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Time-sectioning Cryo-SEM Evidence of the Mechanism of Macrovoid Formation in Phase Inversion Membranes

Sai S. Prakash, Lorraine F. Francis and L. E. Scriven
Coating Process Fundamentals Program
Department of Chemical Engineering & Material Sciences,
University of Minnesota, Minneapolis, MN 55455

Time-sectioning cryogenic scanning electron microscopy (cryo-SEM) is a unique method of visualizing how the microstructure of liquid coating and membrane precursors evolves during processing. Time-sectioning means rapidly freezing (nearly) identical specimens at successively later stages of the process; doing this requires that coating and drying to be well controlled in the dry phase inversion process, and solvents exchange likewise in the wet phase inversion process. With careful control, frozen specimens are fractured to expose internal surface, etched by limited sublimation to enhance topographical contrast, sputter-coated to avoid charge build-up during imaging, and imaged at temperatures of *ca*. -175ºC. Electron radiation damage is avoided by using low voltages and probe currents. The final states of dry and solidified porous coatings, detached from their substrates as membranes, can be examined by conventional cryo-fracture and ambient temperature SEM as many other investigators have done. The cryo-SEM method uncovers the process by which a membrane forms.

The coatings, or cast layers, examined in three case studies were of (1) cellulose acetate of high molecular weight (60,000 $g.mol^{-1}$) in solvent acetone and nonsolvent water, of weight compositions 10, 80 and 10%, respectively, undergoing dry phase inversion in the course of drying; (2) cellulose acetate of low molecular weight (30,000 $g.mol^{-1}$) in acetone and water, of weight compositions 11, 60 and 29%, respectively, undergoing the same process; and (3) polysulfone (20,400 $g.mol^{-1}$) in mixed solvents tetrahydrofuran, dimethylacetamide and nonsolvent ethanol, of weight compositions 22, 31.8, 31.8 and 14.4%, respectively, undergoing dry-wet phase inversion in the course of drying for a limited time followed by immersion in nonsolvent water. All coatings, cast on silicon substrates, were initially homogeneous.

Sequences of images by time-sectioning show that as the higher molecular weight cellulose acetate coating dries, by free convection in air, it nucleates and grows polymer-poor droplets that coalesce and further coarsen into smooth-walled bicontinuous structure underlying a thin, dense skin. Bicontinuity, i.e. interpenetrating multiply-connected material rich in polymer destined to solidify and material rich in solvent destined to depart, was ultimately verified by stereomicroscopy of the final state of dry membrane. Bicontinuity of structure was verified by stereomicroscopy of the dry sample.

Image sequences of the lower molecular weight cellulose acetate coating show that as it dries, also by free convection in air, it phase separates, seemingly spinodally, directly into a bicontinuous structure whose polymer-rich network, evidently stressed by frustrated in-plane shrinkage, ruptures far beneath the skin in some locales to form macrovoids.

Image sequence of the polysulfone coating show that when, after partial drying of 4 seconds by forced convection and 14 seconds by free convection in air, it is immersed in a bath of water, a coagulant, it swells in thickness as it phase-separates. An apparently dense skin less than a micron in thickness overlies a two-phase substructure that is punctuated with pear-shaped macrovoids that grow ultimately to more than half the final coating (membrane) thickness. At early immersion times, this substructure is visibly two-tiered: bicontinuous, or open-celled, near the bath-side, and dispersion-like, i.e. isolated, rounded, solvent-rich droplets in a polymer-rich matrix, near the substrate side. After prolonged immersion, the substructure, excluding the macrovoids, is entirely bicontinuous (open-celled). The bicontinuity presumably results from nucleation and growth of polymer-lean droplets followed by coalescence to form close-packed polyhedral cells whose walls are polymer-rich lamellae most of which are ruptured. Quite strikingly, in time-sections from soon after immersion, *growing macrovoids are present exclusively in regions where phases are bicontinuous*, and are absent where isolated droplets are dispersed in the polymeric matrix. All the evidence appears to support our hypothesis that macrovoids result from an instability caused by a progressive rupture, deeper and deeper beneath the skin, of tensed links of the polymer-rich, multiply connected network, aggravated by tensile stress localization in the rupturing network and a build-up of pressure in the polymer-lean phase (the pore space). A mechanism of this sort seems to have been suspected by Gröbe and Meyer in 1959.