

Polyurea Segmented Multi-Block Copolymers: Structure, Mechanics and Rheology

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While Polyurea segmented multi-block copolymers are widely used impact-resistant coatings, the molecular underpinnings of this application are poorly understood. Due to inter-segmental repulsion that renders the hard (higher glass transition temperature, T_g) and soft (lower T_g) segments in this molecule thermodynamically incompatible, these copolymers exist in a micro-phase separated state over a broad temperature range. We study the tensile properties and rheology of a Polyurea copolymer (containing 19.8 % hard segments by mass) by measuring its stress-strain behavior (on a custom-built large rate tensile tester between 100 1/s and 1000 1/s) and by oscillatory shear rheometry, respectively. Polyurea shows elastomeric mechanical response over a wide temperature range, as the rigid domains physically cross-link the soft domains. The modulus increases, while the residual strain in specimens stretched to failure decreases with increasing strain rate. The linear viscoelasticity (LVE) of Polyurea shows violation of time-temperature superposition, and its modulus is very sensitive to annealing effects. To elucidate how morphology controls mechanical behavior and LVE, we study the morphology of undeformed specimens by temperature-resolved Small-Angle X-Ray Scattering (SAXS); at room temperature Polyurea has two clear scattering intensity peaks, signifying crystallinity in the hard domains (peak at large angles) and micro-phase separated domains (peak at small angles). To determine the effects of deformation on morphology, we perform SAXS on samples stretched to failure: Polyurea specimens quasi-statically stretched to failure show anisotropic scattering, while samples stretched to failure at large strain rates show *isotropic scattering*. Slow (quasi-static) deformation imparts orientation in hard domains while at larger strain rates no molecular reorientation is possible. *These results suggest that deformation effects on morphology are controlled by rigid domain response over the deformation time-scale.*