Polymeric Particle Growth in Mixed Matrix Membranes: Using USANS to Observe Transient Phenomena in Casting Solutions

Rachel R. Ford[1], Joey D. Kim[1], Kunlun Hong[2], Mamadou S. Diallo[1,3], and Julia A. Kornfield[1]

1. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA
2. Center for Nanophase Materials Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN
3. Graduate School of EEWS (Energy, Environment, Water, and Sustainability), KAIST, Daejeon, Korea

Herein we report a kinetic analysis of particle growth in the casting solution of a mixed matrix membrane using ultra-small angle neutron scattering (USANS). The Diallo Group developed a "one-pot" method for the preparation of polyvinylidene fluoride (PVDF) mixed matrix membranes with embedded polymeric particles. Such membranes are being designed to carry out multiple functions (e.g. retention, sorption and catalysis) with improved properties and performance over those of commercial membranes. An essential aspect of these membranes is their combination of function and mechanical stability. In theory, this is achieved by the *in-situ* crosslinking of amine-containing oligomers [polyethyleneimine (PEI) or low-generation polyamidoamine dendrimer (PAMAM)] which enables interpenetration of the PVDF spherulites of the matrix. By characterizing the microstructure of the mixed matrix membranes, we have determined that they contain amine particles ranging from <1–3 μm in diameter, with nanoporous separation layers of average pore diameter on the order of 20 nm. However, characterization of the final solid-state structure raises questions regarding the factors that govern structure formation during processing of the membranes. To elucidate how the micro- and nanostructure develops during membrane preparation, we have conducted an integrated SANS and USANS experimental study of the casting solution and final membranes.

To our knowledge, this was the first **transient** measurement obtained using USANS. Compared to SANS, the intensities are substantially lower, requiring longer acquisition times as compensation (~minutes for SANS; ~hours for USANS). Therefore, USANS was generally only applied to equilibrated systems. However, upon examination of the intensities of the final casting solutions, we determined shorter acquisition times could be used. We ascertained the minimum acquisition time needed to capture all the features without compromising the integrity of the resulting data. For this work, the acquisition times were reduced by roughly one order of magnitude (to about 15 minutes). Using the shorter acquisition times, we observed transient structural changes in the casting solution across a q-range offered collectively by SANS and USANS. For this experiment, we chose two variables to manipulate: amine polymer and concentration of crosslinker. We studied the "dendrimer effect" using three different polymer precursors: randomly branched PEI, zeroth generation PAMAM, and first generation PAMAM. Changing the crosslinker concentration enabled us to determine the extent to which charge-induced phase separation and crosslinking of amine polymer played a role in the overall structure of the membranes. The success of our membranes is partly attributed to the mechanical stability of the membranes, which is provided by the PVDF component. Manipulating these two variables in conjunction with the short acquisition times allowed us to test our theory on the interactions of PVDF and amine polymer as the crosslinking reaction progressed. Thus, we expanded upon the currently assumed limits of USANS—we demonstrated the capability of USANS in analyzing transient structures by studying polymeric mixed matrix membranes.