Tuning the Mechanical Properties of Injectable Physically Crosslinked Hydrogels

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Introduction

Polymeric hydrogels are widely investigated as synthetic scaffold materials for biomedical applications thanks to their suitable properties such as mechanical behavior similar to those of tissue, biocompatibility and biodegradability, and excellent permeability for oxygen, nutrients and metabolites.

Objective

Covalently cross-linked hydrogels are most frequently investigated, but they have several disadvantages:

- Not self healing: Gel breakage is irreversible.
- Not injectable: Gels cannot be liquefied as required for injection.

⇒ Need a material that is strong enough to support cells but weak enough to reform during injection.

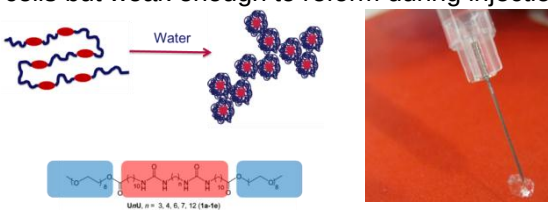

Fig 1. Segmented copolymer with hydrophobic and hydrophilic blocks

Here we present a new physically cross-linked material that fulfills these properties. The material is based on a segmented copolymer containing hydrophilic polyethylene glycol (PEG) domains and hydrophobic domains containing bis-urea groups, which lead to physical cross-linking via hydrogen bonding and hydrophobic interactions (fig1).

Results

At low concentrations, the chains form flower-like structures, with only few links between flowers. By increasing concentration, more links between flowers are formed, resulting in a elastic gel of loosely connected flowers. At even higher concentrations, as the overlap concentration(c^*) of flowers is approached, *crowding dominates the structure and mechanics of the material (fig2(a)).*

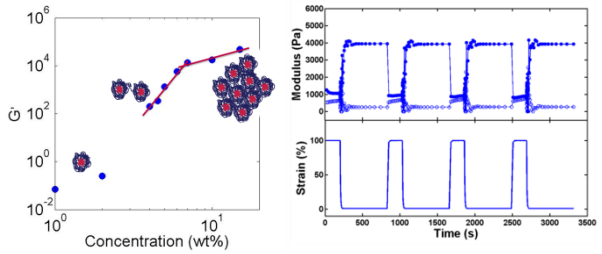

Fig 2. (a) Concentration dependence of the storage modulus: 3 distinct regimes are observed. (b) Self healing

From the data in Fig. 2 we can extract the overlap concentration of flowers, which enables us to estimate the approximate number of segments per flower: $c^*_{soft\ PEG\ block} = \frac{M}{R_g^3 N_A} = 0.1993 \frac{mg}{\mu l}$

$$Number\ of\ PEGs\ per\ flower = c^*_{segmented\ polymer} \frac{2^3}{c^*_{soft\ PEG\ block}} \simeq 3$$

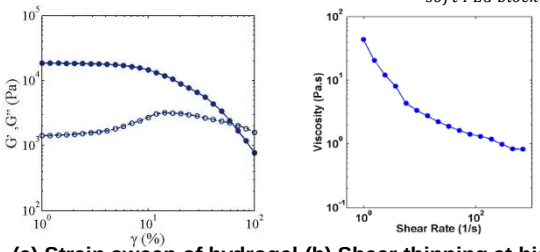

Fig 3. (a) Strain sweep of hydrogel (b) Shear thinning at high shear rates

Self healing: Because the material is a transient network, after fracture at large strains, it recovers its initial elastic-like properties (fig. 2(a)).

Injectability: By applying a large strain, the material exhibits yielding into a liquid-like state (Fig. 3(a)), but still G'' is too large for injection. The key factor that ensures injectability is the dramatic shear thinning of the material, shown in Fig. 3(b).

Conclusion:

Mechanical properties of our physically crosslinked hydrogels are readily tunable by concentration and the material has a high potential to be used as a injectable gel. Our hypothesis of the network structure is supported by the rheological data but should be further investigated using other methods such as scattering or direct imaging techniques.