancing the formation of secondary particles.

Keywords Montmorrilonite · Morphology modifier · Emulsion polymerization · Multiphase latex particles

Introduction

Multiphase latex particles, where two or more organic/inorganic phases coexist within one single latex particle, offer the possibility to prepare polymer films exhibiting properties which cannot be obtained by mechanical mixing of the different constituent lattices [1–4]. These properties greatly depend on the morphology of the composite latex particle, i.e., the shape and the internal structure of the polymer colloid [1–4].

Multiphase latex particles are generally prepared using seeded emulsion polymerization techniques [5–7]. These usually comprise two stages: a first stage in which polymer particles (so-called seeds) are synthesized and a second stage where monomers polymerize in the presence of the seed particles. In the course of the polymerization, phase separation phenomena, which are due to incompatibility between the second-stage and seed polymers in combination with differences in surface tensions, usually occur within the polymer particle leading to a large range of morphologies.

One of the most challenging issues in synthesizing multiphase latex particles is to predict how the different components involved in the synthesis will affect the particle morphology. Latex particle morphology is controlled by both thermodynamics and kinetics. Since Torza and Mason [8], the morphology control initially via thermodynamic considerations has been extensively studied by several research groups such as those of Sundberg [5], El-Aasser [6], and Asua [7]. Their initial approaches were based on the concept that thermodynamically controlled (or equilibrium) morphologies are determined by a minimization of the total Gibbs free energy change, which can be expressed as follows:

$$\Delta G_{P,T} = \sum \gamma_n A_n$$

Where γ_n is the interfacial tension at the nth interface and A_n its corresponding area.

Kinetic factors determine whether the equilibrium morphology will be obtained within a reasonable time (ideally within the time frame of the synthesis of the multiphase latex particles). Both reaction and diffusion rates of polymer species within the latex particle are kinetic factors.

In fact, thermodynamics and kinetics must always be treated together in order to understand the evolution of the

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particle morphology. González-Ortiz and Asua developed a dynamic mechanistic model describing the evolution of the particle morphology based on the migration of clusters (or polymer nanodomains) towards their equilibrium state which is due to a balance of van der Waals forces and viscous (drag) forces [7, 9, 10]. Stubbs and Sundberg have described the morphology development of a composite latex particle by analyzing the probabilities for diffusion and reaction of both polymeric radicals and monomer molecules within the latex particle [11–14]. According to these workers, the particle morphology is determined by the extent of penetration of oligomers formed in the aqueous phase into the latex particle [11]. The depth of penetration will depend on the glass transition temperature (T_g) of the host latex particle: the oligomer radicals will easily penetrate in a "soft" polymer particle having a T_g which is around 20 °C below the reaction temperature. Subsequent phase separation occurs as long as polymer chain diffusion is permitted [13, 14]. The last stage of the morphology formation is a so-called phase consolidation or growth, when the particle phases rearrange themselves in order to reduce the interfacial free energy of the latex system [14].

Most studies found in the open literature deal with the understanding of the morphology development of two-phase latex particles. Despite initial work of Sundberg and Sundberg [15], it is only recently that the preparation of three-phase systems has received much interest [16–19]. A recent study of Herrera et al. [16] highlighted the significant effect of block copolymers PS-block-poly(methyl methacrylate-*co*-styrene) on the morphology of PS/PMMA latex particles. The block copolymers incorporated into the composite latex particles acted like "morphology modifiers" via in situ controlled radical polymerization by allowing a better wetting of PMMA in PS seed particles. Another appealing aspect of this work is that the morphologies of the three-phase latex particles could be well interpreted using the theories explaining the development of two-phase systems.

The morphology of latex particles can also be modified by the incorporation of inorganic compounds such as silica, titanium dioxide, and clay particles [20]. Depending on the nature, size, and shape of the inorganic moiety, the latex particle can adopt unusual morphologies which cannot be obtained otherwise. For instance, the incorporation of clay platelets into latex particles can lead to dumb-bell-like or flat morphologies depending on the conditions of the reactions [21–23]. The potential of inorganic compounds as morphology modifiers has, however, barely been explored in depth in spite of their remarkable effects on particle morphology.

In the work described in this paper, we study the effect of montmorrilonite clay (MMT) platelets on the morphology of PS/PMMA composite latex particles prepared via PMMA-seeded emulsion polymerization of styrene. The clay platelets are incorporated into the PMMA-latex seeds via starved-feed emulsion polymerizations. The conditions for the syntheses of the hybrid PS/PMMA latex particles are such that polymer radical diffusion (i.e., a kinetic factor) limits the development towards the equilibrium morphology which should be an inverted core-shell as PS is much more hydrophobic than PMMA [6, 7, 24]. Also, from a thermodynamic point of view, the clay platelets should be situated at the surface of the latex particles due to their hydrophilicity [19, 25–27]. The relative size of the seed latexes and the mode of operation (batch vs. semi-batch) of the second-stage monomer styrene are varied in order to change the diffusion resistance hindering the evolution of the equilibrium morphology. Some experiments are performed in the absence of clay (blank experiments) in order to better understand the role of the inorganic moiety in the development of the morphologies obtained. Four case studies, classified according to the monomer addition and the relative size of the seed, are described in this paper. For the interpretations of the results, the theories explaining the morphology development of two-phase latex systems are used. The morphologies of the hybrid PS/PMMA latex particles are analyzed via transmission electron microscopy and in some cases in combination with ultramicrotoming.

Experimental

Chemicals

The sodium montmorrilonite (MMT) used in this study was Cloisite® Na^+ kindly provided by Southern Clay Products Inc. (Texas, USA). According to the supplier, the exchange capacity of the clay was 92 meq per 100 g of clay. Styrene (S, Aldrich >99 %) and methyl methacrylate (MMA, Aldrich 99 %) were purified from inhibitors by passing them through a column filled with basic aluminum oxide. Apart from the monomers, all chemicals were used as received. Potassium persulfate (KPS, Aldrich >99 %), ammonium persulfate (APS, Aldrich >99 %) and 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl) propionamide] (VA-086, Wako Chemicals GmbH) were used as initiators. Sodium dodecyl benzenesulfonate (SDBS, Aldrich) and Triton X-100 (TX-100, Aldrich) were used as surfactants and sodium bicarbonate ($NaHCO_3$, Merck, PA) as a buffer. Water was deionized using the Super Q reverse osmosis (Millipore) set up. The other chemicals, *N*,*N*,*N*′,*N*′ tetramethylethylenediamine (TMEDA, Aldrich ~99 %) and potassium hydroxide (KOH, Sigma-Aldrich 90 %) were used as received.

Preparation of the seed polymers

All the following reactions were performed in a 250-mL flat-bottomed, baffled glass reactors, equipped with a mechanical stirrer (45° pitched downflow six-bladed impeller), a temperature indicator, a reflux condenser, and an inert gas inlet. The system was heated by circulating water through the cylinder-jacket of the reactor.

PMMA latexes without clay

The seed latex sp-1 was prepared via a typical batch emulsion polymerization as follows. The reactor was initially loaded with 163 g of distilled water and de-oxygenated in argon gas for a period of 30 min. After addition of a mixture of surfactants (0.24 g of SDBS and 2.71 g of TX-100), the argon flow was reduced to avoid foam formation. Ninety grams of MMA was charged dropwise into the reactor while purging with argon and stirring at a rate of 320 rpm. The reaction temperature (T_r) was slowly raised to 75 °C, and after temperature stabilization, 0.44 g of KPS (having a half-life $t_{1/2}$ of about 4 h at T_r=75 °C) were added. The reaction time was about 2.5 h.

A semi-batch surfactant-free emulsion polymerization was performed to prepare the seed latex sp-2. The reactor was initially charged with 187 g of distilled water and thereafter heated at 80 °C. After addition of 0.47 g of APS ($t_{1/2}$≈4 h), the reaction medium was allowed to stir for 10 min. Thereafter, 66 g of MMA were fed into the reactor at a rate of 0.5 $\mathrm{mL\,min^{-1}}$ using a titrator 776 Dosimat (Metrohm AG). After monomer feeding, the reaction was carried out for an additional 2 h.

PMMA latexes containing clay platelets

The PMMA latex c-sp-1 was prepared using native clay particles. Two hundred fifty milligrams of the inorganic compounds were dispersed ultrasonically using a UP400S Hielscher ultrasonicator (a tip diameter of 22 mm and an energy output of 393 $\mathrm{W\,s\,mL^{-1}}$) in a surfactant solution below the critical micelle concentration (CMC). The CMCs of the surfactants were determined via a surface tension titrator (Data Physics) and found to be 0.13 and 0.6 $\mathrm{g\,L^{-1}}$ at 20 °C for the mixed surfactant system TX-100: SDBS (6:1 *w*/*w*) and pure SDBS, respectively. The clay dispersion was centrifuged at 2,500 rpm for 10 min to remove any possible clay aggregates. The initiator was added to the clay dispersion in one shot after an elevation of the temperature to 80 °C, after which the reaction medium was allowed to stir for 10 min ($t_{1/2}$≈10 h at 80 °C). Then, monomers were slowly added to the reaction mixture with a feeding rate of 17 $\mathrm{\mu L\,min^{-1}}$ by a syringe pump (New Era NE-1000). Before polymerization, all reactants were de-oxygenated by purging with argon for around 20 min. A small pressure of argon was maintained over the reaction medium during the polymerization to avoid oxygen inhibition. Typical recipes of the reactions are given in Table 1.

Table 1 Characteristics of the (hybrid) PMMA seeds used

Seed names	sp-1	sp-2	sp-3[a]	c-sp-1	c-sp-2
D_z (nm)	220	598	392	200	176
PDI[b]	0.02	0.00	0.00	0.12	0.31
MMT loading (wt.%)[c]				3.5	0.5
Solid content (%)	36	26	6	6	8
T_g (°C)	107	106	114	117	113

[a] Prepared using the same protocol as for the preparation of the seed latex c-sp-1 with the exception that the reaction was done in the absence of clay particles

[b] Approximate values to two decimal places

[c] Based on the total amount of monomers

The seed latex c-sp-2 corresponds to a growth of clay-containing PMMA latexes synthesized using the same procedure as for the preparation of the seed latex c-sp-1. The initial reactor was charged with 103 g of water, 1 g of seed latex, 0.02 of $NaHCO_3$, and 0.02 g of SDBS; 11.9 g of MMA and an aqueous solution of KPS (around 2.5 mL at a concentration of around 0.1 M) were fed simultaneously in the reaction medium using two syringe pumps (NE-1000, New Era Pump systems Inc) for 3 h. The stirring rate and the reaction temperature were 300 rpm and 75 °C, respectively.

All the PMMA/MMT latex particles thus produced exhibited anisotropic morphologies (c.f. Fig. 1). The characteristics of the seed polymers are given in Table 1.

Second-stage polymerization of styrene

Semi-batch process

The initial reactor loading consisted of distilled water, surfactant and the seed latex. After warming up the reaction medium to 80 °C, KPS initiator ($t_{1/2}$≈4 h), was added to the reactor at once. Subsequently, styrene was fed at a rate of 3 $\mathrm{mmol\,min^{-1}}$. Stirring and heating of the reaction was kept for 3 h.

Batch process

This second-stage polymerization was initiated by a redox system KPS (oxidant)/TMEDA (reductant). The reactor was initially charged with distilled water, the surfactant, the buffer, and the seed latex. The reaction medium was heated up to 40 °C. After stabilization of the temperature, the total amount of monomer was added at once followed immediately by the addition of an aqueous solution of TMEDA and then of KPS.

The recipes used for the reactions performed are given in Table 2.

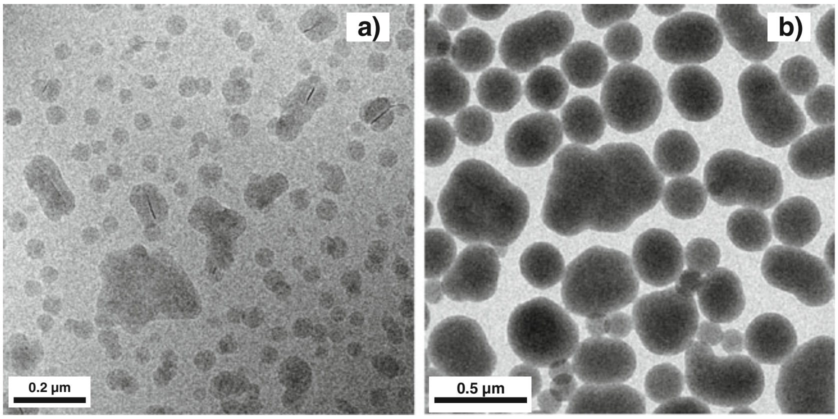

Fig. 1 TEM images of the following seeds **a** c-sp-1 and **b** c-sp-2. The seed latex c-sp-1 was studied at cryogenic temperatures

Characterization

Average particle diameters

The determination of the average particle diameters was performed by the use of a Malvern Zetasizer Nano ZS dynamic light scattering apparatus, with a He-Ne laser as the light source (at a fixed wavelength of 633 nm). This apparatus was used at a scattering angle of 173 °C and at a temperature of 25 °C. The measurements were done after dilution of the samples with deionized water. An indication of the particle size distribution (PSD) was determined with the same equipment. The analysis of the PSD was based on the intensity distribution pattern generated by DLS. It should be noted that the format of the PSD of conventional latexes can be described as equivalent spherical diameter on the *x*-axis and percent on the *y*-axis. It is assumed that the PSD of clay-containing latex particles exhibiting much higher aspect ratio than the conventional ones displays the *x*-axis as length rather than equivalent spherical diameter.

Thermogravimetric analysis

Thermogravimetric analysis was performed using a high-resolution TA-Q500 instrument under nitrogen flow at 50 ml min^{-1}. A scanning rate of 10 °C min^{-1} was used.

Electron microscopy

Cryogenic transmission electron microscopy (cryo-TEM) measurements were performed on a FEI Tecnai 20, type Sphera TEM instrument (with a LaB_6 filament, operating voltage= 200 kV). The sample vitrification procedure was performed using an automated vitrification robot (FEI Vitrobot Mark III). A 3-μL sample was applied to a Quantifoil grid (R 2/2, Quantifoil Micro Tools GmbH; freshly glow discharged for 40 s just

Table 2 Recipes used for the synthesis of the multiphase latex particles and their characteristics

Case studies	1		2		3		4	
Experiment	EP-1	EP-2[a]	EP-3	EP-4	EP-5	EP-6[a]	EP-7	EP-8
Seed name	sp-2	c-sp-2	sp-1	c-sp-1	sp-2	c-sp-2	sp-3	c-sp-1
Water (g)	202.3	98.6	170.2	68.2	212	60.6	59.7	58.9
Seed latex (g)	7.6	2.3	7.5	2.2	11	2.5	1.7	2.2
S (g)	7.6	6.1	19.9	6.4	11	3.1	3.4	3.7
KPS (g)	0.17	0.15	0.15	0.14	0.05	0.008	0.012	0.011
TMEDA (g)					0.02	0.004	0.01	0.007
$NaHCO_3$ (g)					0.13	0.11	0.1	0.12
SDBS (g)	0.03	0.02		0.002	0.03	0.05	0.04	
TX-100 (g)	0.12	0.1		0.08				
S feed rate (mmol min^{-1})	3	3	3	3				
Characteristics								
D_z (nm)	731	–	362	236	731	–	281	142
Polydispersity index	0.03	–	0.06	0.14	0.08	–	0.27	0.18
Solid content (%)	6.8	7.7	9.5	11.8	8.8	7.8	8.3	8.6

[a] The mean particle size could not be accurately determined because of the high polydispersity of the latex particles (above 0.4)

prior to use) within the environmental chamber of the Vitrobot and the excess liquid was blotted away. The thin film thus formed was shot into melting ethane. The grid containing the vitrified film was immediately transferred to a cryoholder (Gatan 626) and observed under low-dose conditions at −170 °C.

For TEM ultramicrotomy, ultrathin sections (70 nm) of dried LCNs were obtained at room temperature using a Reichert-Jung Ultracut E microtome equipped with a Diatome knife. The sections were put on a 200-mesh copper grid with a carbon support layer. The sections were also examined with the Sphera instrument.

Some TEM samples were stained with ruthenium (VIII) tetroxide to enhance the contrast between the phases. RuO_4 was prepared by mixing 40 mg of ruthenium trichloride (Acros) and 10 wt.% aqueous solution of sodium hypochlorite solution (Acros). The PS-rich regions, selectively stained by RuO_4 due to the aromatic structure of PS, should appear much darker than the PMMA-rich regions in the TEM picture [28].

Results and discussion

Case study 1: semi-batch addition of styrene, large seed

In this case study, large-sized seed latexes are used and a semi-batch addition of the second-stage styrene monomers is performed in order to force the second-stage polymerization in the outer region of the host polymers.

Figures 2a, 3a, and 4a show the morphology of the latex particles synthesized for this case study. Some similarities between the conventional and the hybrid latex systems can easily be observed from these images. The latex particles exhibit outer regions composed of several PS domains with a well-defined PMMA-rich core. Obviously, the expected equilibrium morphology which should be an inverted core-shell has not been reached for either type of latex particles [6, 9]. From these observations, it seems that the second-stage monomer preferentially reacted in the outer regions of the latex particles indicating that the penetration of oligomer radicals has been quite restricted during the course of the polymerization [7]. This is actually further evidenced by the observation of similar shape between the resulting multiphase latex particle and the host polymer acting as a morphological template. However, the presence of small occlusions of PS in the interior of the particles also reveals that some reacting species could substantially penetrate in the interior of the seed polymer and that the second-stage polymers could phase separate into small domains (c.f. Fig. 4a). This might have occurred at the early stage of the polymerization due to the initial presence of monomer molecules within the seed polymer [7]. Indeed, the local concentration of monomer, which acts as a plasticizer, was

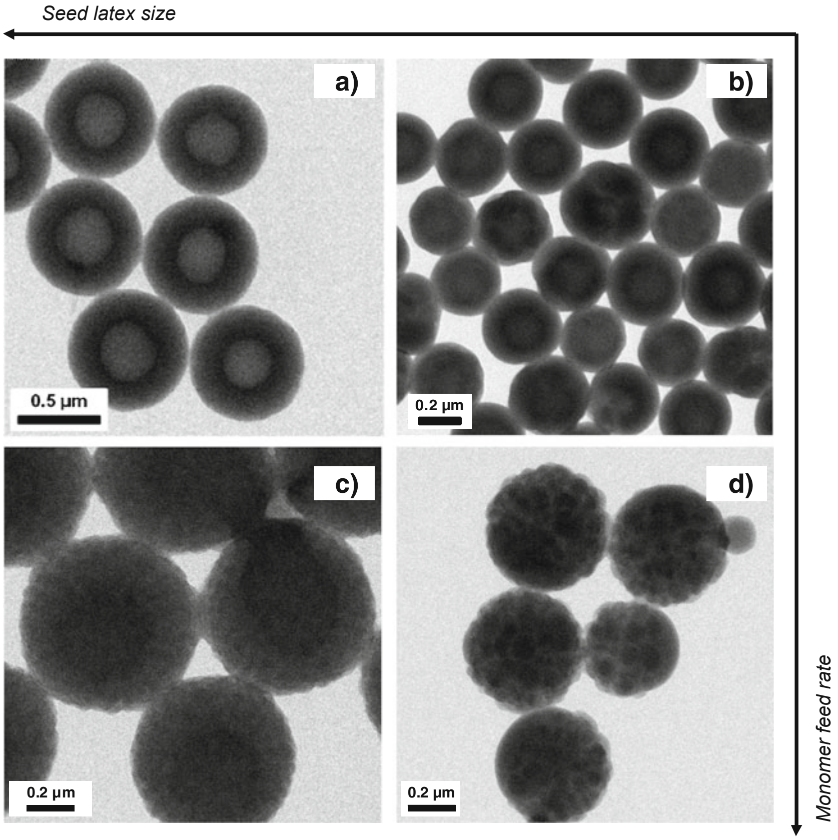

Fig. 2 TEM pictures of two-phase PMMA/PS latex particles prepared using the recipe **a** EP-1 (case study 1), **b** EP-3 (case study 2), **c** EP-5 (case study 3), and **d** EP-7 (case study 4)

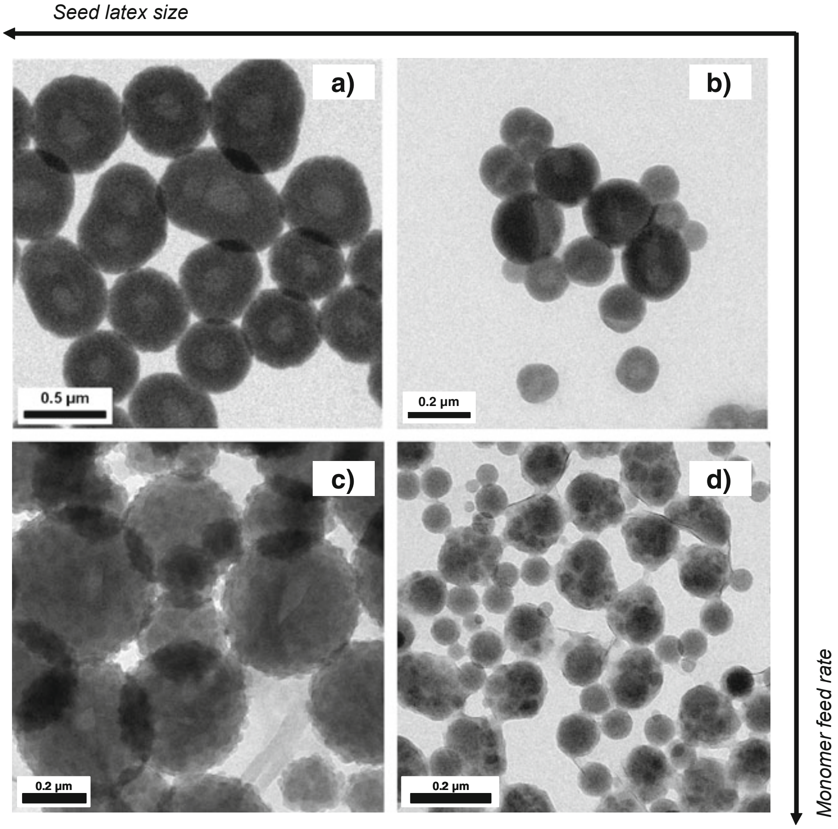

Fig. 3 TEM pictures of multiphase hybrid PMMA/PS/MMT latex particles prepared using the recipe **a** EP-2 (case study 1), **b** EP-4 (case study 2), **c** EP-6 (case study 3), and **d** EP-8 (case study 4)

probably quite high initially due to the fast feeding rate applied for these experiments [7]. This plasticizing effect must have promoted the diffusion of the oligomer radicals [7]. However, the seed polymers were completely depleted of monomer quite rapidly: almost the complete amount of styrene monomer was consumed within 20 min of reaction as determined by gravimetric measurements. Consequently, the host polymer matrix must have quickly recovered its glassy state (its T_g being well above the reaction temperature of around 80 °C) forcing further formation of second-stage polymers around its external regions [12]. The phase consolidation which should occur at the late stage of the reaction has been kinetically inhibited due to the glassy nature of both polymers (the T_g of PS should be around 90 and 110 °C).

In contrast to the conventional latex particles (Figs. 2a and 4a), a split of the PMMA core into two regions can sometimes be observed for the hybrid systems (c.f. Fig. 3a). This unusual configuration, particularly visible for dumb-bell-like hybrid latex particles, might be due to the presence of clay platelets within the polymer matrix. Despite the impossibility to see the inorganic phase in Fig. 3a, the dumb-bell like morphology observed suggests that the clay platelets are located between the two PMMA regions as can be seen in Fig. 1. Also, in a recent work of Voorn et al. dumb-bell-like latex particles were observed when clay particles were present in the core of the polymer particle [21]. TEM analysis of ultramicrotomed sections of the hybrid particles was performed in order to see the orientation of the

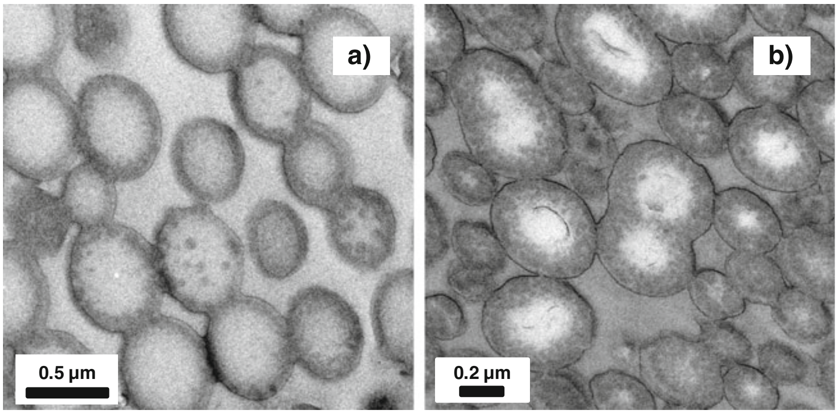

Fig. 4 TEM pictures of cross-sections of **a** two-phase PMMA/PS (EP-1) and **b** multi-phase hybrid PS/PMMA/MMT latex particles (EP-2)

inorganic moieties within the polymer matrix (c.f. Fig. 4b). Surprisingly, except for one particle, a split of the core of the latex particles was barely observed in the TEM picture of the microtomed sections. Such an observation cannot be conclusive because the sample photographed in Fig. 4b may not be representative of the "true" morphological features of the hybrid latex particles: only a few tens of latex particles, cut at random positions, are represented.

Case study 2: semi-batch addition of styrene, small seed

For this case study, second-stage styrene monomers are added semi-batch wise and smaller seed polymers are used compared to the ones of the preceding study. This should permit the second-stage polymers to reach the core of the seed polymer more easily [11, 14].

Figure 2b shows different kinds of morphology for the conventional latex particles. Indeed, some particles seem to have adopted a spherical onion-like morphology composed of a thin black PS-rich region sandwiched between two dark gray regions which probably consist of a mixture of PMMA- and PS-rich polymers. Other particles have a bumpy appearance with larger PS-rich domains in the interior of the particle and a thin PMMA shell.

The observation of different kinds of morphology in one single latex is typical for experiments where the morphologies develop under kinetic control [6, 29]. Although phase separation and phase consolidation have obviously been very limited, the particle structures are apparently closer to the equilibrium state expected for this kind of system. Because of the small size of the seed polymers, the relative depth of penetration of the second-stage polymers are naturally enhanced [11].

In Fig. 3b, similar morphological characteristics can be observed for the hybrid particles. The position of the clay platelets within the latex particle can also be seen in Fig. 5. It can be observed that the clay platelets, which were initially in the core of the particle, seem to have shifted towards the surface of the latex particle. This observation shows that the inorganic particles were quite mobile during synthesis and tried to be in contact with the aqueous phase. The location of the clay particles on the latex particle surface is indeed thermodynamically favorable because of the high hydrophilicity of the inorganic compound [19, 22, 26, 27].

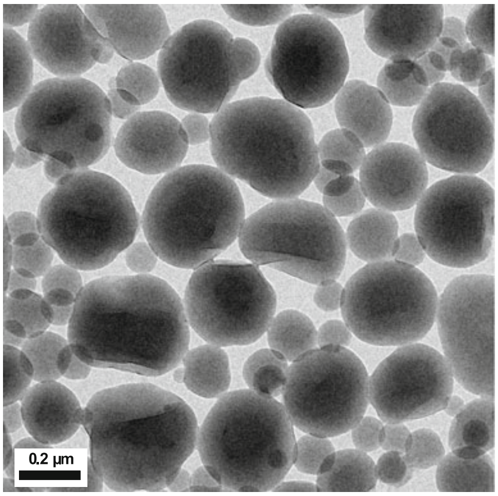

Fig. 5 A TEM picture of unstained multiphase hybrid PS/PMMA/MMT latex particles prepared using the recipe EP-4

In contrast to the blank experiment (Fig. 2b), the synthesis of the hybrid particles seems to have produced a fair number of secondary PS particles as observed in Figs. 3b and 5. The formation of secondary particles might have been promoted by the presence of clay platelets, the only difference with the blank experiment. It has been shown that secondary nucleation (e.g., via homogenous/coagulation mechanism) can occur if oligomer radicals formed in the aqueous phase cannot penetrate into the seed particles [30, 31]. The clay particles, more or less situated on the outer regions of the latex particles, might have prevented the penetration of the second-stage polymer radicals partly because of their impenetratability. Also, the clay platelet, bearing a permanent negative charge on its surface and having a high aspect ratio, might have prevented the diffusion of polymeric radicals in the polymerization locus because of electrostatic and/or hydrophobic repulsions as previously observed for silica particles [32]. Indeed, Sheibat-Othman et al. have shown in recent work that hydrophilic silica particles present on a latex particle could restrict the absorption of styrene oligomer radicals due to their negative charge and their strong incompatibility with the hydrophobic radicals [32]. The limiting absorption of oligomer radicals within the latex particles might have enhanced the formation of secondary particles.

Case study 3: batch addition of styrene, large seed

For this case study, a batch addition of styrene, instead of a feed, was performed in order to obtain a high concentration of monomers within the seed polymers which should allow a good mobility of the particle phases.

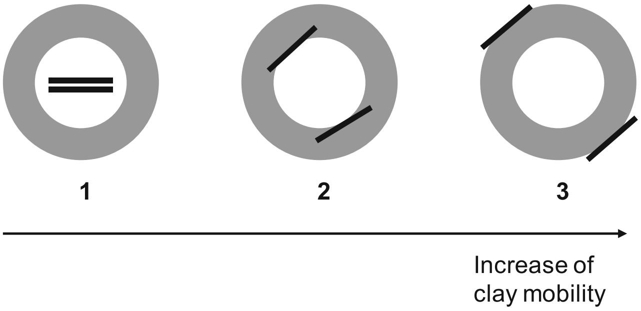

Fig. 6 Schematic representation of the possible morphologies obtained by increasing the clay platelets mobility

From Figs. 2c and 3c it can be seen that both the conventional and the hybrid latex particles have a spherical-like shape with a rough surface. They seem to be filled with many PS domains mixed with the PMMA phase. This observation shows that the second-stage polymers were allowed to significantly penetrate the host polymer particle [14]. This fact is actually further evidenced by a loss of the anisotropic character of the morphology of the hybrid particles, implying that polymerization took place throughout the particle. From these images, however, it is difficult to qualitatively estimate the extent of phase separation due to a poor contrast between the particle phases.

An interesting feature is that some hybrid particles display a PMMA core somehow decorated by several clay platelets exhibiting a core-shell-like morphology. This morphology seems to be the result of a limited diffusion of the clay platelets towards the particle surface as illustrated in Fig. 6. Initially, the clay platelets were in the core of a glassy latex particle (situation 1 in Fig. 6). After addition of the styrene monomers, the clay platelets tried to migrate towards the surface of the latex particle within a more plasticized seed polymer (situation 2 of Fig. 6). This migration of the inorganic compounds has been incomplete probably because of a relatively fast reaction rate and the large size of the seed polymer. Simultaneously, the second-stage radical species could significantly penetrate the seed polymer but could not reach the inner center of the latex particle due to the presence of the clay platelets: the inorganic compounds acted as rigid barriers against polymer radical diffusion.

Case study 4: batch addition of styrene, small seed

Smaller sizes of the seed latexes combined with a batch addition of styrene were used in order to achieve further penetration of the second-stage polymers as compared to the previous cases.

For this case study, the conventional latex particles exhibit an original cauliflower-like morphology (c.f. Fig. 2d). The particles exhibit a rounded part (bud) with a homogeneous PS-rich phase. The flower-like part seems to be composed of small occluded PS domains within a PMMA matrix. In contrast to the case study 3, it appears that the morphology obtained is closer to its equilibrium state which would have probably been hemispherical-like. Indeed, we can see that the "bud" of the particle seems to adopt a convex configuration tending to minimize its contact with water.

In Fig. 3d, the morphology of the hybrid latex particles displays large occlusions of PS domains apparently well-phase separated from a PMMA phase. These morphological characteristics, however, look quite different from the conventional ones. It can also be observed that the clay platelets are situated on the surface of all particles suggesting that the particle phases were highly mobile during polymerization.

Similarly to case study 2, the clay platelets might have acted as physical barriers against polymerization within the seed polymers because a high number of secondary particles can also be observed. This effect of the clay seems actually more obvious here, probably because the migration of the clay platelets towards the surface of the latex particle completely occurred for all particles (c.f. situation 3 in Fig. 6); whereas in case study 2 this migration was incomplete in many instances (c.f. situation 2 in Fig. 6).

In this case study, it becomes obvious that the effect of the clay platelet on the morphology of the PS/PMMA composite latex particles depends on its ability to diffuse during synthesis.

Conclusions

In the work described in this paper, the effect of clay platelets on the morphology of PMMA/PS composite latex particles was studied. The multiphase latex particles were synthesized from clay-containing PMMA-seed latexes via (semi)-batch emulsion polymerizations of styrene. It was found that the particle morphology obtained greatly depended on the ability of the clay platelets to diffuse throughout the seed polymer. Indeed, when the reactions were strictly under kinetic control, i.e., where the clay platelets were unable to diffuse during polymerization, anisotropic core-shell-like morphologies with split core were observed. A better mobility of the clay platelets could more or less restrict the diffusion of the second-stage polymers within the host polymer, leading to original kinetic controlled morphologies. In case of a full migration of the clay platelets on the particle surface, the penetration of the second-stage polymer species in the seed latex was found to be more limited enhancing the formation of secondary particles.

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