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Effect of Cross-Linking on Free Volume Properties of PEG Based Thiol-Ene Networks RAMESH RAMAKRISHNAN, VIVEK VASAGAR, SERGEI NAZARENKO, The University of Southern Mississippi — According to the Fox and Loshaek theory, in elastomeric networks, free volume decreases linearly with the cross-link density increase. The aim of this study is to show whether the poly(ethylene glycol) (PEG) based multicomponent thiol-ene elastomeric networks demonstrate this model behavior? Networks with a broad cross-link density range were prepared by changing the ratio of the trithiol crosslinker to PEG dithiol and then UV cured with PEG diene while maintaining 1:1 thiol:ene stoichiometry. Pressure-volume-temperature (PVT) data of the networks was generated from the high pressure dilatometry experiments which was fit using the Simha-Somcynsky Equation-of-State analysis to obtain the fractional free volume of the networks. Using Positron Annihilation Lifetime Spectroscopy (PALS) analysis, the average free volume hole size of the networks was also quantified. The fractional free volume and the average free volume hole size showed a linear change with the cross-link density confirming that the Fox and Loshaek theory can be applied to this multicomponent system. Gas diffusivities of the networks showed a good correlation with free volume. A free volume based model was developed to describe the gas diffusivity trends as a function of cross-link density.

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