Correlative Mapping with AFM, STEM HAADF, and PF-QNM/SROM of Interpenetrating Networks of Elastomeric and Glassy Polymers

Alyssa J. Fielitz[1*], Jeremy M. Beebe[1], Dongchan Ahn[2], Marius Chyasnavichyus[1], Tyler R Heyl[3], Myoungbae Lee[2], Shane Mangold[2], Carl Reinhardt[1], Kenneth R. Shull[4], Anthony J. Silvaroli[4], and Muzhou Wang[3]

[1.] Core Research & Development, The Dow Chemical Company, Midland, MI, United States.
[2.] Consumer Solutions, The Dow Chemical Company, Midland, MI, United States.
[3.] Department of Materials Science and Engineering, Northwestern University, Evanston, IL, United States.
[4.] Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL, United States.
* Corresponding author: ajmckenna@dow.com

Interpenetrating polymer networks (IPNs) offer a unique opportunity for correlative mapping to trace the microstructural origins of their macroscopic properties, which are often superior to physical blends. IPNs are classified through two main categories based on their synthetic method. An example of a simultaneous IPN is one formed when two monomers are mixed before being polymerized simultaneously. In contrast, sequential IPNs are formed by two main methods. In the first, a first polymer is crosslinked to create a network and that network is subsequently swollen with the second monomer, which is then polymerized. The second method involves a one-pot mixture of two monomers that can each be polymerized through different means. For instance, the first monomer could be polymerized thermally, and the other monomer subsequently photo-polymerized to create the IPN [1-3].

We studied sequential and simultaneous IPNs made from polydimethylsiloxane (PDMS) and methacrylate-based glassy acrylic polymers. Correlative mapping was used to characterize the extent of mixing between the silicone and organic phases. Atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM) high annular dark field (HAADF) revealed that these IPNs phase-separated into a PDMS matrix with organic inclusions. Dynamic mechanical analysis (DMA) confirmed poor miscibility between the components. Peak force quantitative nanomechanical mapping (PF-QNM) showed modulus differences between the distributed domains in the simultaneous and sequential IPNs; specifically, the modulus depended on the synthetic route as well as the degree of mixing. For example, in one system at equivalent polymer ratios, simultaneous IPNs had a higher degree of mixing than sequential, and therefore, the elastic modulus of the methacrylate-rich glassy phase was lower than the modulus of the neat methacrylate polymer and lower than the modulus of the distributed glassy phase in the sequential network. Super-resolution optical microscopy (SROM) experiments were conducted in which a fluorescent tag was added to the PDMS phase. Within the minor phase, the intensity of the fluorophore signal was directly correlated to the degree of mixing between the components, with the brightest regions corresponding to higher concentration of PDMS and the darkest regions to higher concentrations of organic phase. Our work allows us to connect macroscopic conclusions about extent of mixing (i.e., DMA) with maps of local mixing at high spatial resolutions (i.e., PF-QNM/SROM, AFM, STEM-HAADF).

CrossMark

References:

[1] ES Dragan. Chem. Eng. J. **243** (2014), p 572. doi:10.1016/j.cej.2041.01.065
[2] YS Lipatov, TT Alekseeva. Adv. Polym. Sci. **208** (2007), p. 1. doi:10.1007/12_2007_116
[3] LH Sperling in "Encyclopedia of Polymer Science and Technology" 4th ed. Ed. HF Mark (Wiley, Hoboken), p. 272.