Polymer Encapsulation of Single Clay Platelets by Emulsion Polymerization Approaches, Thermodynamic, and Kinetic Factors

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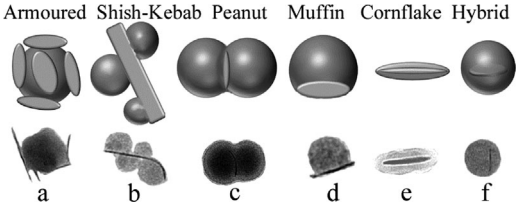
Polymer encapsulation of clay platelets through (mini)emulsion polymerization can be a versatile method to obtain hybrid nanoparticles with several important applications. However, to achieve actual encapsulation of the single clay platelets inside latex particles is relatively difficult. For single clay platelet encapsulation, complete exfoliation and colloidal stability needs to be achieved as well as kinetic and/or thermodynamic control mechanisms to locate and maintain the position of the single clay platelet on the inside of the latex particle. An overview of these mechanisms will be given and an overview of the most relevant attempts in this area will be discussed in retrospect in the context of a systematic mechanistic understanding.



1. Introduction

1.1. Kinetic and Thermodynamic Factors in (Mini)emulsion Polymerization Approaches to Encapsulate Clay

For chemical reactions to proceed, a driving force is needed which basically is the difference in Gibbs free energy (ΔG^0) between initial state (educt) and final state (product). The position of the equilibrium depends on the value of ΔG^0. Starting from an educt, the rate of product formation depends on the Gibbs free energy of activation (to the transition state), $\Delta G^{\#}$(f) for the forward reaction and similar for the rate of backformation of educt from product the Gibbs free energy of activation $\Delta G^{\#}$(b) is determining. If one wants to obtain a certain product then, although the product might be the most stable molecule, it still depends on the kinetics of the reaction whether this product can be obtained from the educt in a reasonable span of time. In some cases, a reaction is kinetically controlled and one can stop the reaction at some point, isolating a molecule that is not thermodynamically stable. A post stabilization reaction might be needed to prevent the molecule to further react to the thermodynamically most stable product. For example, in certain polymers obtained by step growth polymerization reactions (like polyoxymethylene) the backreaction can occur through unzipping of the last unit in the polymer chain, modifying the endgroups prevents the backreaction from occurring, even under conditions (high temperature, aqueous conditions) that normally this polymer would strive to an equilibrium situation which is rich in the undesired monomer.

This concept of kinetic and thermodynamic interplay is also observed and applied in the synthesis of nanostructures in general[1] and in the morphology of seeded emulsion polymerizations in particular.[2] In the conceptual paper of Chen and co-workers,[1] the emphasis is on the use of the concept of kinetic and thermodynamic control during the formation of nanocrystals, although they generalize the concept also to a few examples in soft matter. In the area of seeded emulsion polymerization, both the thermodynamic[3–5] and kinetic aspects[6,7] are well understood. The area of understanding the formation

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of the morphology of hybrid latex particles, a combination of inorganic and polymeric materials in submicron structures, is still in its infancy.

In general, one can distinguish between emulsion and miniemulsion polymerization approaches to encapsulate inorganic particles in general and clay platelets in particular. The principle of miniemulsion polymerization[8,9] is that monomer is emulsified in water with the aid of surfactants and high shear to obtain usually submicron particles that are then polymerized with a water or oil soluble initiator. In this approach, encapsulation of inorganic particles is achieved by hydrophobic modification of the inorganic particles and dispersing them in the monomer before emulsification.

The principle of emulsion polymerization[9] is that monomer is emulsified in water, surfactant is creating micelles and with, in general, a water-soluble initiator, oligomers are formed in the aqueous phase that enter the monomer swollen micelles to create the polymeric latex particles. Often in industrial processes, the micelles are replaced by preformed seed particles in order to have better control over particle number and size. In emulsion polymerization, the encapsulation of inorganic particles can be regarded as a seeded emulsion polymerization. In the emulsion polymerization approach, the inorganic particles are first surface modified (hydrophobized) to make them dispersible with normal surfactants and then an emulsion polymerization is performed, where the locus of polymerization is the hemimicelle, a micelle-like hydrophobic domain around the inorganic particle. In some cases, unmodified inorganic particles can be used where either a bilayer of surfactant is adsorbed on the surface or some in-situ surface modification is occurring through precipitation of oligomers/polymers formed in the aqueous phase.

The thermodynamic controlling factors in seeded emulsion polymerizations are based on the total surface energy of the system composed of the sum of the products of interfacial areas and interfacial tensions for each of the polymers with water and the polymers with each other.[2] Besides the polymers themselves also the addition of surfactant, compatibilizers, and the inclusion of initiator end groups can affect these interfacial tensions.

The kinetic factors are based on rates of diffusion, in the case of the model of Asua[6] of clusters of polymer chains (or polymer nanodomains), in the case of the model of Sundberg[7] based on diffusion rate of oligomeric radicals. In both kinetic models, the viscosity inside the growing latex particles is crucial, this viscosity is, amongst others, connected to the monomer to polymer ratio in the growing latex particles over time which in turn is affected by rates of polymerization.

The main difference looking at these factors in a miniemulsion polymerization approach is that the inorganic particles should already be compatible with the monomer from the onset of the miniemulsion polymerization. In batch miniemulsion polymerization, the inorganic particles are inside a relatively low-viscosity medium early on in the polymerization making the possibility to achieve equilibrium morphologies higher than in, for example, a starved fed emulsion polymerization.[10]

1.2. Free Radical Polymerization Versus Controlled Radical Polymerization for Clay Encapsulation

In free radical polymerization, the radicals are easily susceptible to fast termination and the average lifetime of a radical, from initiation to termination, is no more than in the order of magnitude of seconds. In controlled radical polymerization, radical termination is suppressed by some kind of capping agent like a metal complex or a nitroxide, or a reversible transfer mechanism is operating like RAFT (Reversible Addition Fragmentation Transfer). These mechanisms can be operative also in clay encapsulation.[9]

Either way, the polymer chains are growing for a much longer time, if desired for hours.

The way controlled radical polymerization is aiding the encapsulation of clay is that the long growing chains can be located on the surface of inorganic particles, directing polymer growth to the surface. In principle, attaching a free radical initiator could achieve a similar effect, but in general two radicals are produced from an initiator so at least one radical could freely produce polymer not on the surface of the inorganic particle. Especially RAFT is shown to be very popular to achieve good encapsulation of inorganic particles. The pioneer of this approach is B. Hawkett and together with the group of Van Herk he also applied this method to high aspect ratio inorganic particles for the first time.[11]

The use of ATRP in clay encapsulation is relatively scarce, but in 2012 Khezri et al.[12] reported the use of ATRP in miniemulsion polymerization to obtain PMMA-encapsulated clay.

2. Results and Discussion

2.1. Emulsion Polymerization Versus Miniemulsion Polymerization

As discussed in the introduction, well-established models exist for morphologies of polymer nanoparticles with more than one polymer, taking both kinetic and thermodynamic factors into account.[2–7] The number of papers describing morphologies for hybrid latex particles with the same level of sophistication as that for polymer–polymer nanoparticles is very limited. Asua,[10] in 2014, described a morphology map for polymer–inorganic nanocomposites synthesized by miniemulsion polymerization, based very

much on the same (thermodynamic) factors as that for polymer–polymer nanoparticles. He showed that for several literature examples, the resulting morphology can most often be explained by this morphology map. In some cases, the morphologies obtained were claimed by the original authors to be controlled by kinetic factors, but Asua could convincingly argue that in all these cases the thermodynamics were responsible for the resulting morphologies. This sounds logical as again in miniemulsion polymerizations, during a substantial part of the polymerization, the internal viscosity of the particle is low, creating the conditions for attaining the equilibrium morphology. He restricted himself to low aspect ratio inorganic nanoparticles, although the mapping can still provide some guidance to high aspect ratio clays also. The complicating factors of clay encapsulation through emulsion polymerization are the following:

(1) Most clays like montmorillonite (MMT), cloisite, and hectorite have a strong tendency of stacking, once in aqueous dispersion spontaneous exfoliation often occurs but then the opposite charges of the faces and edges can lead to cardhouse structures and associated gelation. So if no special additives are used, a clay dispersion of MMT of a few percent already leads to a highly viscous system, limiting the level of clay during the emulsion polymerization.
(2) The unmodified clays used in encapsulation are hydrophilic and the nice spontaneous exfoliation is based on the interactions of the hydrophilic surface with water. Hydrophobic modification of the clay, needed for encapsulation, although possible, can lead to stacking again. Even adding surfactant to a hydrophobically modified clay still does not always lead to individual platelets in the aqueous phase. So in case of single platelet encapsulation we have these opposing factors; for exfoliation we like to have the hydrophilic surface, for encapsulation we would like to introduce a more hydrophobic region around the clay (the hemimicelle).

The complicating factors in clay encapsulation through miniemulsion polymerization are the following:

(1) The clay has to be predispersed in the monomer phase and almost always a hydrophobic modification is needed. Obtaining single exfoliated platelets in the droplets is challenging and getting one clay platelet per particle is almost impossible.
(2) Using miniemulsion polymerization is a versatile and alternative method to emulsion polymerization but is not widely adopted in industry yet.

So it seems that both approaches are more or less complementary; emulsion polymerization, as a widely adopted polymerization technique, is able to encapsulate single clay platelets with or without a modification step whereas miniemulsion polymerization, as a more specialized technique, is capable of encapsulation modified clay at high solids, but usually results in encapsulation of multiple (stacked) platelets in the particles.

Asua[10] in his paper on morphology mapping states that the limitation of emulsion polymerizations (and dispersion polymerizations) is that the only two attainable morphologies are either inorganic particles (clay) on the outside of the hybrid particles (armored latex particles) or single inorganic particles inside the latex particles. In many applications, the usage of clay is to enhance mechanical properties, barrier properties, and other physical properties. In many cases, the efficacy of clay is correlated to the extent of exfoliation, this extent is commonly accessed via Xray Diffraction (XRD) measurements. One can argue that the optimal morphology to change properties of a polymer film would be completely exfoliated clay platelets; they have the highest aspect ratio and the highest surface area per weight of clay. The armored latex particles are generally obtained when the interfacial tensions between the clay and the polymer are high. In principle, armored latex particles can also be obtained by physically blending latex and clay in water. Many papers show as a main result either only armored latex particles or these in combination with encapsulated latex particles. An important modeling paper describes different equilibrium morphologies of nanodroplets in the presence of nanofillers, the starting point of miniemulsion polymerization.[13] This paper models the equilibrium morphologies of nanodroplets (not the final nanocomposites) through Monte-Carlo simulations. The model also includes high aspect ratio inorganic particles and it shows that the compatibility between the nanofiller and the monomer and aqueous phases is the key factor that controls the equilibrium morphology of the monomer droplets and in turn, may control the final morphology of the polymer particles synthesized by miniemulsion polymerization. Interestingly also the absolute size of the clay platelets with respect to the droplets is a limitation for encapsulation. Given this information, we can go through the literature and see what morphologies were obtained with encapsulation through miniemulsion polymerization. It has to be remarked that clear identification of a morphology is not easy because of the small thickness of the clay platelets. Both TEM and SEM are used where SEM clearly shows a rough surface when an armored morphology is depicted.

In an early paper (2004), Sun et al.[14] claimed the successful encapsulation of laponite in polystyrene through miniemulsion polymerization. CTAB was used to hydrophobize the clay. In 2010, Leiza and co-workers applied their monomer droplet/clay model[13] to actual encapsulation of clay via miniemulsion polymerization[15]

and showed that they obtained mainly armored morphologies in line with the model for the droplet morphologies. Interestingly, they also observed a limited number of dumbbell or peanut morphologies. In 2013, a two-step polymerization process was introduced, basically using the typical armored morphologies as a seed particle for a second stage feeded emulsion polymerization.[16] In this two-step process, clearly kinetic control over the morphology is obtained through keeping the viscosity high by feeding the monomers slowly in the second step, giving the original equilibrium morphology from the first step no change to equilibrate to armored morphology. In this way, successful encapsulation of clay was achieved. The group of Hartmann and Pasch uses a somewhat different approach where the monomer and the clay are in separate miniemulsions and then are co-sonicated (ad-miniemulsion polymerization technique) to achieve highly filled polymer clay nanoparticles.[17] The process can be described as a polymerization in an adsorbed monomer layer created and stabilized as a miniemulsion.

In emulsion polymerization starting at a clay dispersion in water, obviously, not too high clay levels are possible because of the viscosity limitations. However, on the other hand both modified and unmodified clays have been used successfully to create interesting morphologies. In 2006, Voorn et al.[18] where the first to report on the so-called dumbbell or peanut morphology. In this case, hydrophobic edge modification of the MMT clay platelets was applied with titanates. The mechanisms of formation of these peanut-shaped particles are not fully clear but one theory is that polymerization starts at the edges and at some point the faces are engulfed with the polymer. This morphology can also nicely be verified by looking at the SEM images observing the non-spherical particles, but in TEM the same challenge exists that it is sometimes difficult to observe the location of the clay. For that reason, in some cases thicker high aspect ratio platelets were used like gibbsite.[11]

Both conventional and RAFT radical polymerization have been applied in emulsion polymerization. Like in miniemulsion polymerization, the use of ATRP is scarce although also some work is ongoing in that direction.[19]

Initially most of the work was focused on hydrophobized clay and in some cases clay with reactive groups like monomer functionalities. In the work of Voorn, it seemed that edge modification worked best to fully encapsulate the clay,[20] later also unmodified clay was successfully encapsulated.[21]

The modification of the clays was either ion replacement on the faces of the clay or edge modification through reaction with the hydroxyl groups.[18] The solids contents were relatively low due to the initial limitations of the concentration of clay in water. Later also solid contents up to 40% were achieved with emulsion polymerizations. The more successful approach for clay encapsulation through miniemulsion polymerization is in a two-step process where first the clay is included (mainly at the surface) of latex particles and then in a second starved feed seeded emulsion polymerization the clay is really encapsulated. Similar to that, one can envisage a first step where emulsion polymerization is used to create a clay-encapsulated seed followed by a second step being again the seeded emulsion polymerization.[22] In this way, the initial high viscosity of the clay is no longer a limitation to the production of high solids encapsulated clay.

One drawback of the emulsion approach is that the modified clays are exposed for a longer time to aqueous conditions and that, for example, for the titanate-modified clays, hydrolysis of the bonds between the clay and the titanate can take place.[21]

Overall, the variety of morphologies obtained for clay encapsulation through emulsion polymerization is richer than that for miniemulsion polymerization.

2.2. Possible Clay Nanocomposite Morphologies Obtained Through the Various Approaches

We would like to categorize the different morphologies obtained in both emulsion and miniemulsion clay encapsulation. First of all, it is noticed that the size and size distribution of the clay platelets are important parameters in the obtained morphologies, it is clearly observed that in encapsulation of a polydisperse clay different sizes of the clay are associated with different morphologies.[20,21]

The modification of the clay is another important parameter together with a possible reactivity of the clay modification with the polymerizing system. Often double bonds are incorporated in the surface modification, making the clay platelets part of the covalent polymer network. Cross-linking reactions can also be used to capture a certain non-equilibrium morphology.

The most common morphology found in the literature is that of the armored latex particles, clay platelets located at the surface of the polymer nanoparticles (Figure 1a). Typically, the clay platelets are in the same size range as the latex particles in that case and one often can observe parts of the clay sticking out in the aqueous phase through the use of cryo-TEM. In SEM, this morphology can easily be identified by a rough edgy surface in the dried sample.

In case the clay platelets are much larger than the latex particles, the so-called shish-kebab morphology can be formed (Figure 1b). Latex particles seem to be attached to the surface of the larger clay platelet. The shape of the latex particles is sometimes flattened in contact with the clay platelets. The peanut morphology is where two deformed latex particles seem to be connected by a single clay platelet (Figure 1c). Also clay particles with only one side covered

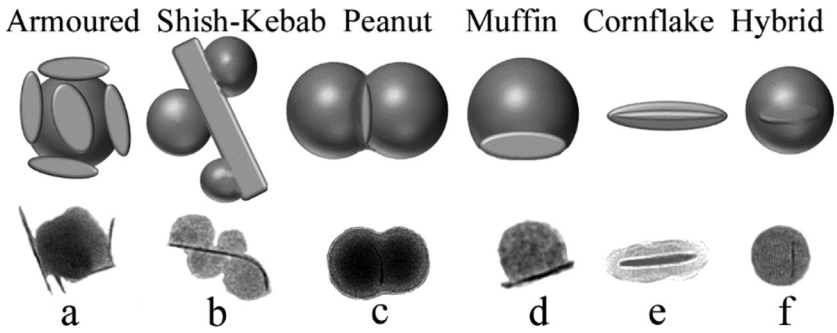

Figure 1. Overview of the different morphologies that can be formed in clay encapsulation in emulsion and miniemulsion polymerization. Top images schematic drawing of the morphology, bottom drawings how these morphologies might actually show up in TEM images.

Studying the effect of the polymerization process, surface modification, and added surfactants amongst others is simplified by using relative monodisperse clay samples. Depending on the conditions, either single clay platelets or stacks of several clay platelets may be found and abovementioned morphologies. In general, a combination of morphologies is found in the resulting materials after clay encapsulation and it is relatively uncommon to find only one morphology.

can be seen in some samples,[19] we coin this morphology the muffin morphology (Figure 1d).

Then, arguably one of the most interesting morphologies is the cornflake morphology (Figure 1e) where a thin layer of polymer is covering the clay. The interesting feature of this morphology is that the anisotropy of the clay platelet is directly translated in anisotropy of the nanocomposite. Similarly, in the peanut morphology the clay platelet is oriented perpendicular to the long axes of the nanocomposite. In both cases, orientation of the nanocomposites in, for example, a film will also lead to strong orientation of the clay platelets themselves. In the case of the cornflake morphology, the clay would be oriented parallel to the film direction which is known to give, for example, maximum barrier properties.

If the amount of polymer covering the clay platelet is large, the particle in the end will strive to a spherical morphology again and the link between the clay platelet orientation and the particle morphology is lost, we call this the hybrid latex particle (Figure 1f). In many cases, several of these morphologies can be seen resulting from one encapsulation reaction, often the different morphologies are coupled with the different clay particle sizes. In the majority of cases, miniemulsion polymerization leads to the armored latex particles or to hybrid latex particles (usually in the two-step process or the special ad-miniemulsion process). In emulsion polymerization the peanut, shish-kebab, armored latex particle, and muffin morphology are mostly seen. Of course, reactions also lead to separate latex particles and separate clay platelets sometimes. It is not always clear whether separate latex particles are formed separately and then coalesce with the clay platelets to form morphologies like the shish-kebab or peanut morphology. It has also been shown that by controlled heterocoagulation, one can encapsulate, for example, gibbsite platelets.[23] Heterocoagulation could in some cases explain the formed morphologies also, in competition with surface polymerization.

2.3. Interplay of Kinetic and Thermodynamic Factors in Clay Encapsulation Through Emulsion Polymerization

As in polymer–polymer core shell particle formation, the interplay of thermodynamic and kinetic factors is also operating in clay encapsulation through (mini)emulsion polymerization. Looking from the starting point of miniemulsion polymerization, thermodynamically the clay has to be modified hydrophobically to make it miscible with the monomer initially.[12–17,24–31] But the interfacial tensions change during the polymerization and the resulting morphology can still be armored latex particles. An interesting example is given by Chakrabary and Singha[25] where the use of neutral functional monomer, in combination with a fluorinated acrylate in miniemulsion polymerization, led to encapsulated Cloisite hybrid latex particles (multiple clay platelets per particle) whereas the use of a positively charged functional monomer led to armored morphology. In emulsion polymerization, one would like to create an affinity of the monomer for the clay particle surface, this is typically done by creating a hemimicelle around the clay, using surfactant absorption on a more or less hydrophobized clay surface.[11,18–23,32–34] Unfortunately, complete hydrophobization will lead to stacking of the clay platelets again because of the loss of favorable interactions between the clay surface and water that have led to the spontaneous exfoliation in the first place. This is the reason that edge modification seems to be a logical choice as a compromise between both factors.[18,23] After formation of a hemimicelle, the monomer (and sometimes also the initiator) is added under starved feed, keeping the viscosity of the particle as high as possible so as to prevent the thermodynamically most favorable morphology from forming, especially in the case of unmodified or partially modified clay. The same strategy is followed in the two-step miniemulsion polymerization approach after creating seed particles with miniemulsion polymerization.[17] In the case of unmodified clay platelets, the

question is how in the initial stage of the polymerization a hydrophobic layer of polymer is created around the clay platelet.[21] Usually the emulsion polymerization is conducted well below the CMC of the surfactant, making homogeneous nucleation most likely. The initial oligomers produced in the water phase are still relatively hydrophilic, depending on the type of monomer and the initiator, and might therefore have an affinity to the clay surface and adsorb. This absorbed (or precipitated) polymer layer is then gradually creating a hydrophobic polymer layer around the clay facilitating further growth on the surface. This mechanism is supported by the kinetic studies of Bourgeat-Lami and coworkers.[32] Other mechanisms with which one can direct the polymerization to the surface are modification with polymerizable groups,[33,34] adsorption of RAFT,[11,20] or ATRP[12,19] oligomers followed by chain extension hemimicelle formation on hydrophobically modified clay or through adsorption of bilayers.

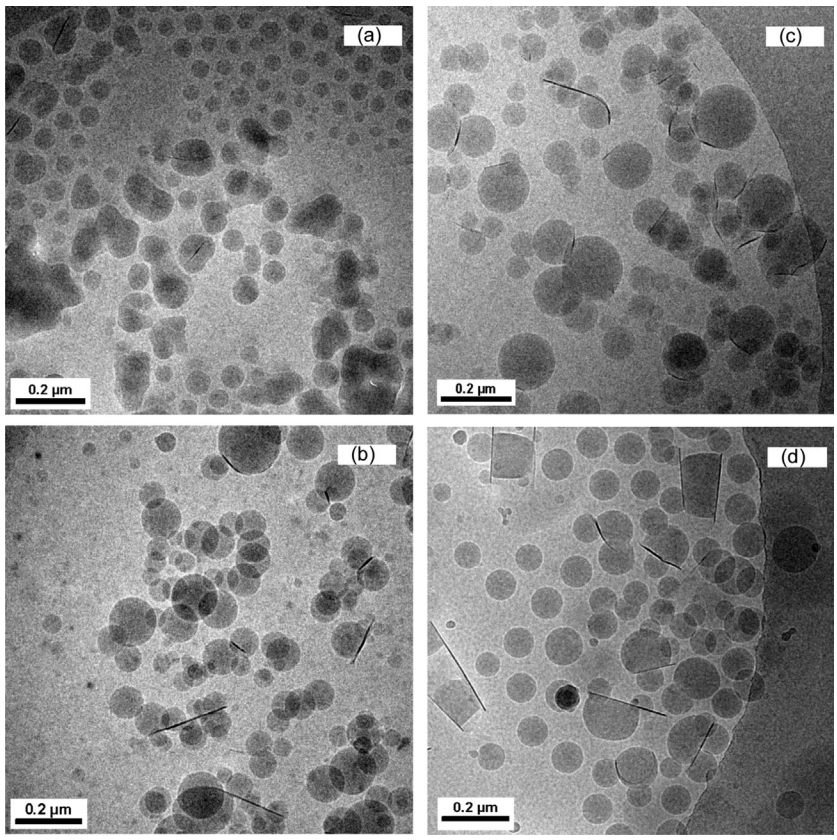

Figure 2. CryoTEM pictures of the latex/clay nanocomposites synthesized by varying the monomer feed composition ratio (by weigh) as such: (a) MMA:BA (1:0), (b) MMA:BA (3:1), (c) MMA:BA (3:2), and (d) MMA:BA (0:1). Experimental conditions: H_2O (100 g), monomer (7.05 g), VA-086 (0.14 g), native clay (3.5 wt% based on monomer), SDBS (0.056 g), a monomer feed rate of 16 mg min^{-1}, and a reaction temperature of 80 °C. Reproduced with permission from ref.[21]

Retaining a non-equilibrium morphology can then be achieved by either keeping the internal particle viscosity high during the polymerization process or creating chemical bonds between the clay and the polymer (cross-linking or through copolymerization of functional groups on the clay surface with the growing polymer). Often by varying the conditions during the polymerization reactions, one can analyze whether an equilibrium or a non-equilibrium morphology has been formed. Increasing the monomer feed rate, in case of a non-equilibrium morphology, will often result in armored latex particles again.

Changing the glass transition temperature of the formed (co)polymer, in this case changing from MMA to BA, we see a shift from cornflake morphology to shish-kebab and muffin morphologies (Figure 2).[21] Also heating up particles for a longer time can show a change in morphology toward the equilibrium morphology, as shown in Figure 3.[21]

The use of the different encapsulated morphologies in films has shown improvement of mechanical properties,[26,27] water vapor, and oxygen barrier properties[26,33] and thermal stability.[29,33] The ultimate film morphology where all the encapsulated (cornflake) clay platelets are strongly oriented parallel to the film has not been achieved so far. A general overview of clay encapsulation with unmodified and modified clay in emulsion and miniemulsion polymerization can be found in ref.[35]

3. Conclusion

Polymer encapsulation of clay platelets through (mini)emulsion polymerization can be a versatile method to obtain hybrid nanoparticles with several important applications. However, to achieve actual encapsulation of the single clay platelets inside latex particles is relatively difficult. Other than for the encapsulation of lower aspect ratio inorganic nanoparticles, several additional complicating factors play a role in clay encapsulation. For single clay platelet encapsulation, complete exfoliation and colloidal stability needs to be achieved as well as kinetic and/or thermodynamic control mechanisms to locate and maintain the position of the single clay platelet on the inside of the latex particle. In many cases, both in miniemulsion and in emulsion polymerization,

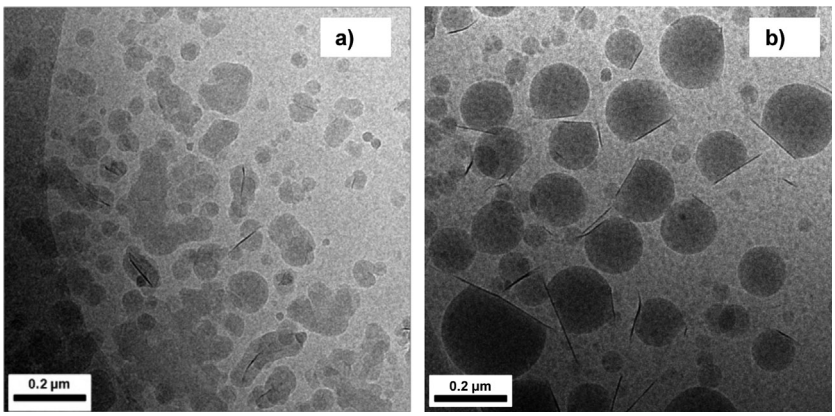

Figure 3. Cryo-TEM pictures of PMMA-latex/clay nanocomposites (a) before and (b) after heat treatment at 130 °C for ≈20 h. The experimental conditions used to synthesize the LCN are as follows: H_2O (100 g), monomer (7.05 g), VA-086 (0.14 g), native clay (3.5 wt% based on monomer), SDBS (0.056 g), a monomer feed rate of 16 mg min^{-1}, and a reaction temperature of 80 °C. Reproduced with permission from ref.[21]

non-equilibrium morphologies are obtained and usually successful encapsulation strategies rely on preventing the morphology to go to equilibrium. Several interesting morphologies can result from the clay encapsulation reaction and it has been shown that several properties, like mechanical and barrier properties, can be improved by these morphologies. Here, we have made an attempt to label the different morphologies observed and we have mapped some of the factors that control the formation of these morphologies. Future challenges would comprise the synthesis of desired morphologies at high solid contents as well as with high loadings of clay, using industrially viable processes.

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Keywords: clay encapsulation; emulsion polymerization; hybrid latex; miniemulsion polymerization; nanocomposites

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