Morphologies of Fast-Frozen and Freeze-Fractured Latex Coatings during Drying

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Cryogenic scanning electron microscopy (cryo-SEM) is used to visualize the microstructure of latex dispersions and latex coatings at different stages of drying. A key step in preparing specimens for these studies is freeze-fracture, which reveals the interior microstructure of the dispersion or coating. Cryo-SEM images of these specimens show unusual morphologies. In freeze-fractured dispersions, polymer particles plastically deform when the fracture front propagates through them. This ductile failure occurs at temperatures far below the glass transition temperature of the polymer, and forms features called "pullouts". These pullouts generally have elongated stems connected to a hemispherical base. As a coating of latex dispersion dries and forms a film, freeze-fracture behavior differs. We hypothesize that the different pullout morphologies map directly onto seven stages of film formation: early consolidation, later consolidation, early compaction, compaction with partial coalescence, later compaction, early coalescence and later coalescence.

Early Consolidation: latex particles are fully consolidated from the suspension. All the pore-spaces between close-packed particles are filled with water and air invasion hasn't begun yet. Upon cryo-fracture, frozen ice matrix holds latex particles strongly and plastically deform them to form mushroom-shaped, spool-shaped or awl-shaped pullouts, as reported by Ge et al. in 2006.

Later Consolidation: the air invasion starts and the pendular rings form at interparticle contacts. The adhesion between the frozen individual pendular rings and latex particles is not strong enough to hold the particles upon fracture and plastically deform them to form pullouts, nor can the van der Waals force at either point of slightly flattened particle-particles contacts. The fracture front propagate through the interfaces between the remaining frozen water and latex particles, leaving latex particles unfractured. No pullouts form in this stage.

Early Compaction without Coalescence: the degree of flattening between the contacting latex particles advances and the coating becomes well compacted. No water is left at this stage. The only adhesion force between flattened latex particles is the weak van der Waals force at interparticle contacts, which is not strong enough to hold latex particles together upon fracture. No pullouts form in this stage as the fracture front will go through the flattened latex particle boundaries.

Compaction with Partial Coalescence: as the interdiffusion starts at flattened latex particle boundaries, the polymer chains are entangled with one another, which significantly enhanced the adhesion between latex particles. This stronger adhesion causes the pullouts to re-appear upon cryo-fracture. Pullouts are mostly from individual particles at this stage, but could also be bridged too.

Later Compaction with High Degree of Coalescence: as the degree of coalescence increases, although the interparticle boundaries may still be visible, the degree of interdiffusion and polymer chain entanglement between adjacent particles is much higher than previous stage. This will directly result in forming pullouts from plastic deformation of several adjacent particles that are "coalesced" together, while no longer from individual latex particles.

Early Coalescence: in the early coalescence stage, the degree of inderdiffusion and polymer chain entanglement is very high. But pullouts still can form due to the existence of local difference of the degree of coalescence. As the latex particle boundaries become indistinct, it is difficult to identify if the pullouts are pulled from individual particles anymore. They appear to be a mesh-like network structure.

Later Coalescence: the coating is fully coalesced so it will act like a bulk of polymer film. No pullouts will form upon fracture at this stage.

Closure: Drawn from our experimental observation, the freeze-fracture behavior of a drying latex coating can be used to identify the progress of film formation during drying, from consolidation to fully coalesced.