Electronic Supplementary Material (ESI) for RSC Advances.

Energetic Hybrid Polymer Network (EHPN) through Facile Sequential Polyurethane Curation Based on the Reactivity Differences between Glycidyl Azide Polymer and Hydroxyl Terminated Polybutadiene

(Supporting Information)

Crosslinking density (γ) can be defined as the number of moles in the effective network chain per cubic centimeter, and is generally obtained from the volume fraction of the swollen polymer in a solvent (ϕ) and the gel fraction of the swollen polymer (ω) according to the following eq. (1). Moreover, the parameters of φ and ω can be calculated as the following eqs. (2) and (3), respectively.

$$\gamma = \phi^{5/3} . \omega \quad (1)$$

$$\phi = (m_0/ \rho_2) / [m/ \rho_1 + m_0 (1/ \rho_2 - 1/ \rho_1)] \quad (2)$$

$$\omega = m_1 / m \times 100\ \% \quad (3)$$

Where ρ_1 and ρ_2 are respectively the densities of solvent (0.87 gcm^{-3} for toluene) and ρ_2 is the density of testing specimen (mean value of 1.27 gcm^{-3} for GAP based specimens) while m_0, m, and m_1 represent the weights of the initial, swollen, and deswollen states of the specimen respectively. For the measurement of crosslinking density, the soluble substances in the testing specimen were firstly extracted by acetone for four days, and then the specimen was dried and its density (ρ) was measured by the method of specific gravity bottle. Subsequently, the testing specimens were placed in toluene for 7 days for swelling. Finally, the swollen specimens were weighed after removing the solvent attached on the specimen surface with filter paper. Furthermore, the absorbed solvent of swollen specimens evaporated for re-weighing the deswollen specimen.

Figures 1 and 2 (Supporting information) show almost the same trend of crosslinking density where crosslinking density increased with the increase in NCO/OH ratio while swelling ratio decreased. The increase of crosslinking points can inhibit the swelling behavior. The crosslinking density is presumably to be maximum at the curing ratio (NCO/OH) of 1, which would give the highest reaction completion of every functional group, e.g. NCO and OH-groups. Any ratio deviating from this unity will lead to remaining of the functional groups and the initial formed PU structure became the steric hindrance. In general, higher crosslinking density results in higher tensile strength and lower elongation at break, that's why with the increase in NCO/OH ratio, crosslinking density increased with an increase in tensile strength while the breaking elongation decreased with the decrease in swelling ratio as shown in figure 1 and 2 (Supporting information).

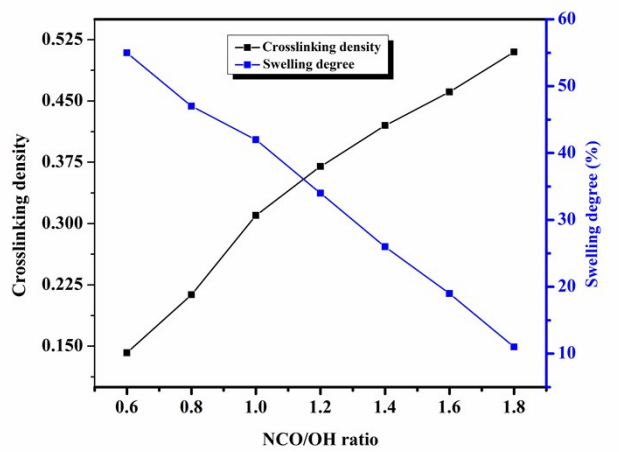

Fig: 1. Effect of NCO/OH ratio on the crosslinking density of HTPB

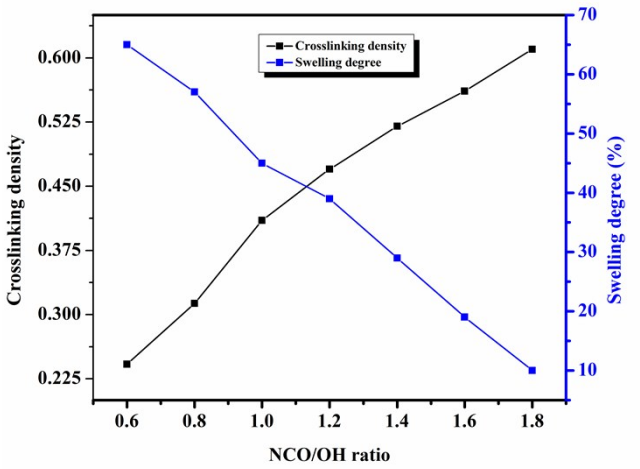

Fig: 2. Effect of NCO/OH ratio on the crosslinking density of GAP

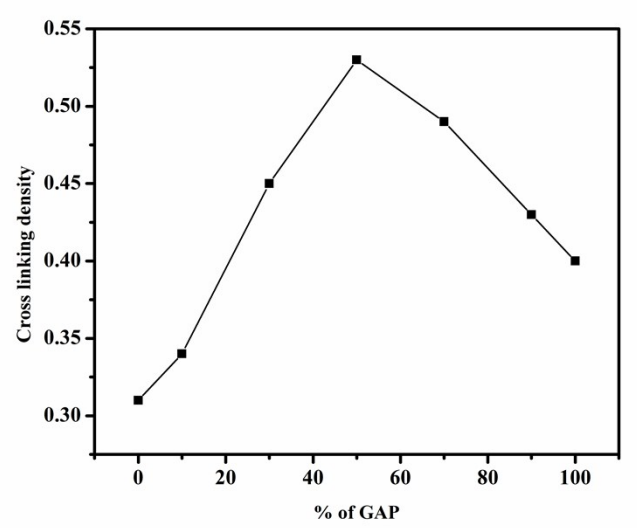

Figure 3: Effect of % of GAP on the crosslinking density of GAP-HTPB EHPNs