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Double-Network Strategy Improves Fracture Properties of Chondroitin Sulfate Networks

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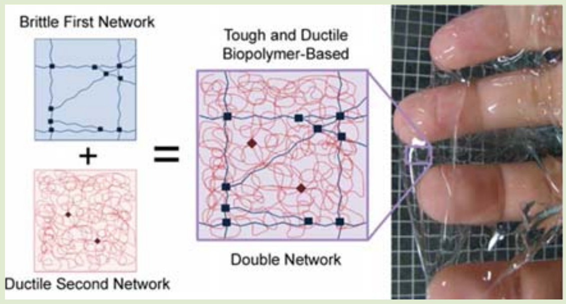
S *Supporting Information*

ABSTRACT: A tough and ductile, ultrathin film, double-network (DN), biopolymer-based hydrogel displaying the yielding phenomenon was synthesized from methacrylated chondroitin sulfate (MCS) and polyacrylamide (PAAm). The DN of MCS/PAAm exhibited a failure stress more than 20 times greater than the single network (SN) of either MCS or PAAm and exhibited yielding stresses over 1500 kPa. In addition, the stress−strain behavior with a yielding region was also seen in a hydrogel of MCS and poly(*N*,*N*-dimethyl acrylamide) (PDMAAm). By replacing PAAm with PDMAAm, interactions known to toughen networks are removed. This demonstration supports the idea that the brittle/ductile combination is key to the DN effect over specific interactions between the networks. The MCS/PAAm and MCS/PDMAAm DN hydrogels had comparable mechanical properties to the archtypal DN hydrogels of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)/PAAm. In addition, these tough and ductile, biopolymer-based, double-network hydrogels demonstrated a substantial yielding region.



In general, materials undergo either a yielding phenomenon or a brittle failure, and the strength of the material is determined by which process occurs first.[1] Many materials display yielding, however, synthetic, chemically cross-linked hydrogels always have a brittle fracture, with the exception of double-network (DN) hydrogels of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)/polyacrylamide (PAAm), which also have extraordinary fracture stresses.[1,2] Anisotropic gels such as poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide) (PBDT)/PAAm DN hydrogels have also shown yielding.[3] Recently, Sun et al. created hybrid gels of ionically cross-linked alginate and covalently cross-linked PAAm.[4] These alginate/PAAm hydrogels displayed high extensibility, 20 times their initial length, and a yielding region, but the fracture strength was only ∼160 kPa.[4] Synthesizing tough and ductile biopolymer-based hydrogels that demonstrate the generality of yielding could lead to materials resistant to catastrophic failures, especially important in areas such as tissue engineering.[5] The goal of this work is to create a tough biopolymer-based DN hydrogel system with a yielding region using PAMPS/PAAm DN as a model and to test the hypothesis that the double-network effect is due to the combination of brittle and ductile networks. We first replaced PAMPS with MCS, thus exchanging a sulfonated synthetic polymer with a sulfonated biopolymer synthesized by cross-linking a linear polymer and then replaced PAAm with poly(*N*,*N*-dimethyl acrylamide) (PDMAAm) to eliminate the two protons of the amide group. This research shows that a biopolymer-based DN hydrogel can be designed to have high toughness and a distinct yielding region.

DN hydrogels are formed from a highly covalently cross-linked, brittle and stiff, polyelectrolyte first network with a lightly covalently cross-linked, soft and ductile, neutral polymer second network.[2c,d,6] The second network has a molar concentration 20−30 times greater than the first network.[2c,d,6]

DN hydrogels have significantly improved toughness in comparison to either single-network (SN) alone. The improved toughness is believed to be due to the fracturing of the first network, which dissipates the strain energy, while the ductile second network holds the bulk hydrogel together and supports high strains.[2d,7] Ultrathin film DN hydrogels (∼100 μm thick) are comparable to bulk, solution-cast DN gels in mechanical properties such as toughness, yielding, and necking. Thus, they have a toughening mechanism similar to the toughening mechanism found in bulk, solution-cast DN gels. However, ultrathin DN hydrogels have experimental advantages of allowing for observation of the tearing mechanism, requiring less material and equilibrating more rapidly with solutions.[2f,8]

Previously reported DN hydrogels made from PAMPS/PAAm have three characteristic regions, preyielding, yielding, and hardening, and display a clear yield point (transition between preyielding and yielding regions).[2c,d,f] The preyielding region is a region in which the brittle network starts absorbing

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