142i Dynamic Relaxation Characteristics of Crosslinked Poly(Ethylene Glycol) Networks and Composites

Sumod Kalakkunnath, Haiqing Lin, Scott T. Matteucci, Benny D. Freeman, and Douglass S. Kalika

The dynamic relaxation characteristics of various families of crosslinked rubbery networks based on poly(ethylene glycol) diacrylate [PEGDA] have been investigated using dynamic mechanical thermal analysis and broadband dielectric relaxation spectroscopy. The focus was on elucidating the underlying molecular processes associated with the sub-glass and glass-rubber relaxations observed for these materials, and the correlation of these processes with composition, network structure, and gas transport properties. Of particular interest are the effects associated with the inclusion of nanoscale particles in the networks, and the influence of these particles on relaxation dynamics, crystallization, and bulk transport.

Three series of rubbery networks were investigated, with systematic variations in backbone structure and composition, crosslink density, and nanoparticle loading. For the unfilled networks, specimens with varying crosslink density were prepared by introducing different amounts of water into the initial PEGDA polymerization mixture, or by copolymerization with monoacrylate species. In the case of the composite materials, commercially-available MgO particles were introduced into the reaction mixture over a wide range of loading.

Dynamic mechanical studies were undertaken to establish the glassy and rubbery modulus values for these networks, as well as their glass transition characteristics; the rubbery modulus for the various films was related to the apparent molecular weight between crosslinks according to classical network theories. In the case of the dynamic mechanical measurements, time-temperature superposition was used to establish master curves across the glass transition and these were fit according to the Kohlrausch-Williams-Watts stretched exponential function. Broadband dielectric spectroscopy measurements provided detailed information as to the molecular origin and intensity of the sub-glass and glass-rubber relaxations, as described by the empirical Havriliak-Negami relaxation function. The sensitivity of the dynamic mechanical and dielectric methods proved especially valuable for exploring the onset of crystallization in the various composite formulations as a function nanoparticle loading.