Tuning Mechanical Properties of Chondroitin Sulfate-Based Double-Network Hydrogels

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Summary: High strength double-network (DN) biopolymer-based hydrogels were created using copolymers of methacrylated chondroitin sulfate (MCS) and poly (ethylene glycol) diacrylate (PEGDA) as the first network and polyacrylamide (PAAm) as the second network. The concentration and cross-linking of the networks were adjusted to control the mechanical properties including the failure stress, failure strain, Young's modulus, and yielding behavior. First, we increased the cross-linking of the first network both by increasing the MCS concentration from 13 to 20 wt% and by copolymerizing MCS with 2 to 6 wt% PEGDA. The additional cross-linking increased the Young's modulus as much as five times, reaching 3.3 MPa, and the failure stress up as much as four times, reaching 2.9 MPa. However, this also reduced failure strain from a high of 2.9 mm/mm to a low of 0.12 mm/mm and diminished the yielding region. Changes in the concentrations of acrylamide or its cross-linking with N,N′-methylenebisacrylamide (BIS) in the second network had a lesser effect on the DN properties. We hypothesized that to obtain a yielding region which results in high toughness, we need to alter the cross-linking of the first network such that the yield stress of the MCS-PEGDA/PAAm DN does not exceed the failure stress of PAAm network. Because of the wide range of mechanical properties achieved in these DNs with limited changes in the swelling degrees, unlike conventional single-network gels, the DN approach allows attainment of a much greater range of mechanical behavior than is possible with single networks.

Keywords: biopolymers; chondroitin sulfate; double-network gels; hydrogels; mechanical properties; polyacrylamide

Introduction

Although the high water content and three dimensional structure of hydrogels makes them great candidates for use as tissue engineering scaffolds and other applications, the high water content dilutes the load-bearing polymer component, making them inherently low in strength and toughness.[1] Thus there is an ongoing need to improve their mechanical properties.

We have shown that it is possible to create hydrogels with high strength and toughness by employing the double-network (DN) strategy. We have previously created DN hydrogels of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)/polyacrylamide (PAAm), where we have seen significantly improved toughness to either single network alone.[2–9] The strategy of DN hydrogels is to combine a brittle, stiff and highly cross-linked polyelectrolyte first network with a ductile, soft and lightly cross-linked neutral second network, where the molar concentration of the second network is in excess relative to the first.[5,6,8,10] DN hydrogels have stress-strain behavior that is unlike other hydrogels, as illustrated in Figure 1. As shown in the figure, the DN of PAMPS/PAAm can have three characteristic regions: pre-yielding,

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