Microstructure and Stress Development in Complex Latex Coatings

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Latex coatings are used in a wide variety of applications, including adhesives, paints, paper coatings, and tougheners. These coatings dry in a series of well characterized stages: consolidation, compaction, and coalescence, which are collectively known as film formation (1). In the first stage the latex particles begin well dispersed in the aqueous media. As water evaporates from the surface of the coating, the particle concentration increases. This stage, consolidation, typically continues until the particles contact each other, at about 60-70 volume percent. The second stage, compaction, begins when the particles come into irreversible contact. For some latexes, especially ones with low glass transition temperatures (T_g), the particles begin to deform against one another during this stage. During coalescence, polymer chains from adjacent particles interdiffuse, particles boundaries become less distinct, and the film gains mechanical properties (2).

Film formation is affected by material properties, like T_g, as well as processing factors, such as drying temperature. Of particular interest to this research is the study of latexes with complex internal structure. Currently little is known about how the nanostructure inside the particles themselves influences film formation. In this research, several characterization techniques have been used to study the effects of nanostructure on film formation of latex coatings, including cryogenic scanning electron microscopy (cryo-SEM), atomic force microscopy (AFM) and stress measurement (3, 4, 5).

Cryo-SEM is an innovative technique that allows imaging of coatings at different stages of the film formation process. A controlled volume of latex is dropped onto a silicon substrate using a

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micropipette, and the coating dries for a set period of time. Then, the sample is plunged into liquid ethane, which vitrifies the structure. After vitrification, the sample is held at a temperature of -160°C, fractured, and heated to -96°C for ten minutes to sublime away water. This is necessary to view the internal structure of the coating. Finally, the sample is coated with platinum and imaged. Cryo-SEM is advantageous because specimen preparation halts dynamic processes that occur during drying and allows the sample to be viewed under the high vacuum requirements necessary for SEM.

Two types of latex particles were studied in this research. The first is a triblock copolymer—poly(methyl methacrylate)-b-poly(butyl acrylate)-b-poly(methyl methacrylate) (PMMA-PBA-PMMA). Nitroxide mediated controlled radical polymerization in emulsion was used to synthesize this triblock copolymer latex at Arkema Inc. Latexes with 60:40 and 50:50 ratios of PBA:PMMA were characterized. The expected block copolymer structure is a layered ring structure of alternating blocks pf PMMA and PBA (6). To observe the effects of particle nanostructure on film formation, cryo-SEM and AFM were mainly used. Results show that this latex undergoes the anticipated stages of film formation: consolidation, compaction and coalescence. One drawback of electron microscopy is that the different blocks of polymer are indistinguishable, i.e. the PMMA and PBA within the particles cannot be differentiated from each other. In order to view the nanostructure of the film, AFM was used on fully formed films to determine their final microstructure. There was phase separation of the different polymers in the system, but no long range order was found and particles boundaries were indistinguishable. Work is underway to characterize internal particle structure as film formation takes place.

The second latex studied is a blend of polyvinylidene fluoride (PVDF) and acrylic. This blend was used to study stress development and cracking along with morphology development. Two blends were studied: a 70/30 and a 50/50 PVDF to acrylic ratio. The morphology of the particles themselves is a mix of the two polymers. Cryo-SEM studies have shown that coatings made of the 50/50 ratio fully coalesce at room temperature, while coatings of the 70/30 ratio tend to crack and particle boundaries are always distinguishable, even in the fully dried film. This result indicates that the film is not completely coalesced, and stresses that development during drying causes cracking. Using a cantilever stress measurement apparatus cracking and stress development in these coatings is under investigation in order to develop a better understand of how to link particle structure to performance.

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