

Impact of Network Architecture on the Microstructure of PDMS/PMMA Hybrid Elastomers

Jeremy Beebe¹, Tyler Heyl², Anthony Silvaroli², Dongchan Ahn³, Shane Mangold³, Myoungbae Lee³, Alyssa Fielitz³, Kenneth Shull² and Muzhou Wang²

¹The Dow Chemical Company, Midland, Michigan, United States, ²Northwestern University, United States, ³The Dow Chemical Company, United States

Silicone elastomers often find application due to their optical transparency and excellent thermal stability. However, the use range of these materials is limited to some extent by their low toughness. Organic elastomers are less thermally stable and often yellow upon exposure to heat and UV radiation. However, they are generally tougher than silicones. Hybrid silicone-organic elastomers therefore offer the potential to create materials with better toughness than silicone-only elastomers while maintaining desired optical properties. We have demonstrated that it is possible to form optically transparent PDMS/PMMA interpenetrating polymer networks (IPNs) and that the Young's modulus and fracture energy of these materials scale as a function of PMMA concentration [1]. We constructed these IPNs using both sequential and simultaneous synthetic routes. These two routes led to materials with similar mechanical properties but different optical properties.

In this presentation we discuss how scanning transmission electron microscopy (STEM) and atomic force microscopy (AFM) have been used in conjunction with dynamic mechanical thermal analysis (DMTA) to understand the connection between microstructure, optical properties, and phase mixing in these materials. Due to differences in average atomic number, the continuous PDMS phase and the distributed PMMA phases show strong contrast in STEM high-angle annular dark field (STEM-HAADF) imaging. STEM-HAADF images show differences in both the shape and the size distribution of PMMA domains between the two IPNs. The simultaneous route leads to spherical PMMA domains that become larger as the PMMA concentration increases. The sequential route leads to clusters of irregularly-shaped PMMA domains with a size that scales inversely with PMMA concentration.

The nanostructure of the distributed domains also depends on synthetic route. The mechanical property differences between the PDMS and PMMA phases lead to substantially different AFM tapping mode phase angles. Phase contrast images of the simultaneous IPNs reveal that the distributed phases consist of nanoscopic domains of PDMS trapped within PMMA spheres. The domains present within the sequential IPNs do not show similar nanostructure. Peak force quantitative nanomechanical mapping (PF-QNM) experiments were conducted to analyze the local mechanical properties of the different IPNs. We find the modulus of distributed domains in the simultaneous IPNs (mixed PDMS/PMMA) is approximately one order of magnitude lower than the modulus of the distributed domains in the sequential IPNs (pure PMMA). An interesting finding from this work is that even though there are strong differences in local material composition and mechanical properties within the distributed phases of these IPNs, there is little difference in their bulk mechanical properties.

The PMMA glass transition temperature was also found to reflect the microstructural differences between the IPNs. In the sequential IPNs, there is a gradual slight decrease in PMMA glass transition temperature with increasing PMMA concentration. The loss tangent peak maxima in these materials decrease from 155 °C at 15% PMMA loading to 140 °C at 50% PMMA. In the simultaneous IPNs, two separate glass transitions are observed with perturbations in loss tangent extending from 60 °C to 180 °C, and the relative

contributions of these transitions scales as a function of PMMA concentration. At 10% PMMA, the glass transition is quite broad and has a loss tangent maximum near 105 °C. At 50% PMMA concentration, two peaks are clearly resolved, with loss tangent maxima near 85 °C and 160 °C. Based on the differences in microstructure observed by AFM phase contrast imaging and PF-QNM, we are able to interpret these peaks as corresponding to mixed versus pure PMMA phases, respectively.

Reference

[1] A.J. Silvaroli *et al.* “Tough, Transparent, Photo-curable Hybrid Elastomers.” *ACS Appl. Mater. Interfaces* **2020**, *12*, 44125–44136.