Presented at the 14th International Coating Science and Technology Symposium[1]
September 7-10, 2008, Marina Del Rey, California

Drying and Collapse of Hollow Latex

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Introduction

Often the most expensive component of a latex paint is the opacifier, used to improve the whiteness of the coating. Hollow latex is one of the most promising alternatives to titanium dioxide, the most common opacifier. It is less expensive per gallon, less prone to agglomeration, and produces a more scrub resistant coating than TiO_2.[1,2] Since its invention in the 1980's, hollow latex has grown into a highly profitable specialty product for paints and paper coatings.

A typical hollow latex particle has an outer diameter of 500 nm with a central void, which is approximately 40% of the volume of the entire sphere[3]. In addition to the central void, some hollow latex particles also contain small pores that penetrate through the outer shell. These perforated particles are referred to in this study as "porous" hollow latex. When a suspension containing hollow particles is first cast down onto a substrate, the hollow particles are filled with water. During film formation the voids dry, leaving an air bubble in the center of each. The difference in refractive index between the air void and the polymer shell causes light scattering, making the film opaque.

Although hollow polymer has been profitable commercially for almost two decades, the individual particles are prone to buckling when dried under certain conditions (Figure 1). This collapse reduces the scattering efficiency of the latex.[2] The purpose of this work is to explore the process by which a hollow latex particle dries and deduce a mechanism by which particle collapse occurs. A full publication on this topic is in preparation.[4]

[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

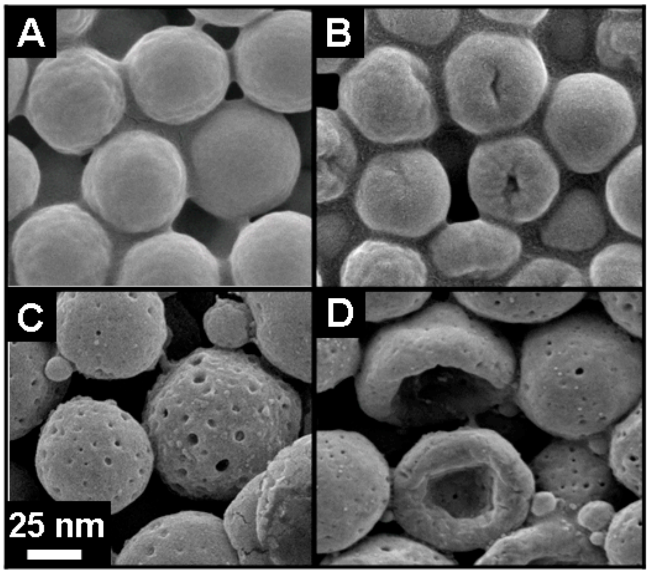

Figure 1: Room temperature SEM images of dry hollow latex particles. Nonporous (A and B) and porous (C and D) particles are imaged in not collapsed (A and C) and collapsed (B and D) states.

Experimental Results

Porous and nonporous samples of hollow latex were donated by Rohm and Haas and Dow Chemical. These samples were known to be more collapse prone than current state-of-the-art technology. Polyvinyl acetate latex was used as a low glass transition temperature (T_g) polymer binder, necessary to hold the high T_g hollow latex particles together in a coating.

Film Formation of Hollow Latex Cryogenic scanning electron microscopy (cryo SEM) was used to image coatings prepared from dispersions of hollow latex (50-60 effective vol%) and polyvinyl acetate latex binder (20 solids wt%) in intermediate drying stages of film formation. Sample preparation follows that of Ma *et al.*[5]

Four primary drying stages were identified using cryo SEM. Initially, large hollow particles and small latex binder are fully submerged and evenly distributed in water. As drying proceeds, particles concentrate until they make contact. Fingers of air descend from the coating top surface, appearing as open pockets in the coating porespace. In the second stage, air invades all of the way to the substrate and residual water is left hanging in pendular rings at the contact points between particles. The smaller binder particles move with the water and gather in rings surrounding each contact point. In the third stage, van der Waals and surface tension forces deform the low T_g binder particles. Individual binder particles are no longer distinguishable, and very little water is detectable within the porespace between particles. Finally, the remaining water in the particle voids dries. Collapsed hollow latex particles are only found in the last drying stage, suggesting that failure occurs as individual particles dry to the porespace.

Effects of Drying Condition on Collapse To determine important parameters that affect particle failure, drying temperature (15 – 72 °C), binder concentration (0 – 30 solids wt%) and relative humidity (20 – 70%) were all explored. High temperature, high humidity levels, and low binder concentrations all increased collapse in nonporous latex. If the hollow latex shell was porous, temperature and humidity had little effect, whereas binder increased collapse.

Proposed Theoretical Model for Particle Drying

In the dispersed state, hollow latex particles encapsulate water and also dissolved air. For a nonporous particle to dry, water must diffuse out of the void through the particle shell wall and from the coating. The escape of water lowers the pressure within the particle. If the pressure decreases sufficiently, a gas bubble will nucleate within the encapsulated water. The particle will be dry when this gas bubble is the only phase left within the hollow particle. However, The Young-Laplace equation states that there is a large thermodynamic penalty for creating a vapor bubble of nanoscale radius, r_{bub}, in a fluid with surface tension σ:

$$P_{cavitation} = P_{vap} - \frac{2\sigma}{r_{bub}} \qquad (1)$$

If the critical pressure for bubble nucleation is lower than the critical buckling stress of the particle, the hollow latex will collapse. Further information on the model and comparison to experiments is presented elsewhere.[4]

References

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