Microstructure of Wet Dispersions and Drying Particulate Coatings by Cryo-SEM

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Presented at the 13th International Coating Science and Technology Symposium[1]
September 10-13, 2006, Denver, Colorado

The microstructure – down to nanometer scales – of coatings based on hard particles and polymeric binders develops through the drying process from the liquid-borne dispersion that is layered on the substrate by a coating flow. This research demonstrates how cryogenic scanning electron microscopy (Cryo-SEM)[1-2] can be used to document the original dispersion structure and its evolution as the coating solidifies by drying. Two systems were studied: (i) aqueous dispersions of latex particles (polyvinyl acetate-co-acrylic, polydisperse with volume-average diameter ~300nm) and ceramic nanoparticles (antimony-doped tin oxide ATO, or tin-doped indium oxide ITO, ~15 – 20nm) and (ii) non-aqueous dispersions of needle-like iron nanoparticles (e.g. 100 × 10nm) in an organic polymer solution (polyvinyl chloride and polyurethane in a mixture of organic solvents).

Aqueous dispersion samples (total solid content 2 vol%, ceramic concentration in final dried coating 15 vol%, pH = 3) confined between two copper freezing hats (i.e. diameter: 3mm, depth: 100 and 200 μm) were frozen within 8 milliseconds at 210 MPa in a high-pressure freezing machine. Wet aqueous coatings, after deposition and partial drying, were frozen by hand plunging into liquid ethane. Frozen dispersions and coatings were then broken open to expose internal structures, sublimed to increase topographical contrast, coated with a few

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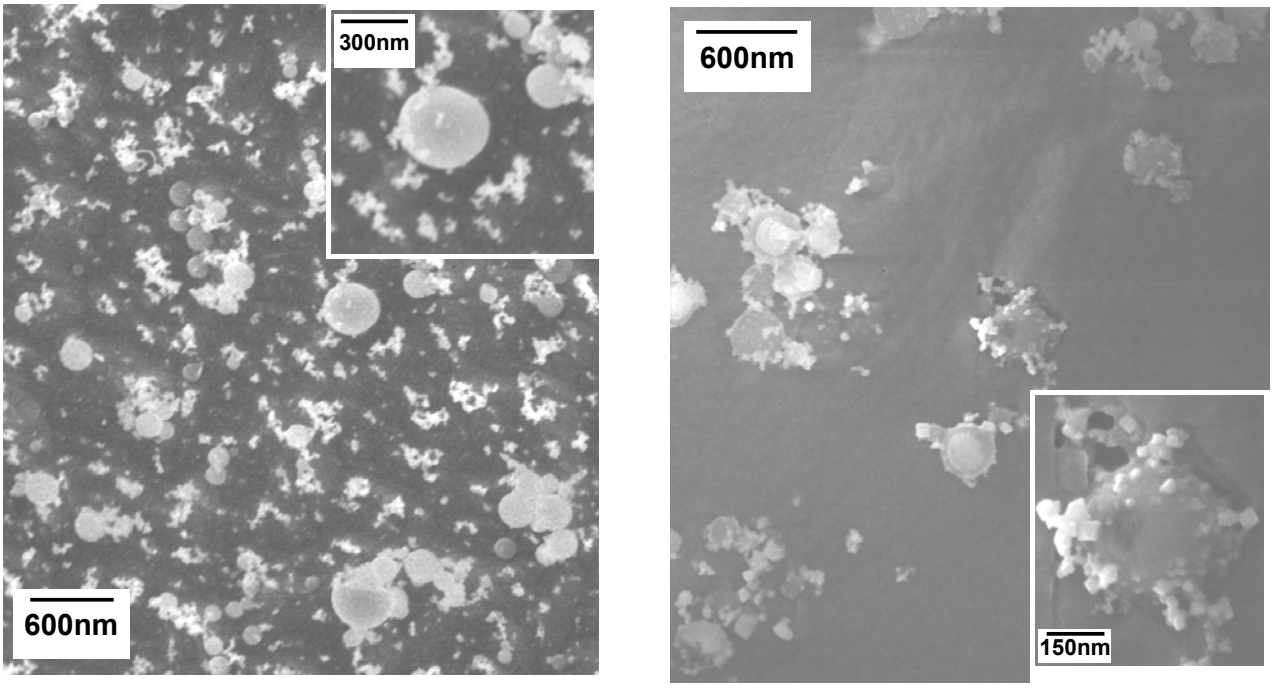
nanometers of platinum to increase their surface conductivity, and imaged at -160°C in a high-resolution Field Emission SEM equipped with a cold stage.

Cryo-SEM images of the ATO/latex dispersion showed that small clusters of ATO and individual latex particles were homogeneously distributed in frozen water. The images of the ITO/latex dispersion showed that ITO particles adsorbed onto surfaces of latex particles. Electrostatic repulsion between negatively charged ATO and negatively charged latex particles stabilizes the ATO/latex dispersion, whereas in ITO/latex dispersion, positively charged ITO particles are attracted onto surfaces of negatively charged latex particles. These results are consistent with Sun et al's hypothesis from DLVO calculation of interaction potentials[3].



(a) (b)

Figure 1. Cryo-SEM images of ATO/latex dispersion (a) and ITO/latex dispersion (b).

Visual observation of ATO/latex coating showed it dried from the edge inward. Cryo-SEM images of a partially dried ATO/latex coating showed the microstructure varied at the

lateral drying front. Moreover, these images revealed different drying regimes — concentrating suspension, consolidation, compaction and partial coalescence. As water evaporated and particles concentrated, small ATO particles were trapped in the water-filled spaces between large latex particles. With more drying, latex-latex particle contacts flattened, voids shrank and ATO particles were forced to pack closely in the interstitial space, forming an interconnected network. Finally, partial coalescence occurred among latex-latex contacts. Coalescence was further evidenced by SEM images of a coating after pyrolysis of the latex.

Samples of the non-aqueous magnetic dispersion were confined between copper freezing hats and fast frozen by hand plunging into liquid ethane. Frozen dispersions were then broken open, and sputter coated with about 5 nm platinum before imaging at -160 °C in the SEM. Cryo-SEM images of microstructures exposed in the fractured surfaces showed individual iron particles embedded in frozen organic solvent/polymer matrix. Moreover, the iron particles appeared to be oriented randomly in the dispersion.

In parallel, partially dried coatings prepared on-line and off-line were examined for degree of orientation of magnetic particles. On Imation's pilot line, a partially dried commercial magnetic coating was fast-frozen and collected by a cryo-punch apparatus. The apparatus was located between the pre-drier, where magnetic field is applied, and the drying oven. During set-up, the punch chamber was purged by nitrogen gas to remove moisture. To collect a sample, the coating line was suddenly stopped, liquid nitrogen was immediately discharged onto the coating surface to freeze it, and a hollow punch simultaneously descended to cut free a disk of coated web. This sample was conveyed to a Dewar by a flushing of liquid nitrogen. Off-line, the magnetic dispersion was drawn down by a wire-wound rod by hand onto a silicon substrate, and

partially dried for about 50s at room temperature in absence of magnetic field. This partially dried coating was then hand plunged into liquid nitrogen for imaging by cryo-SEM.

The cryo-SEM images of these partially dried coatings during drying showed that the acicular particles tend to rotate from random 3D orientation into planes parallel to the substrate due to the shrinkage of the coating in the thickness direction[4-5]. When early drying was in a magnetic field, the particles tended toward unidirectional alignment in those planes, whereas without the field they retained random in-plane orientations.

This research shows the utility of cryo-SEM technique for microstructure development studies of both aqueous and non-aqueous particle-based dispersions and coatings.

Acknowledgements

The authors thank Peter Silbernagel, Gaylord Hibl, Gary Huelsman of Imation Corporation for the cryo-punch sample, and the industrial sponsors at the Coating Process Fundamentals Program.

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