 DOI: 10.1002/masy.200651384

Encapsulation of Platelets by Physical and Chemical Approaches

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Summary: The Eindhoven group on emulsion polymerization has contributed to the field of encapsulation of many types of particles like pigments, fillers and clay particles, preparation of hollow multicompartment particles and encapsulation of nanotubes with latex particles. All these developments are very relevant for the next generation of coatings in which, more than in the past, improved properties are related to nanostructuring of the components in the coatings. Recently, interest has grown for the encapsulation of natural layered silicates, better known as clay platelets, and the formation of subsequent polymer-clay nanocomposites. In this paper we summarize our recent successful attempts to encapsulate platelet particles by a physical approach (controlled heterocoagulation of gibbsite and polymer latex particles, followed by thermal annealing of the polymer) and a chemical approach (starved-feed, surfactant-free emulsion polymerization in the presence of covalently modified clays).

Keywords: cryogenic TEM; emulsion polymerization; encapsulation; heterocoagulation; polymer-clay nanocomposites; surface modification

Introduction

In polymer community there is a continuous trend towards the development of materials that are stronger, tougher, durable, as well as readily accessible and processable. For the coatings applications such demands are also becoming standard. (Micro) encapsulation is the process of obtaining small solid particulates, liquid droplets, or gas bubbles with a coating.

The encapsulation of pigment and filler particles is an important area of research, both in the academic world and in industrial laboratories. Many activities in the past decade have been aimed at obtaining inorganic powders, coated with an organic polymer layer. Such systems are expected to exhibit properties other than the sum of the properties of the individual components. In general, several benefits from this encapsulation step can be expected when the obtained particles will be applied in a polymeric matrix, *e.g.* plastics or emulsion paints:

- Better particle dispersion in the polymeric matrix
- Improved mechanical properties
- Improved effectiveness in light scattering in a paint film
- Protection of the filler or pigment from outside influences
- Protection of the matrix polymer from interaction with the pigment
- Improved barrier properties of a paint film

The applications of these encapsulated particles relate to the above mentioned benefits and can be found in filled plastics, paints, inks, paper coatings etc.

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Polymer-clay nanocomposites, by incorporating just a few percent of clay nanoparticles, have demonstrated improvement in mechanical properties, thermal stability, and barrier properties. The challenge is to incorporate single clay platelets in latex particles and then impose anisotropy on the final coating film. Barrier properties and scratch resistance may benefit from such an anisotropic film. The way to obtain anisotropic film formation would be to have non-spherical latex particles in such a way that, during coalescence in the film formation process, most of the clay platelets align parallel to the substrate surface. Since the hydrophilic clay layers can be readily exfoliated in the aqueous phase, emulsion polymerization appears to be a very attractive route. We have shown that the usual outcome of efforts to encapsulate clay platelets is that the clay is on the outside of latex particles.

Results

The Physical Approach: Controlled Heterocoagulation of Platelets and Spheres

Heterocoagulation is generally driven by electrostatic interactions of oppositely charged species that generate a stable composite particle. In general, the smaller shell-forming particles (SFP) with a relatively low T_g are adsorbed onto the surface of the larger core-forming particles (CFP). Eventually, a monolayer of small particles forms on the surface of the large particle. In the subsequent step of the formation of core-shell composite particles, the heterocoagulated particles are heated to a temperature higher than the T_g of the SFP but lower than the T_g of the CFP.[1–4] The controlled heterocoagulation process and subsequent annealing of polymer to obtain anisotropic particles are schematically shown in Figure 1.

Polymer-clay nanocomposites have been synthesized by the heterocoagulation approach,[5,6] but these papers only discussed the final nanocomposite material and not the stability of the particle dispersions. In this work, we show the heterocoagulation between charged spheres and oppositely charged platelets. For the heterocoagulation with clay platelets, cationically charged latex spheres with different sizes and charge densities have been synthesized.[7] Clay platelets appeared to be highly susceptible to destabilization effects as a result of the presence of oppositely charged latexes and this resulted in aggregation and even flocculation (see Figure 2). Heterocoagulation between the cationically charged latexes and large montmorillonite platelets or smaller synthetic Laponite RD platelets occurs. Nevertheless, control over the platelet coverage and the formation of single platelets completely covered by latexes has not been obtained. The experiments indicate that heterocoagulation between clays and oppositely

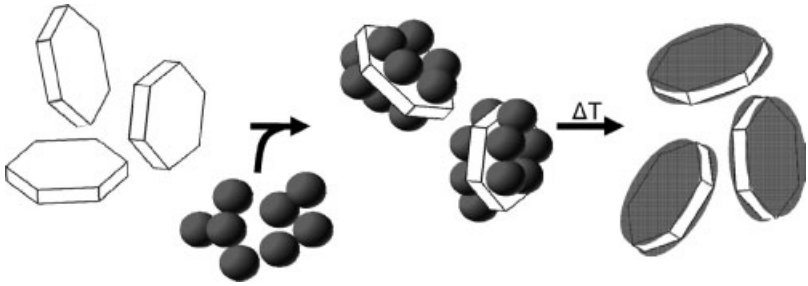

Figure 1.
Schematic illustration of the heterocoagulation between gibbsite platelets and spheres. Stable gibbsite platelets covered with one layer of spherical particles are formed and after a heat treatment the spheres are annealed and form a polymeric film at the surface of the platelets.

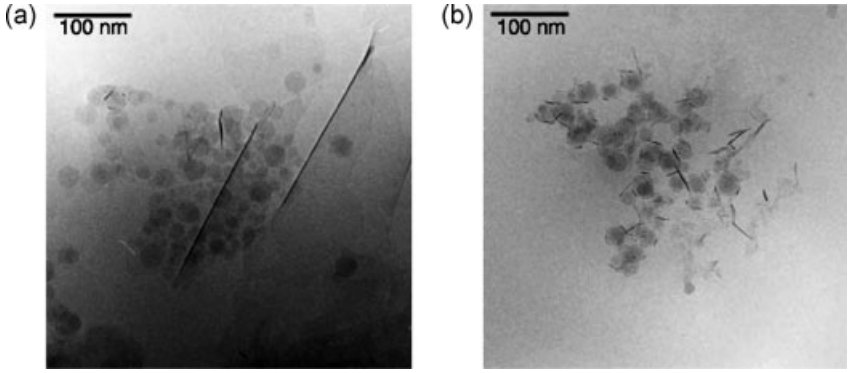

Figure 2.
Cryogenic transmission electron microscopy micrographs of cationic latexes heterocoagulated with montmorillonite clay platelets (a) and synthetic Laponite RD platelets (b).

charged latexes is possible. However, the control over the colloidal composite particle appeared to be difficult. The formation of stable heterocoagulated colloidal particles was not achieved.

Model colloidal platelets (gibbsite) are much thicker than clays and have a more controlled size distribution. These model platelets are much easier to visualize by scanning or transmission electron microscopy. Heterocoagulation experiments were conducted with anionically charged spheres and cationically charged gibbsite platelets.[8] Synthetic gibbsite platelets have a width in the range of 100–400 nm and a thickness increasing from 7–15 nm, respectively, depending on the processing conditions. The thickness of gibbsite allows direct visualization with electron microscopy and atomic force microscopy (AFM).

Heterocoagulation experiments of different spheres in the presence of gibbsite platelets were performed at solid contents between 0.005 and 0.02 wt%. Heterocoagulation experiments were conducted by varying the number ratio between the small and large particles (N_S/N_L) at a constant ionic strength. It appeared from visual observations that stable dispersions were obtained for the sphere-plate heterocoagulation experiments. We used AFM to observe the morphology of heterocoagulated particles.[8] From the height profile of the image we can derive that there is also a monolayer of spheres beneath the platelet. This clearly indicates that heterocoagulation takes place in the water phase and that the observed morphology is not the result of the precipitation of gibbsite platelets followed by the "snowing" of the surface with latex spheres.[8]

We also used cryo-TEM to examine the particle morphology. These analyses showed that there was no aggregation between the gibbsite platelets and the oppositely charged spheres. Based on cryo-TEM observations, the formation of stable, heterocoagulated gibbsite/latex particles has been confirmed.

The heterocoagulated gibbsite/PBMA colloidal particles were heated to 80 °C for 8 to 24 h and analyzed by cryo-TEM. Figure 3 shows the annealing and sintering of latex particles adsorbed to the surface of the gibbsite platelet after 24 h of heating at 80 °C (shown by the black arrows). The number ratio N_S/N_L for this system is 230 to ensure high fractional coverage of the gibbsite platelets by latex spheres. The black arrows indicate the PBMA polymer layer, which is lighter than the gibbsite. This formation of the polymer layer suggests that the encapsulation of gibbsite platelets and the formation of anisotropic latex-based particles are feasible by the heterocoagulation process.

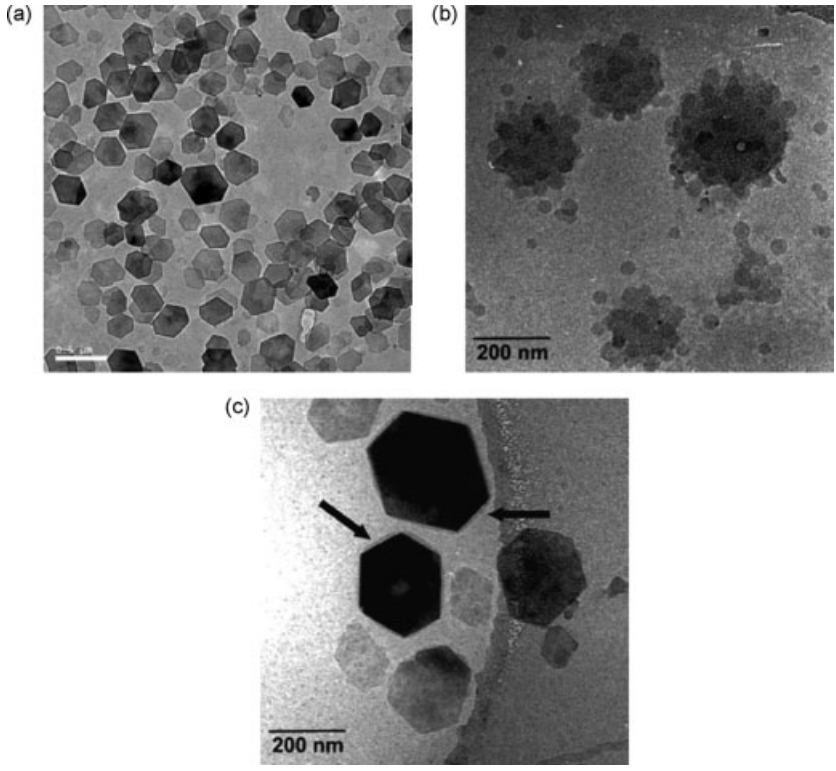

Figure 3.
(a) TEM micrograph of the colloidal gibbsite platelets. (b) Cryo-TEM micrograph showing gibbsite platelets covered with a layer of PBMA latex particles. (c) The formation of a PBMA layer on the surface of gibbsite after 24 h of heating at 80 °C.[5]

Chemical Approach: Starved-Feed, Surfactant-Free Emulsion Polymerization of MMA onto Covalently Modified, Polymerizable Clay Platelets

Conventional emulsion polymerization in the presence of clay and modified clay platelets have prepared polymer-clay hybrid particles,[9] but only armored particles (clay being located at the particle surface) have been obtained. Encapsulation of clays in dispersion by polymer appears to be very challenging. Bourgeat-Lami *et al.*[11] have shown that only face modification using exchange of the stabilizing cations by cationic initiators or monomers in a seeded emulsion polymerization would also produce armored latex particles. Alternative to face modification by cation exchange, functionalization of the clay surface using covalently bonded molecules enables the tuning of its hydrophobicity and functionality. Recent studies[12–18] have reported the covalent modification of clay platelets with the grafting of alkoxysilanes. The edges of the clay contain hydroxyl groups from the silanol or aluminol groups. These edge groups can be treated as conventional Si–OH groups and can be modified with silanes or titanates.[19]

For the chemical approach we have used sodium montmorillonite (MMT), which is a natural clay with an average platelet diameter of approximately 150 nm, obtained after 2 steps of centrifugation.[20] The MMT almost completely exfoliates in water when using mechanical mixing. The clay was first modified on the sides in dichloromethane with the silane or titanate coupling agent[20] (see Figure 4).

After the modification of the sides of the clay platelets encapsulation in water using starved-feed, surfactant free emulsion poly-

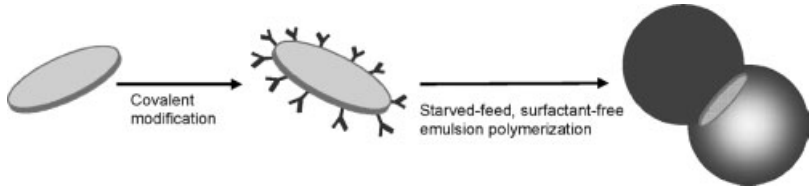

Figure 4.
Schematic illustration of clay platelet modification and encapsulation via emulsion polymerization with a vinyl monomer.

merization (initiator VA-086) turned out to be possible without introducing stacking of the clay platelets again. Scanning electron microscopy (SEM) analysis of latex particles can provide information on the location of the clay platelets. As already shown in one of our previous publications,[21] clay platelets located on the surface of the latex particles produced rugged surfaces, whereas clays inside latex particles would produce smooth latex particles. At first glance, Figure 5a shows ''normal'' spherical latex particles with a minor fraction of non-spherical latex particles. However, a thorough inspection of the micrograph reveals that more than 50% of the latex particles depicted in Figure 5a have a dumbbell or snowman-like shape, or are at least non-spherical. The variation of the particle shape may be the result of the broad size distribution of the modified MMT: particles containing smaller MMT platelets tend to be spherical while those with larger platelets are more likely non-spherical 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.[10,21] This confirms that the clay platelets are not located at the surface of the latex particles and, instead, they are completely encapsulated inside the latex particles. SEM micrographs from higher dilutions provided detailed information about the dumbbell structures, see Figure 5b. Figure 5b shows dumbbell-like latex particles which contain MMT platelets. These micrographs of Figure 5 clearly demonstrate that the dumbbell-like particles vary in particle size from 200 to 400 nm.

Cryo-TEM was used to examine the particle morphology of the montmorillonite encapsulated latex particles in the wet state.ÂThe black lines in Figure 6 are covalently modified montmorillonite platelets encapsulated in latex particles. The dumbbell shape is caused by the presence of a clay platelet (between 80 and 130 nm in length) inside. The unique dumbbell, non-spherical shape[22,23] of the latex particles cannot be obtained via emulsion homopolymerizations in one single step;[10,11,24–26]

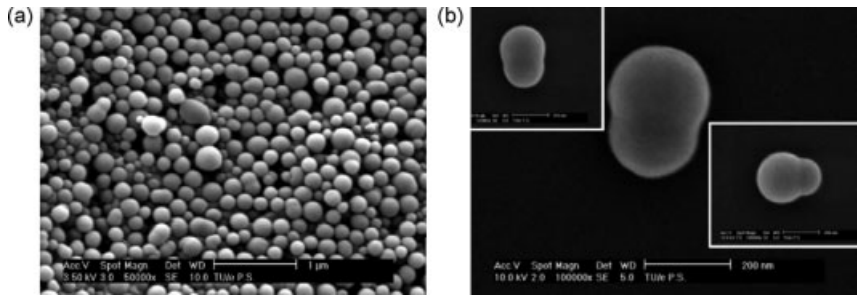

Figure 5.
(a) Nanocomposite latex particles observed with scanning electron microscopy. (b) A magnification of single dumbbell-shaped clay encapsulated latex particles from a highly diluted.

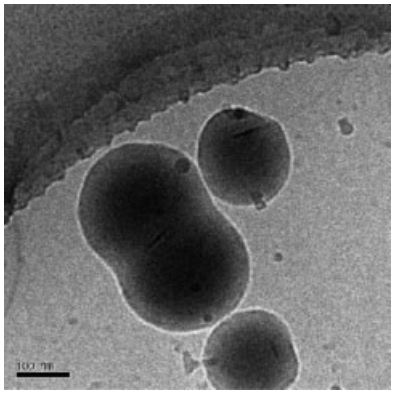

Figure 6.
Cryo-TEM micrograph of PMMA latex particles containing covalently modified montmorillonite clay platelets prepared by starved-feed emulsion polymerization.

batch emulsion polymerization in the presence of unmodified[10] or covalently modified[11] clays led to latex particles surface covered with clay platelets. The starved-feed, surfactant-free emulsion polymerization conditions,[24,26] combined with covalent edge modification, appear to be the key to obtain clay encapsulation.

Although clay platelet orientation was not in the desired direction, X-ray analysis of the latex did not show any clay aggregates in the final film. The X-ray diffraction patterns of the polymer-clay nanocomposite films from LRD containing latex particles (DV01) and Na-MMT containing latex particles (DV05) are shown in Figure 7. Both nanocomposite films were obtained after heating for 24 h at 120 °C. The diffraction patterns reveal no observable clay basal spacing in the polymer films and complete exfoliated polymer-clay nanocomposite films are achieved.

Conclusions

In this work two routes have been followed: (1) controlled heterocoagulation of inorganic and polymeric particles or (2) direct emulsion polymerization on the surface of hydrophobized inorganic particles.

We have demonstrated the formation of anisotropic latex-based particles by the heterocoagulation between gibbsite platelets and spherical particles. Dynamic light scattering measurements as well as microscopic visualization have confirmed the formation of heterogeneous colloidal particles. AFM and cryo-TEM micrographs revealed the uniform distribution of adsorbed latex spherical particles on both sides of the gibbsite platelets. Heat treatment of the heterocoagulated particles led

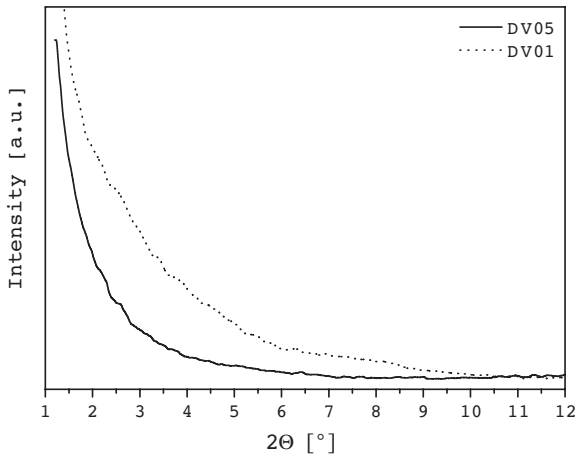

Figure 7.
X-ray diffraction patterns of polymer-clay nanocomposite films from LRD containing latex particles (DV01) and Na-MMT containing latex particles (DV05).

to the formation of a layer of polymer at the surface, covering the whole gibbsite platelet, hence creating a gibbsite-encapsulated, anisotropic particle. With this procedure we have shown that polymer-coated, anisotropic nanocomposite particles can be readily produced via heterocoagulation between spheres and platelets without any surface modifications.

The emulsion polymerization directly on clay platelets imposed more problems; it turned out to be very difficult to force the clay platelets inside the latex particle. Both with normal and inverse emulsion polymerization of hydrophilic and/or hydrophobized clay platelets the outcome is usually that the clay platelets are partitioned on the outside of the latex particles.

Only after special modification of the side of the clay platelets it turned out possible to force them inside the latex particles through starved-feed, surfactant-free emulsion polymerization. This process results in anisotropic particles in the form of dumbbell shaped latex particles with one or a few clay platelets per particle.

Acknowledgements: Prof. Dr. G. de With, Dr. J. Meuldijk and Dr. J. Laven of Eindhoven University of Technology are thanked for their constructive discussions. We thank Henk Woestenberg for SEM analyses and Macro Hendrix for XRD measurements, both from the Eindhoven University of Technology. Special thanks are extended to Dr. P. M. Frederik and P. H. H. Bomans (University of Maastricht, The Netherlands). The Foundation of Emulsion Polymerization (SEP) and Dutch Polymer Institute (DPI) are thanked for their financial support.

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