Understanding Fracture in Physically Crosslinked Hydrogels

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The development of hydrogels for cell culture applications has focused on controlling their linear elasticity and viscoelasticity. As cells exert tensile and compressive forces on their surroundings, it is crucial to also consider the non-linear responses of these materials. However, the complexities of non-linear deformation and hydrogel fracture remain inadequately understood. Our goal is to correlate linear and non-linear bulk hydrogel responses with the molecular properties of the hydrogel constituents. Employing a bottom-up approach, we synthesize hydrogels entirely composed of molecularly characterized building blocks. Using star-shaped polyethylene glycol with terminal crosslinking units, we create a material where the contour length of each crosslinked network chain is similar [1-3]. The crosslinks consist of self-assembling coiled coil forming peptides. Utilizing a library of coiled coils with tunable thermodynamic, kinetic, and mechanical stabilities [1,4], we investigate how these parameters correlate with the linear and non-linear properties of the resulting hydrogels.

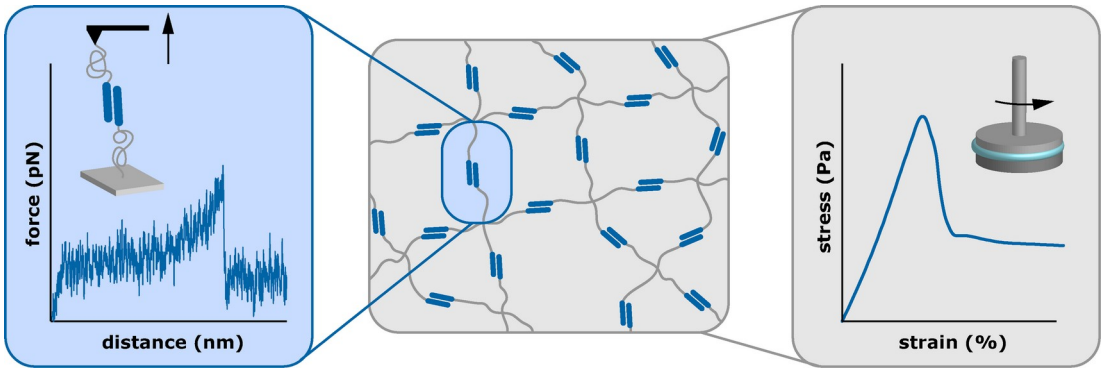

Figure 1. Structure and characterization of coiled coil-crosslinked star-PEG hydrogels. Single-molecule force spectroscopy yields information about the dynamic mechanical behaviour of individual crosslinked chains, whereas rheology provides complementary information about material failure and self-healing at different strains and strain rates.

Oscillatory shear rheology in the linear viscoelastic range reveals that the relaxation times are governed by the equilibrium properties of the crosslinks. More importantly, rotational stress-strain experiments reveal that fracture can be tuned when using crosslinks with different non-equilibrium bond rupture properties. A theoretical model for hydrogel fracture allows for extracting molecular bond rupture parameters of the crosslinks. These parameters are reproduced using atomic force microscope-based single-molecule force spectroscopy, underscoring our ability to link molecular and bulk mechanical properties. Our next step is to introduce a fluorescent reporter system to monitor the crosslink assembly state. This will ultimately enable the visualization of network topology and crosslink rupture in real-time.

Keywords: hydrogel, fracture, rheology, single-molecule force spectoscopy

References

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