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Controlling the Morphology of Composite Latex Particles

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research article

Controlling the Morphology of Composite Latex Particles

—Douglas Holmes

Latex plays an important role in many common products such as household paints, surgical gloves, various adhesives, coatings, and shock absorbent materials. A latex is a type of polymer, which is a large molecule made up of thousands (or even millions) of small molecules, called monomers, attached in a long chain. The chemical process by which these polymers are made is known as polymerization. Latex particles are unique in that the polymer chains polymerize to form particles in water, where most other polymers exist as independent chains in different solvents but rarely in water. Many different factors play a role in the polymer's final properties, and it is of great importance to manufacturers to be able to control these properties. With a latex, many of these properties are controlled by how two or more different types of polymers arrange themselves inside the particles; this arrangement is known as the particle's morphology. Being able to control the particle's morphology is important to the product's final properties; however, how to have this control is still not well understood. This project was designed to investigate one of the ways of controlling the particle's morphology. We hope that this investigation will help improve our ability to predict and direct latex particle morphologies in the future.

One way to control the particle's morphology is to change the glass transition temperature of one of the polymers in the particles. This is where I focused my research. The glass transition temperature (T_g) is a property somewhat unique to polymers, but is similar to properties like a melting or a boiling temperature. Polymers don't crystallize like liquid water does into ice; instead, they go from a rubbery phase to a glassy phase. For instance, the rubber that makes up your car tires is a polymer that is above its glass transition temperature at room temperature and, therefore, is rubbery; while the plastic used in soda bottles is below its glass transition temperature at room temperature and is, therefore, hard and brittle.

In my experiments I polymerized two different polymers within the same latex particles to form a composite latex particle. To control the composite latex particle's morphologies, I varied the glass transition temperature of the second polymer, or second stage, while keeping the glass transition temperature of the first polymer, or seed latex, constant. I kept my seed latex with a constant T_g while varying the second stage polymer's T_g . Previous studies had been done doing just the opposite, that is, varying the seed latex T_g while keeping the second stage polymer's T_g constant. I also kept the temperature at which the polymerization was performed constant. This meant that, in some experiments, the reaction temperature was above the second stage polymer's glass transition temperature so the polymer was soft. In other experiments, when the reaction temperature was below the second stage polymer's T_g , the polymer was hard. We believed that this property of the hardness or softness of the second stage polymer plays a large role in controlling the final composite latex particle morphology.

Another important factor in these experiments was that the polymerization was done in water. The seed latex used was hydrophilic (water-loving) and, therefore, wanted to be in contact with water; while the second stage

polymer was hydrophobic (water-fearing) and did not want to be in contact with the water. This means that if both the seed latex and the second stage latex were very soft (making them very mobile), then the second stage polymer would form on the inside of the particle and the seed latex would form on the outside.

One of the techniques we used to investigate the morphology of the composite latex particles formed was Transmission Electron Microscopy (TEM). The resulting images showed that, when the second stage polymer was hard, it formed a "core-shell" morphology on the outside of the polymer because it was too immobile to penetrate the seed latex or move around on the surface. The most interesting results came when the second stage polymer was very soft and mobile. Since the seed latex was still hard, the second stage polymer couldn't penetrate it; but because it was mobile, it was able to move around on the surface of the particle to form lobes. The reason it does this is because these lobes allow for more of the hydrophilic polymer to be in contact with the water and less of the hydrophobic one. These results gave us a better understanding of what controls latex particle morphology and will help industry better control their polymer systems to produce polymers with the properties they want.

Emulsion Polymerization

Emulsion polymerization is a special type of polymerization process in which the end result is a stable aqueous dispersion of polymer particles, typically 50-500nm in diameter. The simplest recipe for this involves water, monomer, initiator, surfactant (soap), and a pH buffer (baking soda). The surfactant molecules have a hydrophilic end and a hydrophobic end. Since they are in water, many surfactant molecules get together and form small spheres with the hydrophilic ends on the outside, in contact with the water, and the hydrophobic ends on the inside, protected from the water. These spheres of surfactant molecules are known as micelles. Since the monomer being added is also hydrophobic, it forms inside the micelles with the other hydrophobic molecules. The initiator being used thermally dissociates into free radicals, lone electrons that are very reactive. These radicals begin propagating by adding monomer units in the water phase until they reach a certain length, z , at which they become surface active. Once the radicals reach this length, the z -mers enter the micelles and continue the free radical polymerization, which results in the nucleation of a polymer particle. Polymerization results in the formation of a new particle phase, which is made up of both monomer and polymer, and is stabilized by surfactant. An example of a latex particle being stabilized by surfactant molecules is Figure 1.

Figure 1. *Surfactant molecules stabilizing a latex particle*

To have better control of the final latex particle size and distribution, a seeded emulsion polymerization with a previously prepared seed latex is used. Once the seed latex is formed, it can be used in second stage polymerizations (1) to form composite latex particles by polymerizing a second monomer, different from the seed polymer, or (2) simply to grow larger particles by polymerizing the same monomer. Figure 2 shows how a composite latex particle can form its final morphology in a seeded emulsion polymerization.

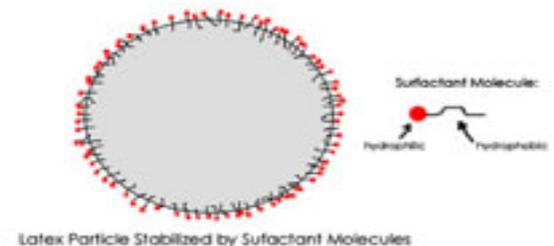


Figure 2. *How a composite latex particle forms from the initial seed particle*



Thermodynamic and Kinetic Effects on Particle Morphology

Controlling the final morphology of composite latex particles is of prime importance to industry since their product's properties largely depend upon this morphology, that is, the arrangement of the polymers within the particle. Various types of morphologies have been identified, such as core-shell, inverted core-shell, core-shell with internal occlusions, hemispheres, sandwich structures, and raspberry-like structures. Figure 3 shows examples of these structures.

Figure 3. *Thermodynamically vs. Kinetically controlled morphologies.*

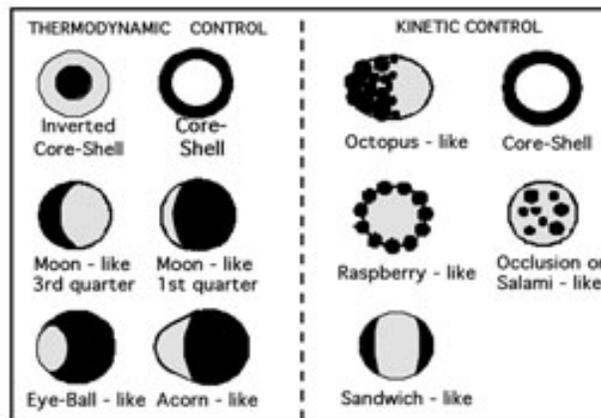
Particle morphology will be determined by either thermodynamic or kinetic factors, depending on the polymerization conditions (1,2). Thermodynamic control means that the molecules want to minimize their overall energies, such as surface energy and energy from molecular interactions. This desire for to minimize the system's free energy often, but not always, results in the more hydrophilic, or polar, polymer forming on the outside of the particle, which keeps it in contact with the water. If the reaction temperature is well above the T_g of the polar seed latex, then the particles are soft. This allows the nonpolar second stage polymer to penetrate more deeply into the particle, thus increasing the likelihood of forming the equilibrium morphology. Nonequilibrium conditions often occur when the diffusion rate of radicals into particles, the phase separation, and the rearrangement of the polymer chains are slow compared to the rate of polymerization. The development of morphology is, then, kinetically controlled.

Nonequilibrium morphologies are most likely to occur when the T_g of at least one of the polymers is close to or above the reaction temperature, and the monomer is fed slowly throughout the second stage polymerization. These conditions make for an extremely high viscosity within the seed particles which, in turn, makes it difficult for the two polymer phases to rearrange themselves into their thermodynamically favorable, or equilibrium, morphology.

Effect of the Entering Radical's Mobility on Particle Morphology

The nonequilibrium particle morphology of composite latex particles is very dependent on the mobility of the entering oligomeric radical. (An oligomer is a chain of monomer units, not long enough to be considered a polymer.) Oligomeric radicals enter from the water phase and then must diffuse, or penetrate, into the particles. If their diffusion rate, or mobility, is limited, the second stage polymer will form on the outside of the particle, making a core-shell morphology more likely. The extent of the radical's mobility is dependent on the relationship between the reaction temperature (T_r) and the seed polymer T_g . Previous studies had examined the relationship between the two properties by changing the T_g of the seed latex while keeping the T_g of the second stage polymer constant. These studies helped to provide a better understanding of the relationship between the seed T_g and the T_r and its effect on the ability of an entering radical to penetrate the latex particle.

The next step in understanding particle morphology is to maintain the reaction temperature and the seed latex characteristics throughout a series of experiments while changing the T_g of the second stage polymer, which is the focus of the work here. The basic conditions of the study include using a polar seed polymer and then polymerizing a nonpolar second stage monomer within the seed particles. This often indicates that the equilibrium morphology of this system should be an inverted core-shell. To reach these conditions, a seed



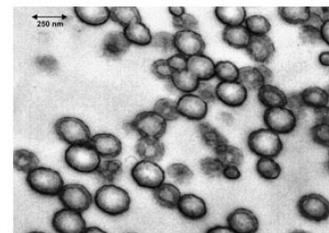
copolymer of methyl acrylate and methyl methacrylate with a Tg of approximately 80°C was used. The second stage consisted of a styrene/n-hexyl methacrylate copolymer. The second stage comonomer ratio was varied from 100% styrene to 13% styrene and thus varied the second stage Tg from 104°C to 5°C.

Analysis of Particle Morphology through Transmission Electron Microscopy

The morphologies of the final latices were observed using transmission electron microscopy (TEM), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and surfactant titration. The results from the TEM studies are discussed here. TEM is a electron microscopy technique that bombards the sample with an electron beam and generates an image of the sample by detecting where the electrons are transmitted. This, then, allows us to see through the latex particles. The best way to picture this is to imagine looking at an egg under a microscope. Since a normal microscope will allow you to see only the surface, you will have no way to judge how the yoke is arranged inside the egg's shell. Using this transmission technique, we would be able to see the morphology, or arrangement, of the two materials inside the egg: the egg white and the yoke. This analogy can be applied to the composite latex particles we are examining: we are left with a cross-section of the particle, so, essentially, we can see inside it.

Initial morphology simulations for this set of experiments predict that even by making the Tg of the second stage polymer very soft, it will still be highly kinetically hindered, forcing it to form on the outside of the particles. When the second stage polymer was glassy or moderately glassy, with Tg's ranging from 104°C to 60°C, it formed a shell on the outside of the particles. Figure 4 shows a TEM image of particles with this morphology.

Figure 4. TEM image showing the second stage polymer forming as a shell



When the Tg of the second stage polymer became significantly less than the reaction temperature (Tg = 35°C, Tr = 70°C), lobes began to form on the surface of the particles. This composite latex morphology is shown in Figure 5. These lobes are formed because the soft second stage polymer is more mobile on the surface of the particle than the glassy second stage polymer. This increased mobility allows it to form a more thermodynamically favorable morphology.

Lobes offer this more thermodynamically favorable morphology since they reduce the amount of surface area of the second stage, nonpolar polymer that is in contact with the water phase. This also allows more of the polar seed polymer to come in contact with the water, which helps to create a more thermodynamically favorable morphology.

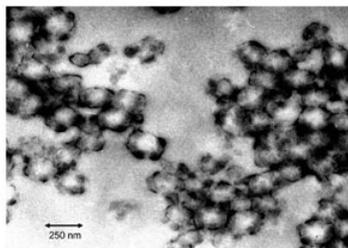


Figure 5. TEM image showing the second stage polymer forming as lobes on the outside of the particles

Conclusions

The results from these experiments have given us an increased knowledge of how the relationship between the reaction temperature and the glass transition temperature of the polymer affect the final composite latex morphology. This knowledge will be useful in industry to help companies better control the morphology of their latex particles and therefore the properties which their latex has. This study is on-going, and similar experiments are underway which will help to further our understanding in this area.

I would like to thank my advisor Dr. Don Sundberg and fellow scientist Jeff Stubbs, my immediate advisor, for taking me into their lab, sparking my interest in polymer science, and continually supporting me over the years. Without their teachings and inspiration I would not consider myself a scientist. I owe a great many thanks to Jeff for working closely and patiently with me throughout the years while I developed lab experience and scientific knowledge from the little I had when I first arrived.

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Author Bio

As a sophomore at UNH, Douglas Holmes joined Don Sundberg's Polymer Research Group, then later spent a summer doing similar work in Australia. He returned to UNH with a desire to conduct independent research. His latex polymer work began as a senior thesis project for his BS in Chemistry, which he received in 2004. The result of his project will be published this year in a scientific journal; however, he wanted to publish in Inquiry to show readers the research undergraduates were doing as well as to introduce them to polymers, which are all around them. The research process, he says, "taught me a lot about research and even more about myself. I quickly and continually learned how to fail and how to learn from those failures . . . Most importantly, I learned how to think like a scientist." At present, Doug is in a doctoral program in polymer science and engineering at the University of Massachusetts. He hopes one day to become a professor.

Mentor Bios

Donald Sundberg, Ph.D., has been at UNH since 1978. During that time he has had the pleasure of directing more than 25 undergraduates in his research laboratory. An associate professor of Materials Science, he specializes in polymeric materials and is director of the Nanostructured Polymers Research Center at UNH. Sundberg feels that Doug's work in his lab was a positive experience for the whole group: "I surrounded him with a number of people, all of whom served as mentors to him, and created a professional and positive atmosphere." Sundberg aided Doug in the many revisions needed to make their complex subject accessible to non-scientists.

In May, Jeffrey Stubbs will finish his Ph.D. in Materials Science. No stranger to UNH, Mr. Stubbs received his undergraduate degree here, also, and for the past four years has been a research scientist in the Materials

Science Program. His areas of specialization are polymer lattices made by emulsion polymerization, nanoscale morphology control in latex particles, and free radical polymerization kinetics. Doug Holmes joined an ongoing project in his lab, which is funded by several large companies. According to Mr. Stubbs, "The work performed by Doug is an excellent example of the fine contributions that good undergraduates can make to important projects such as this one."