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### **Structural Interplay - Tuning Mechanics in Peptide-Polyurea Hybrids<sup>1</sup>**

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Utilizing cues from natural materials, we have been inspired to explore the hierarchical arrangement critical to energy absorption and mechanical enhancement in synthetic systems. Of particular interest is the soft domain ordering proposed as a contributing element to the observed toughness in spider silk. Multiblock copolymers, are ideal and dynamic systems in which to explore this approach via variations in secondary structure of nature's building blocks – peptides. We have designed a new class of polyurea hybrids that incorporate peptidic copolymers as the soft segment. The impact of hierarchical ordering on the thermal, mechanical, and morphological behavior of these bio-inspired polyurethanes with a siloxane-based, peptide soft segment was investigated. These peptide-polyurethane/urea hybrids were microphase segregated, and the beta-sheet secondary structure of the soft segment was preserved during polymerization and film casting. Toughness enhancement at low strains was achieved, but the overall extensibility of the peptide-incorporated systems was reduced due to the unique hard domain organization. To decouple the secondary structure influence in the siloxane-peptide soft segment from mechanics dominated by the hard domain, we also developed non-chain extended peptide-polyurea hybrids in which the secondary structure (beta sheet vs. alpha helix) was tuned via choice of peptide and peptide length. It was shown that this structural approach allowed tailoring of extensibility, toughness, and modulus. The sheet-dominant hybrid materials were typically tougher and more elastic due to intermolecular H-bonding facilitating load distribution, while the helical-prevalent systems generally exhibited higher stiffness. Recently, we have explored the impact of a molecular design strategy that overlays a covalent and physically crosslinked architecture in these peptide-polyurea hybrids, demonstrating that physical constraints in the network hybrids influences peptide hydrogen bonding and morphology. These structural features correlated well with systematic changes in modulus, extensibility, and hysteresis. Complementary to this effort is the design of PEG-based peptide-polyurea hybrids with tunable and responsive as structural and injectable hydrogels.

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