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Title

Resilient Polymer Networks Via Thiol-Norbornene Chemistry: Mechanical and Adhesive Properties

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Abstract

Hydrogels, a class of materials composed of polymer networks swollen with large amounts of water, have gained increasing attention in a range of fields, from tissue engineering to food science. However, synthetic hydrogels are known to be brittle and have poor mechanical properties, including low extension ratios and fracture toughnesses. It has been a great challenge to develop synthetic hydrogels with improved mechanical properties and correlate with their network composition. In this dissertation we developed two robust well-defined synthetic hydrogel systems by two simple strategies--thiol-norbornene chemistry and ring opening metathesis polymerization (ROMP). The swelling and mechanical properties were systematically characterized and correlated with their network structures.

The PEG/PDMS hydrogels synthesized by the simple, efficient, photo-initiated thiol-norbornene chemistry have improved mechanical properties. By manipulating the volume fractions of the PEG and PDMS, a large range of water content (54%-97%) was achieved. The Young's modulus (E) was significantly improved by increasing the volume fraction of PDMS in the hydrogel, and the Voigt and Reuss models were used to quantify the relationship between the volume fraction and E . In addition, increasing the volume fraction and molecular weight of the PDMS led to tougher hydrogels with G_c more than 100 J/m^2 . Furthermore, a high resilience (more than 97%) was maintained across the entire range of strains, regardless of the composition of the PEG/PDMS hydrogels.

Controlled polymerization provides another method to synthesize gels with improved mechanical performance. The properties of the ROMP-based gels were tuned by varying the initial molar ratio of the monomer to cross-linker from 7.5% to 20%. The mechanical properties of the gels were characterized via the cavitation rheology technique (CRT), which demonstrated a transition from reversible to irreversible deformation with the increase of the molar ratio. By combining CRT and contact mechanics, E and G_c for these gels were quantified. As the amount of the cross-linker increased, E increased while G_c slightly decreased.

Soft tissues with hierarchical structures share similar properties as synthetic hydrogels. The study of their mechanical properties would provide useful information in designing synthetic hydrogels with novel network structures. Eye lens was chosen in this study. The anisotropic mechanical properties of bovine eye lenses were measured using CRT over a range of length scales. E of the nucleus and cortex of the lens were determined, as approximately 11.8 and 0.8 kPa, respectively, on macroscopic length scales. We also measured the mechanical properties of the lens on a length scale of a single cell, suggesting that the stiffness significantly decreased from that in the bulk measurements for both the nucleus and cortex. In addition, during the growth of the cavity anisotropic propagation in the cortex was observed, while in the nucleus, the propagation was isotropic. We further explored the elasticity of the cavity deformation, showing both elastic and inelastic deformation occurred in the nucleus with equal contributions while deformation in the cortex was elastic and reversible.

Lastly, we investigated adhesive properties of polymer networks with the thiol-norbornene chemistry to explore their possible applications. The mechanical and adhesive properties of these PDMS networks were quantified by the contact adhesion test (CAT), as well as DMA and compressive measurements. E of these end-linked PDMS measured by CAT was comparable with that measured by the compressive test. In terms of the adhesion properties, the energy release rate was described as a function of crack velocity. A higher molecular weight between cross-links led to a higher adhesion energy over a range of crack velocity for the PDMS with the same end-linking chemistry. Sylgard PDMS with 18 to 1 ratio was chosen to compare the mechanical and adhesive properties to the end-linked PDMS. With the similar Young's modulus and resilience, the adhesion energy of the Sylgard PDMS was comparable to that of the end-linked PDMS with 5 kDa molecular weight, which was likely to result from the comparable molecular weight between cross-links.

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