Clay Platelets Encapsulated Inside Latex Particles

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There has been increasing interest for encapsulation of fine inorganic powders with organic molecules or polymers to afford various desired physical properties. Inorganic platelets such as layered silicates have been extensively investigated as polymer−clay nanocomposites over the past decade.[1] One often-employed strategy to modify inorganic clay is the exchange of stabilizing alkali by organic cations such as alkylammonium, making the clay organophilic and compatible with polymers.[2] Melt intercalation and in situ polymerizations in the presence of organically modified clays have been used to produce polymer−clay nanocomposites with improved mechanical and thermal properties of the polymer.[3] Emulsion polymerization in the presence of clays was employed to prepare polymer/clay hybrid particles,[4−6] but only armored particles (clay being located at the particle surface) were obtained. Encapsulation of clays by polymer appears to be very challenging. We previously reported a physical approach, heterocoagulation, to encapsulate gibbsite (much thicker than individual clay) platelets by polymer.[7] In this communication, we present the encapsulation of clay platelets by polymers via emulsion polymerization.

Clay platelets, including synthetic Laponite RD (LRD, $D = \sim$25 nm) and natural sodium montmorillonite (MMT, $D = \sim$150 nm; very large particles were removed by centrifugation), were first covalently modified in dichloromethane (Figure 1 and Supporting Information) by using silane or titanate containing polymerizable (meth)acrylic moeity.[8] Both silane and titanate led to primarily edge modification of the platelets.[6,8] After the silane modification, slightly turbid dispersions were obtained for both MMT and LRD ($D_z = 161$ and 32 nm, respectively, as determined with dynamic light scattering, DLS). The titanate modification also led to slightly turbid platelet dispersions in dichloromethane ($D_z = 169$ and 32 nm for MMT and LRD, respectively). For the silane modification, it was shown from thermogravimetric analysis (TGA, Figure S1, Supporting Information) that about 4.9 and 8.1 wt % of silane was grafted to MMT (MMT−Si) and LDR (LDR−Si), respectively, in agreement with values reported in the literature.[6,8a] The titanate modification yielded about 6.9 and 11.3 wt % increase for MMT (MMT−Ti) and LRD (LRD−Ti), respectively. After drying, the modified platelets could be dispersed in water, but the dispersions were more turbid than the unmodified clay dispersions, likely due to the hydrophobization of clay platelets.

Emulsion polymerizations of methyl methacrylate (MMA) in the presence of unmodified LRD and MMT platelets did not result in encapsulation of the clay platelets by latex particles.[5]

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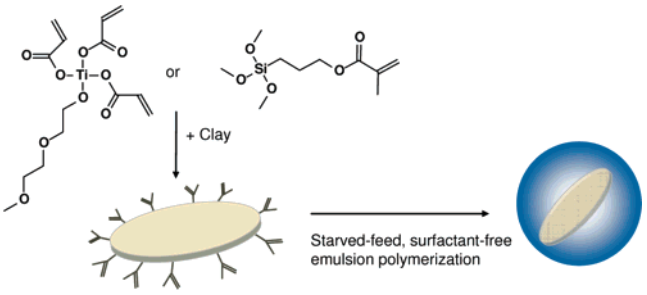

Figure 1. Schematic illustration of clay platelet modification and encapsulation via emulsion polymerization with a vinyl monomer.

Table 1. Characteristics of Clay-Encapsulated Latex Particles[a]

entry	modified clay type	modified clay (wt %)[b]	clay content in latex particles (wt %)[c]	D_n[d] [nm]	D_z[e] [nm]	PDI[e]
DV01	LRD−Ti	6.2	3.0	67 ± 15	96.2	0.18
DV02	LRD−Si	6.2	3.6	59 ± 14	93.7	0.21
DV05	MMT−Ti	5.9	3.8	285 ± 87	351	0.32
DV06	MMT−Si	6.4	4.8	327 ± 69	298	0.27
DV09	(control)			284 ± 35	296	0.16

[a] The MMA concentration was 6.9−7.2 wt % based on the total charge, and the concentration of a nonionic water-soluble initiator VA-086 (2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]) was 0.15 wt % for all polymerizations. [b] Clay content based on the total solid content from the recipe. [c] Actual clay content in the latex particles determined by TGA. [d] Particle sizes determined by TEM; the longest length was measured in the case of nonspherical particles. [e] *Z*-average particle diameter, obtained by DLS measurements, and polydispersity index (PDI) is calculated from cumulant analysis as described in the International Standard ISO 13321.

Attempts to encapsulate organocationically modified clays by emulsion polymerization also failed. Batch emulsion polymerizations in the presence of covalently modified platelets and surfactants were attempted by Herrera et al.,[6] but the platelets were observed to cover the latex particles. In this study, covalently modified clay platelets were successfully encapsulated inside latex particles via *surfactant-free*, *starved-feed* emulsion polymerization. If a surfactant-free, batch-emulsion polymerization was used, only a small fraction of clay platelets were encapsulated, but the vast majority of the platelets were located at the surface of latex particles.

Table 1 lists some characteristics of clay-encapsulated PMMA latex particles. The particles containing MMT inside appeared to have similar size to the control sample (DV09, with no clay platelets). The size of LRD-encapsulated particles, about 60 nm in diameter, was significantly smaller, indicating the PMMA particle growth is apparently affected by the presence of modified LRD platelets. During the polymerization, the modified clay platelets may behave like templates, and the final latexes would be influenced by the initial platelet size. Furthermore, the PDI of the clay-containing latexes appeared to be strongly related to the PDI of the clay platelets. LRD is a synthetic clay with a narrower size distribution than MMT; consequently, the PDI of LRD-containing latex particles is smaller than their MMT-containing counterparts (Table 1). It is also shown in Table 1 that 48−75 wt % of clay platelets were successfully encapsulated inside latex particles (nonencapsulated clay platelets were removed by centrifugation; see Supporting Information).

Cryogenic TEM (cryo-TEM) was used to examine the particle morphology in the wet state. Figure 2 shows representative cryo-

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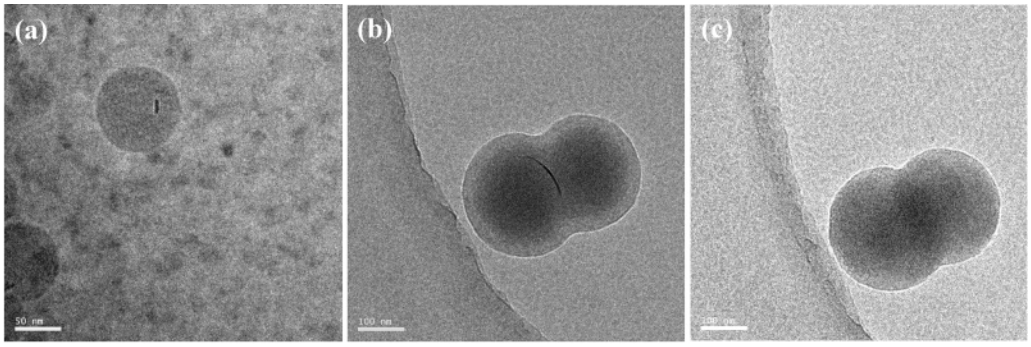

Figure 2. Cryo-TEM micrographs of PMMA latex particles by emulsion polymerization containing (a) LRD−Ti and (b) MMT−Ti; (c) the same particle as in (b), but viewed at a tilt angle of −25° (see text for details).

TEM images of PMMA latex particles containing LRD−Ti and MMT−Ti. The black line in Figure 2a is a LRD−Ti platelet with its basal plane parallel to the electron beam (entry DV01, Table 1). The individual LRD platelet is disk-shaped, with a lateral diameter of ∼20 nm and a thickness of ∼1 nm. Depending on the defocus of the objective lens, Fresnel fringes appear on both sides of the diffracting platelets, which may artificially increase the platelet thickness value.[6] The image defocus can aid in examining the particle morphology. Contrast differences and Fresnel fringes of the latex particles and the platelets differ significantly and suggest that the LRD−Ti platelets are encapsulated.

MMT−Ti platelets were encapsulated by the same procedure as the LRD−Ti platelets. Figure 2b shows the unique, dumbbell-like shape of a PMMA/MMT−Ti hybrid latex particle examined by cryo-TEM (entry DV05). The black line in Figure 2b corresponds to a MMT−Ti platelet, with its basal plane oriented parallel to the electron beam. As a result of this orientation, a sharp black line was observed. The dumbbell-like shape is due to the presence of a clay platelet (about 130 nm in length) inside. The unique dumbbell-like, nonspherical shape of the latex particles cannot be obtained via emulsion homopolymerizations *in one single step*;[9] batch emulsion polymerization in the presence of unmodified[5] or covalently modified[6] clays led to latex particles with surface covered by clays. The starved-feed, surfactant-free emulsion polymerization conditions,[10] combined with covalent clay modification, appear to be the key to obtaining clay encapsulation. As mentioned earlier, both silane and titanate modification are believed to lead to primarily edge modification,[6,8] but a recent report showed that face modification is also possible.[11] During the starved-feed, surfactant-free emulsion polymerization, the PMMA chain would likely start growing from the methacrylic moiety at the edge (to a certain extent from the face as well) of the modified MMT after the initiation in the aqueous phase and then grow along both sides of the platelet. When the clay platelet is large enough, as in the case of MMT−Ti, the presence of the platelet would prevent the uniform growth of the latex particle, resulting in nonspherical particles. For the much smaller LRD−Ti, the effect of the platelet on the particle shape appeared to be less significant, leading to spherical particles (Figure 2a). In both cases, complete encapsulation of clay platelets in latex particles was successfully obtained.

It was found from cryo-TEM analysis that not all dumbbell-like or snowman-like particles "appeared" to contain clay platelets inside. To clarify the presence of the clay platelets inside latex particles, micrographs at several tilt angles of the cryostage between −45° and +45° were obtained. The MMT−Ti platelet, clearly visible in Figure 2b, appeared to "disappear" completely at a tilt angle of −25° (Figure 2c). The tilting of the stage made the basal plane orientation of MMT−Ti more perpendicular to the electron beam and reduced the diffraction contrast of the platelet, effectively making it invisible. In addition, we checked a number of dumbbell-like particles in the tilt angle range from −45° and +45°; the "sticking-out" of the platelet from the particle surface was never observed. The dumbbell-like or snowman-like shape of the latex particles, irrespective of the "visibility" of clay inside the particle by TEM, further corroborates the encapsulation of clay platelets inside latex particles.

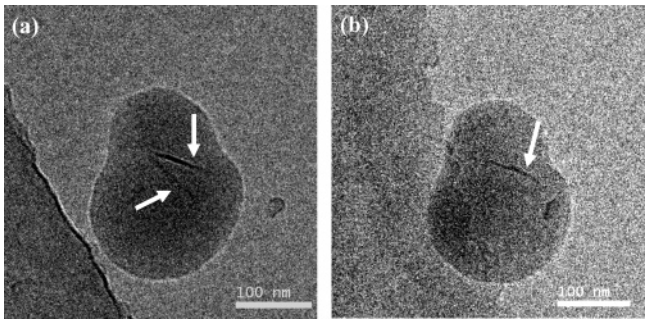

Figure 3. Cryo-TEM micrographs of PMMA latex particles containing (a) MMT−Si, as indicated by arrows, and (b) the same particle as in (a), but viewed at a tilt angle of 45°.

MMT−Si platelets were also successfully encapsulated inside snowman-like PMMA latex particles (entry DV06), as depicted in Figure 3. We found that it was possible to obtain latex particles with more than one clay platelet inside (Figure 3a); when the sample was tilted at 45°, it was interesting that only one platelet was visible (Figure 3b), again due to different platelet orientation. The presence of the clay platelets inside the latex particles apparently had a significant influence on the shape of the hybrid latex particles (see also another image, Figure S2 in Supporting Information).

Environmental scanning electron microscopy (ESEM) analysis of latex particles can provide additional information on the location of the clay platelets (Figure 4). At first glance, Figure 4 shows "normal" spherical latex particles with a minor portion of nonspherical latex particles. However, a close examination of the micrograph reveals that more than 50% of the latex particles depicted in Figure 4 are dumbbell-like/snowman-like in shape, or at least nonspherical. The variation of the particle shape may be the result of the broad size distribution of the modified MMT: particles containing a smaller MMT platelet tend to be spherical, while those with larger platelets are more likely nonspherical in shape, as discussed earlier. The surface of the latex particles is perfectly smooth, which differs with the rugged surface observed for clay-covered particles.[5,12] This confirms that the clay platelets are not located at the surface of

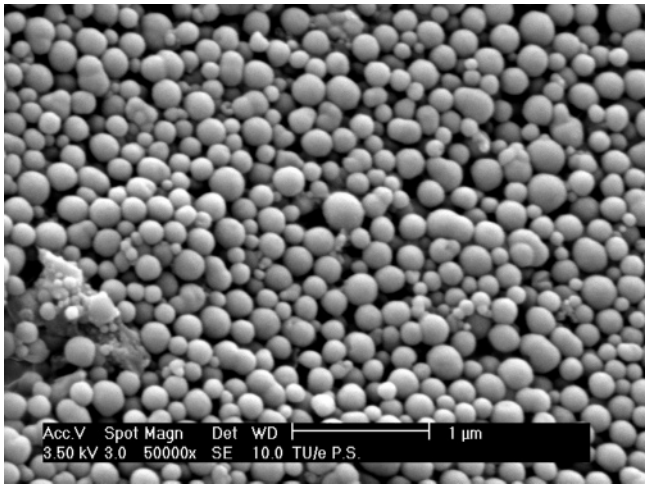

Figure 4. ESEM image of MMT−Ti-encapsulated PMMA latex particles (DV05).

the latex particles, and instead, they are completely encapsulated inside the latex particles.

It should be noted that, from both TEM and SEM images, a considerable amount of spherical particles are present when modified MMT was used for emulsion polymerization. Some of the spherical particles are free of clay platelets (nonetheless, the spherical shape does not necessarily imply there is no clay platelet inside). On the other hand, it is very difficult to determine exactly the amount of particles with or without clay inside. TEM may offer an indication on the number of particles with clay, but the "visibility" of clay by TEM observation strongly depends on its basal plane orientation, making the counting of clay-containing particles very difficult. (To make sure if a particle contains clay or not, the cryostage can be tilted for examination, but this is a very tedious procedure to account for all the particles).

In summary, we demonstrated direct encapsulation of covalently modified clay platelets via surfactant-free, starved-feed emulsion polymerization. With cryo-TEM and SEM, we showed that small LRD platelets were encapsulated inside spherical latex particles, whereas larger MMT platelets were encapsulated inside dumbbell-like or snowman-like nonspherical latex particles. Further investigations on the film-forming and other properties of clay-encapsulated latex particles are under way.

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Supporting Information Available: Experimental details; TGA analyses for modified clays; cryo-TEM image for clay-encapsulated PMMA particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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