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Cryo-SEM studies of latex/ceramic nanoparticle coating microstructure development

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Abstract

Cryogenic scanning electron microscopy (cryo-SEM) was used to investigate microstructure development of composite coatings prepared from dispersions of antimony-doped tin oxide (ATO) nanoparticles (∼30 nm) or indium tin oxide (ITO) nanoparticles (∼40 nm) and latex particles (polydisperse, D_V: ∼300 nm). Cryo-SEM images of ATO/latex dispersions as-frozen show small clusters of ATO and individual latex particles homogeneously distribute in a frozen water matrix. In contrast, cryo-SEM images of ITO/latex dispersions as-frozen show ITO particles adsorb onto latex particle surfaces. 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 calculations of interaction potentials from past research. Cryo-SEM images of frozen and fractured coatings reveal that both ceramic nanoparticles and latex become more concentrated as drying proceeds; larger latex particles consolidate with ceramic nanoparticles in the interstitial spaces. With more drying, compaction flattens the latex–latex particle contacts and shrinks the voids between them. Thus, ceramic nanoparticles are forced to pack closely in the interstitial spaces, forming an interconnected network. Finally, latex particles partially coalesce at their flattened contacts, thereby yielding a coherent coating. The research reveals how nanoparticles segregate and interconnect among latex particles during drying.

Keywords: Cryo-SEM; Microstructure development; Dispersion; Coating; Ceramic nanoparticle; Latex; Drying

1. Introduction

Cryogenic scanning electron microscopy (cryo-SEM) is a powerful tool for characterizing the microstructure of liquid containing specimens, which are ordinarily unstable in the high vacuum of the microscope. For cryo-SEM studies, liquid-containing specimens are first rapidly frozen, and fractured. The fractured surfaces are differentially sublimed for topographic contrast, and a few nanometers of conducting metal are deposited to avoid charging. The fractured surfaces of the frozen specimens are then imaged in a SEM equipped with a cryo-stage. Through rapid freezing, the original microstructure of the liquid-containing specimen is immobilized. Moreover, the vapor pressure of the resulting solid is lowered to the level of vacuum in the microscope.

Cryo-SEM is widely used to explore the hydrated microstructures of biological specimens [1–3], and is finding increasing application in materials science [4–8]. For example, the technique was used to investigate microstructures of concentrated ceramic particle suspensions [4], microstructures of self-assembled organic hydrogels [5], distributions of polymer nanoparticles on fractured surfaces of bitumen/polymer blends [6,7], and distributions of silica nanoparticles in an immiscible polymer blend [8]. In these studies, cryo-SEM provided direct evidence of colloidal structures. Another important application of cryo-SEM is the study of microstructure evolution of coatings prepared from liquid solutions and dispersions. Prakash et al. [9] used cryo-SEM to study evolution of microstructures of cellulose acetate coatings during drying. Their "time-sectioned" images, captured at successive stages of drying, reveal the progression of structural changes caused by drying-induced phase separation. Cryo-SEM has also been instrumental in uncovering the microstructure development in

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coatings prepared from latex dispersions, and latex composites, including pigmented paint "films," i.e., coatings.

The application of cryo-SEM to the study of latex film formation began in 1990 [10]. The technique provided direct visualization of microstructure development, beginning with the aqueous dispersion and throughout the drying of hydrated coatings [11–16]. Ming et al. [11] and Huang et al. [12] froze latex coatings that had been dried for successively longer times to study the structural development. Their images revealed not only the starting suspension structure, but also the three stages in the film formation process: consolidation, compaction and coalescence. Latex film formation was described as follows from the images. First, drying concentrates latex particles until they are closely packed with each other to become consolidated, i.e. fixed in relative position—consolidation stage. Next, the particles begin to flatten against one another at their contacts if the drying temperature is around or higher than the nominal glass transition temperature (T_g) of the latex in bulk; the initially spherical latex particles deform nearly or even completely into polyhedron—the compaction stage. Meanwhile, adhesion strength develops through surface forces at the flattened contacts, so that the compact may be able to withstand in-plane tensile stress of drying that develops concomitantly. Finally, polymer chains of latex particles in contact interdiffuse, welding them together—the coalescence stage. The cryo-SEM results confirm the widely accepted description of the three stages film formation, which was originally proposed on the basis of other evidence and reasoning [17,18]. In their study, Ming et al. [11] showed that deformed but not coalesced latex particles after rehydration that breaks interparticle adhesion might rebound back to spherical shape. This rebound indicates elastic deformation of latex particles during the compaction stage, not the long-assumed viscoelastic deformation. Using the "time-sectioning" technique, Sutanto et al. [13] revealed the progression of the consolidation top-down from the drying free surface of a suspension. Ma et al. [14] captured the progression of an air invasion front during drying of bimodal latex coating.

In addition, the progression of microstructures from the edge in of drying latex coatings provides another way of studying the stages of drying in the same coating. Indeed, many academic investigations have used such narrow coatings or small circular drops of coatings that they have not observed truly "top-down" drying [19,20]. Sutanto et al. [13] and Ge et al. [15] imaged sequences of laterally advancing stages of drying near the edges of flat drying drops of latex coatings. At growing distance from the edge of the coating, the concentration changed abruptly from dispersion to consolidate in a lateral consolidation front.

Cryo-SEM is also a proven method for exploring development of microstructures in coatings prepared from dispersions of latex and inorganic particles. Sheehan and Whalen-Shaw [10] used it to study the influence of the extent of carboxylation of latex on stability of latex/calcium carbonate dispersions. Ma [16] used it to visualize the distribution of titanium dioxide particles in stable and flocculated latex/pigment dispersions.

In the research reported here, cryo-SEM has been used to document microstructure evolution in latex/ceramic nanoparticle coatings. Antimony-doped tin oxide (ATO) and indium tin oxide (ITO) were the ceramic nanoparticles employed. ATO and ITO are transparent and n-type semiconductors, and often used as transparent, conductive coatings [21]. Fig. 1 shows a regular room temperature SEM image of the cryo-fractured cross-section of a completely dried ATO/latex coating. ATO nanoparticles form a network in a network-like polymer matrix formed by partially coalesced latex particles. The segregated microstructure of conductive fillers in contact lowers the coating's percolation threshold for conduction without detracting much from its inherent transparency [22]. However, it has been unclear how this desirable final microstructure develops from the initial dispersion state in the course of drying. Grunlan et al. [23] and Sun et al. [22] postulated that the small conductive particles are restricted to interstitial spaces between large latex particles during consolidation, compaction, and partial coalescence to form the segregated structure. Furthermore, Sun et al. [24] speculated that different colloidal states developed in the starting ATO/latex and ITO/latex suspensions and during subsequent drying because of different particle–particle interactions. The cryo-SEM images of this paper reveal how the conductive fillers and latex particles distribute in the starting dispersions, and then how the composite coating microstructures evolve during drying.

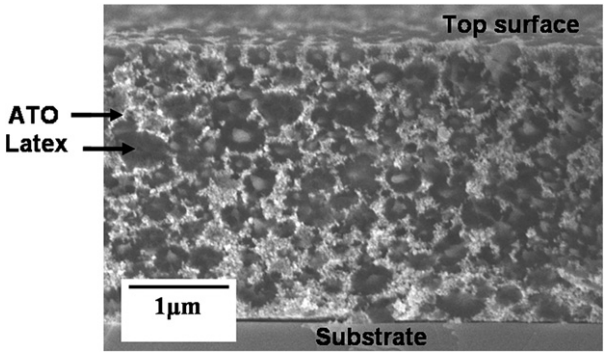

Fig. 1. Cross-sectional microstructure of a dried ATO/latex composite coating. Small ATO particles form a segregated network in the polymer latex matrix.

2. Materials and methods

2.1. Materials

Antimony-doped tin oxide (ATO) and indium tin oxide (ITO) nanoparticles were used as conductive and transparent fillers. Spherical ATO particles (Nanophase Technologies, Romeoville, IL) range in size from 22 to 58 nm with an average particle size of approximately 30 nm, as reported by the manufacturer and confirmed by SEM measurement. The manufacturer's density of the ATO is 6.8 g/cm^3. ITO particles (Nanophase Technologies, Romeoville, IL) range in size from 20 to 100 nm with an average size of 40 nm, as confirmed by SEM measurement. The smaller ITO particles are spherical, medium-sized ones are faceted, and larger ones are octahedral in shape. The manufacturer's density of ITO is 7.1 g/cm^3.

Flexbond 325 (Air Products, Allentown, PA), an aqueous dispersion of poly(vinyl acetate-co-acrylic) polymer latex (55 wt%) that is stabilized by a non-ionic surfactant was the