Morphology of Hydroxyapatite as Suspension Stabilizer in the Polymerization of Poly(styrene-co-Butadiene)

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Synopsis

The morphology of the layer of hydroxyapatite that surrounds the polymer beads during the suspension polymerization of a random copolymer of styrene and butadiene is described. The layer is actually composed of two distinct parts: a thin layer made of very uniformly distributed hydroxyapatite primary particles and a second layer, usually much thicker, which is made of agglomerates of hydroxyapatite which are loosely packed. This second layer contains very small polymer beads, about 1 to 2 microns in diameter, that have polymerized at the droplet interface. Some of these smaller beads migrate into the bulk of the polymer during the polymerization contributing to the contamination of the polymer.

INTRODUCTION

Suspension polymerization processes have been used since the beginning of the century.[1,2] The idea of dispersing fine monomer droplets in aqueous suspension was probably conceived from the fact that native rubbers are found as latexes in nature.[3] In typical suspension polymerization, the monomer, usually a water-insoluble organic phase, is dispersed into droplets in an aqueous phase. Stirring is maintained as polymerization occurs. When the reaction is completed, the solid beads are isolated. Today, polymerizations carried out in aqueous media have great industrial importance.[4] Their main advantages over ordinary large-scale bulk polymerization processes are their efficiency in transferring the heat of reaction and the facility with which the small spheres can be handled after the reaction is completed. Suspension polymerization produces relatively large particles, of high purity, which can be directly filtered or centrifuged.

A crucial problem arising in the suspension polymerization process is related to the coalescence and the agglomeration of the beads during the polymerization. There are many collisions occurring during the agitation which results in a notable dispersion in which coalescence and break up of the droplets take place. As the reaction proceeds, the viscosity of the organic phase changes, and the droplet becomes tacky, favoring agglomeration upon globule collision. Small amounts of suspension stabilizers, sometimes also called suspending agents, are used to hinder the coalescence of the monomer droplets and the agglomeration of the beads which have become more viscous.

They are of two main types of suspension stabilizer used in suspension polymerization: (i) water-soluble organic polymers and (ii) insoluble finely divided inorganic materials. These agents which locate themselves at the

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water–monomer interface are effective in forming a layer around the bead. The mechanism of action of these materials—at least for the inorganic powder—is not known with certainty, but it is believed that the inorganic suspending agents hinder the approach of monomer droplets.[4]

One of the most extensively used inorganic particulate suspending agents for suspension polymerization is hydroxyapatite [3 $Ca_3(PO_4)_2 \cdot Ca(OH)_2$] often called tricalcium phosphate. Usually it is used in conjunction with a soap or surfactant.[5] This material is currently used in the suspension polymerization of styrene. Figure 1 shows a transmission electron micrograph of a sample of hydroxyapatite powder which was simply dispersed in methanol and deposited onto a carbon-coated copper grid. Note the platelet shape of the primary particles. They are about 200 nm in length and are relatively uniform in size. However, the majority of the pigment exists as aggregates of these primary particles. The size of the aggregates varies widely within the sample and we have observed differences in aggregates' size distribution between different batches of hydroxyapatite.

It is somewhat surprising that no information can be found in the current literature on the morphology of the layer of hydroxyapatite which surronds the beads during the polymerization. Since the process is of high commercial importance, we are convinced that there perhaps exists a wealth of information on the morphology of the layer of inorganic suspension stabilizers as well as how it affects the final product. Obviously this information is kept proprietary.

We were interested in characterizing the morphology of this material as it surrounds the droplets during the copolymerization of styrene and butadiene by a suspension polymerization process invented in our laboratory.[6] Transmission electron microscopy study was undertaken to examine the polymer beads which were taken from the reactor at the end of the reaction, but before any washing was performed to remove the hydroxyapatite. In this paper, we describe the morphology of hydroxyapatite layer surrounding the beads and speculate on its role in this process.

EXPERIMENTAL

Polymer Fabrication

The detailed procedure for the preparation of the polymers is described elsewhere.[6] Basically, hydroxyapatite and a soap (Alkanol XC from DuPont) were stirred in the water phase. The monomers and the initiator (organic phase) were then added and the reaction was initiated. After the reaction was complete, the polymer was filtered and a sample taken for microscopic characterization, prior to acid washing of the hydroxyapatite. The beads were dried in air prior to characterization.

Characterization

Scanning electron micrographs of the beads, mounted on an aluminum stub and coated with about 20 nm of gold using a sputter coater were taken using a Philips scanning electron microscope model SEM 505.

Fig. 1. Transmission electron micrograph of hydroxyapatite powder. Note the elongated shape of the primary particles. Although isolated particles are observed, most of them are aggregated. Scale bar is 0.5 μm.

The dry polymer beads were embedded in an epoxy resin (Araldite 6020, Ciba-Geigy), and allowed to cure at room temperature for at least 48 hours. They were then sectioned at room temperature using a diamond knife mounted on a Reichert-Jung ultramicrotome model "Ultracut E." Sections of about 0.2 μm thick were collected on a carbon-coated copper grid and then examined using a Philips transmission electron microscope model EM 400, operated at 100 kV. For the examination of the hydroxyapatite powders, the pigments

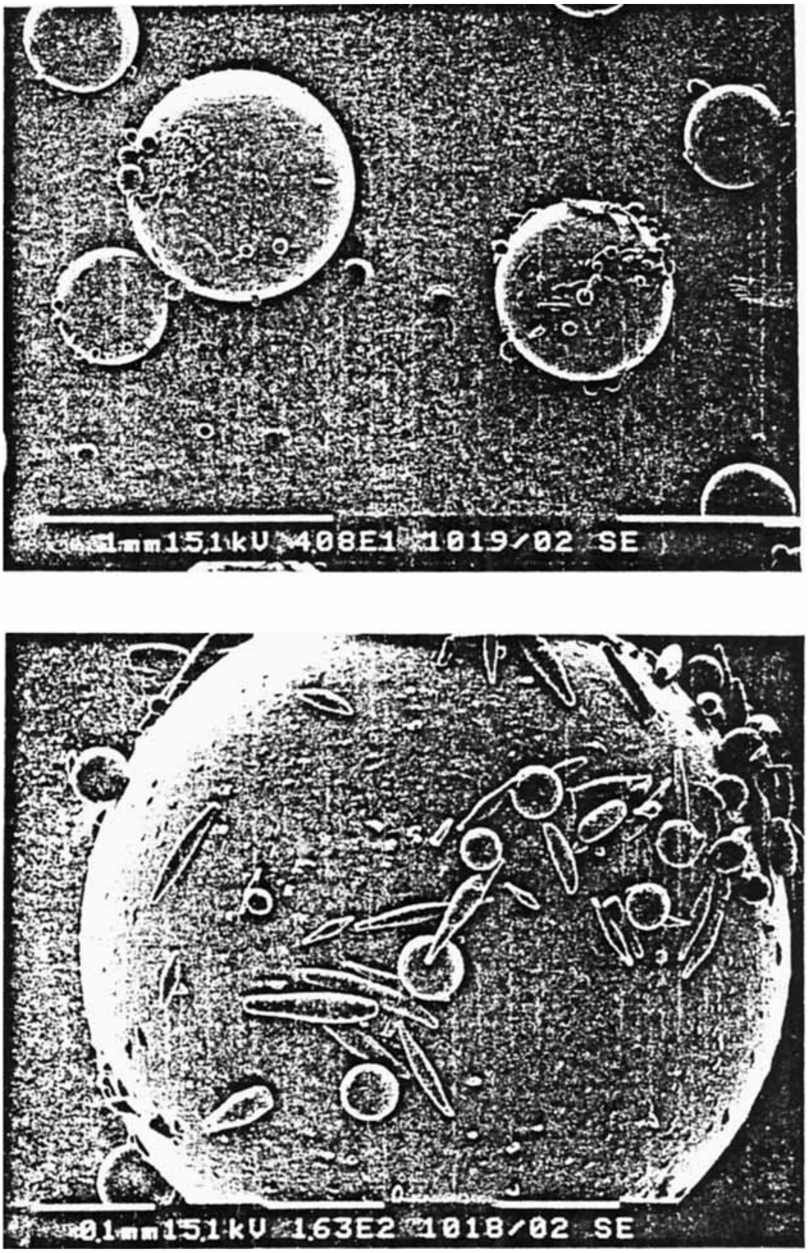

Fig. 2. Scanning electron micrographs of a typical bead of poly(styrene-co-butadiene). The beads have a diameter of about 500 μm. Smaller satellite beads having a spherical or elongated shape are seen at the surface.

were dispersed in methanol using an ultrasonic bath for two minutes. A drop of the suspension was then deposited on a carbon-coated copper grid for transmission electron microscopy (TEM) examination.

RESULTS AND DISCUSSION

Suspension polymerization processes usually yield larger beads (diameter > 50 μm) than emulsion polymerization (diameter < 10 μm). Figure 2 shows a pair of scanning electron micrographs (taken at two different magnifications) of typical beads of poly(styrene-co-butadiene) from the suspension polymerization process. The beads are spherical and their surfaces are relatively smooth. The presence of smaller beads at the surface of the large beads is obvious. These small "satellites," which do not always have a spherical shape, have an average diameter of about 100 μm and are found loosely attached—probably via electrostatic forces—to the surface of the large bead. It has been postulated by Wenning[7,8] that their presence is related to an excess of surfactant.

The morphology of the layer of suspending materials is easily observed through transmission electron microscopy (TEM). It is clearly seen (Fig. 3) that the layer is actually composed of two distinct parts. Firstly, a thin inner layer whose thickness is very uniform around the bead and which is made of uniformly distributed small primary particles of hydroxyapatite that are packed densely around the bead. The flat morphology of the particles and the narrow size distribution are probably responsible for the formation of a thin and uniform packing. On the other hand, the second layer, which is much thicker, does not uniformly coat the bead. This layer is composed of aggregates of various sizes instead of isolated platelets. Since these large aggregates have no particular shape and cannot be broken easily, they cannot pack very efficiently. This creates voids within the layer, which will be filled with either water or monomer during the reaction. Consequently, this layer represents a disordered region where monomer and initiator, trapped inside the layer, can polymerize independently of the rest of the bead. Small polymer beads having diameters between 0.5 and 2 μm are clearly seen within the layer. Interestingly, these beads are also coated with a thin layer of hydroxyapatite which acts as stabilizer. Note the these small beads should not be confused with the "satellite" beads mentioned earlier which are much larger. The morphology of the layer surrounding these satellites was found to be of the same nature as the large beads.

Most of the small beads that form within the hydroxyapatite layer do not really represent a serious problem since they are likely to stay there during the reaction and be washed away during the acid washing. Once washed, these small beads will simply not be retained on the filters during the filtration of the final product. However, it has been observed that some of these beads find their way inside the large beads durings the reaction, and eventually get trapped inside them. Figure 4 shows a small bead found many microns away from the surface of the bead. Usually, many of these beads can be found within the same large bead. It is believed that they were projected inside the bead during the agitation. Although most of them probably return to the surface due to surface tension effects, some will eventually be trapped inside

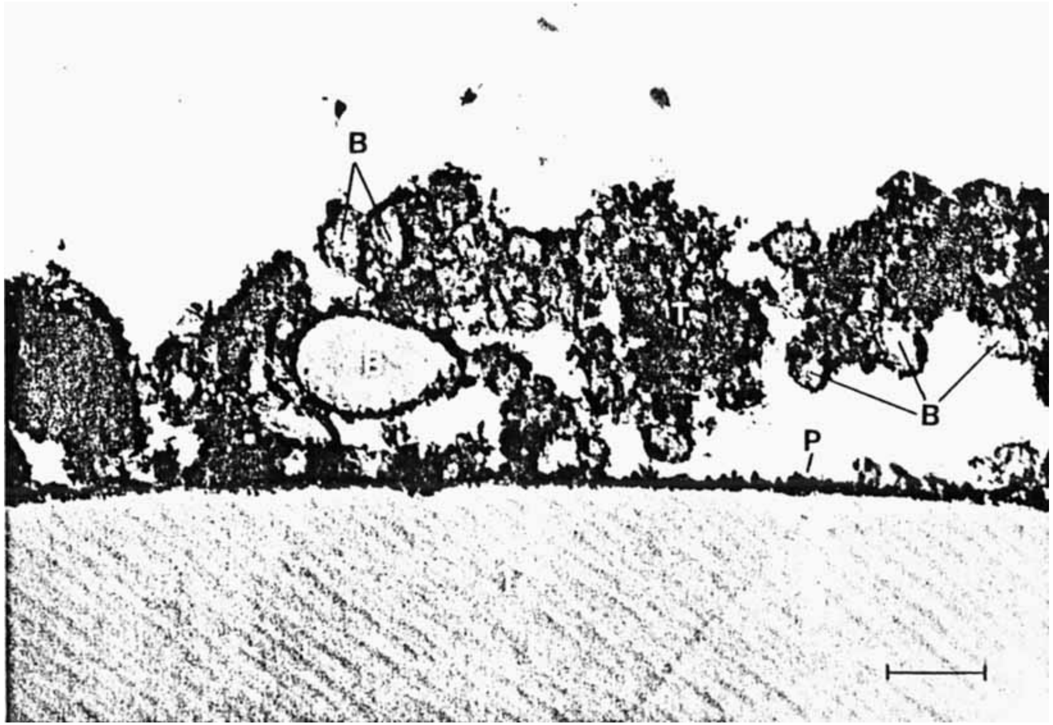

Fig. 3. Transmission electron micrograph of a cross-section of a poly(styrene-co-butadiene) bead showing the two distinct layers that make the suspension stabilizer layer. Legend: I: Bead interior, P: Thin uniform layer of primary particles of hydroxyapatite, T: thicker outer layer made of hydroxyapatite agrregates. B: Small polymer bead within the hydroxyapatite layer. (See text for explanation.) Scale bar is 1 μm.

Fig. 4. Transmission electron micrograph of a cross-section of the interior of a poly(styrene-co-butadiene) bead. Note the small bead (about 2 μm in length) which is only partially covered with hydroxyapatite. It is believed that these small spheres form within the hydroxyapatite layers, diffuse inside the bead, probably due to bead collision, and are finally trapped inside as the reaction proceeds and the viscosity of the polymer increases. Scale bar is 1 μm.

as polymerization progresses and the viscosity of the medium increases. Interestingly, as the TEM micrograph shows for that particular bead, many of these beads were only partially covered by hydroxyapatite and their inside surface is similar to that of the polymer of the large bead. The favorable interaction between the large bead and the exposed interior of the small bead may have favored their migration toward the inside of the bead rather than toward the surface. It should be pointed out that, although they are found in small quantities, these trapped beads are a source of contamination since the acid washing step will not remove the trapped hydroxyapatite. It is also reasonable to suggest that by reducing the thickness of the second layer of hydroxyapatite, the number of these beads will be reduced.

The presence of the two layers around the polymer beads raises two interesting questions. Are both layers needed to achieve a stable suspension? Is it possible to operate with less hydroxyapatite? At the present time we can only speculate on possible answers to these questions. It has been postulated by Wenning[8] that the surface of the bead must be totally covered by the suspending agent in order for the particles to be stabilized, although nothing has been said about the ultimate thickness of this layer. It can be suspected that at the beginning of the reaction, when the monomer beads, which are still fluid, coalesce and reseparate, only the thin layer is sufficient to keep the suspension from collapsing. But as the reaction proceeds and the beads become more viscous and tacky, the second layer probably plays an important role in keeping the beads separated and hindering coalescence. Depending on the vigor of the agitation, a thin layer itself may not be strong enough to hinder coalescence of viscous beads which would not be easy to separate.

At this stage, it is probable that the thick layer is more efficient in acting as shock absorber and stabilizing the suspension late in the process. Consequently, it is likely that both layers are needed to achieve a stable suspension. The complete coverage of the bead is provided by the thin layer while its strength is provided by the second layer.

The knowledge of the ultimate thickness of the second layer is probably an important factor in this process since this layer is the area of formation of the small beads of polymer which represent a potential contamination problem. Additionally, for a thin layer, less hydroxyapatite is needed, and consequently, less acid will be needed to wash the pigment away. Obviously, a lesser quantity of hydroxyapatite and acid will reduce the cost of the process.

Even though we have no definite information on the ultimate layer thickness, these observations raise more questions. What would be the appropriate agglomerate size to obtain the proper layer thickness? Is there an optimim "primary particle to aggregate" ratio that can generate the best inner/outer layer combination? Can this ratio be changed by better dispersion of the pigments prior to the addition of the organic phase? Again, we have no information at the present time to unambiguously answer these questions. However, experiments conducted under identical conditions, with two different batches of hydroxyapatite of identical chemical composition, yielded different bead size. In addition to having identical chemistry, the size of the primary particles of hydroxyapatite was also identical in both cases. However, the level of aggregation was different. This may suggest that the relative quantities of single primary platelets to aggregates has an influence on the morphology of the layer and consequently on the final product.

CONCLUSION

Obviously we do not know the exact role of both parts of the hydroxyapatite layer nor the ultimate thickness for each of them. Although there are many factors that affect the suspension polymerization process, such as the chemistry and kinetics of the reaction, the relative quantity of soap used with hydroxyapatite and the energy incorporated during agitation, the nature of the dispersing agent is also known to play a significant role in the suspension polymerization by affecting the average particle size. The dispersing agent is also a major factor influencing the collapsing of the suspensions inside the reactor. We feel that more controlled experiments in which hydroxyapatite of various sources and having different aggregates size are used, would shed more light on this subject and could lead to useful and perhaps, totally unexpected information that could be applied to the polymerization of many polymers.

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