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## TOUGH HYDROGELS BASED ON DOUBLE NETWORK CONCEPT

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Biointerphases. Gong presently is concentrating on the developing of novel hydrogels with high mechanical performances, including high strength and toughness, self-healing, shock-absorbing, low surface friction, adhesion and bonding, and the application of the hydrogels as bio-tissues, such as cartilages.

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A hydrogel, consisting of cross-linked macromolecules and water, is a soft & wet material. As a combination of solid and liquid components, hydrogels have a high permeability to small molecules and undergo reversible volume change by exuding or absorbing water in response to a wide range of stimuli, such as light, temperature, pH, ionic strength, chemical reactions. In the past three decades, sensing and actuating properties of hydrogels have been extensively studied based on the volume changes. Owing to the similarity between hydrogels and soft tissues, recently, bulk hydrogels have drawn great attention as biomaterials, such as extra-cellular matrix, artificial bio-organs, and phantom tissues in medical device development.

However, conventional hydrogels, which are usually composed of single network (SN) of hydrophilic polymer, are soft, weak, and brittle. They usually fail at a tensile stress less than sub-MPa and strain less than 100%. In 2003, we succeeded in developing novel hydrogels with extremely high mechanical strength by introducing a double-network structure (DN), consisting of a densely crosslinked polyelectrolyte network, poly-2-acrylamido-2-methylpropanesulfonic acid (PAMPS), and a loosely crosslinked neutral network, polyacrylamide (PAAm) [1]. These gels, containing 80-90wt% water, possess hardness (elastic modulus of 0.1-1.0 MPa), strength (nominal tensile failure stress 1–10 MPa, strain 1000-2000%; nominal compressive failure stress 20-60 MPa, strain 90-95%), and toughness (tearing fracture energy 100-1000 J/m<sup>2</sup>) (Figure 1). The toughness of DN gels is 100–1000 times larger than that of normal PAAm gels (10 J/m<sup>2</sup>) or PAMPS gels (10<sup>1</sup> J/m<sup>2</sup>) whose polymer concentrations are similar to those of DN gels. These excellent mechanical performances of DN gels are comparable to that of rubbers and cartilages. Because of the anomalously high mechanical strength and high water content of DN gels, they are expected to have various applications, especially in the field of regenerative medicine (for fabricating artificial tissues and cartilage, etc.).



Figure 1 Tough DN gel containing 90wt% of water [1]

The fundamental toughening mechanism of DN gels is of great interest to researchers. Many experimental and theoretical studies have been performed to explore the mechanism [2-7]. Yielding and necking deformation [2] that was observed through tensile tests (Figure 2) and rate-independent hysteresis [3] observed through cyclic loading tests have indicated that DN gels can accumulate internal damage before the occurrence of macroscopic fracture; after damage accumulation, the DN gels become much softer. On the microscopic level, yielding is caused by the partial breakage and fragmentation of the brittle first network and interconnection among the fragments by the polymer chains of second network [2]. Brown [4] and Tanaka [5] have proposed similar models that can qualitatively explain the anomalously high fracture energy, assuming that the DN gel is locally damaged (yielded) around the crack tip and that the energy dissipated for damage accumulation enhances the effective fracture energy. According to their models, the size of the damage zone could reach the order of several hundred µm, while the fracture energy could reach the order of several hundred  $J/m^2$ . Using AFM measurements [6], the existence of softened regions just below the fracture surfaces was successfully detected, which supports the assumption of localized damage accumulation. Later, using a 3D color laser microscope, the damage zone was directly observed [7]. A linear relationship between the thickness of the vielding zone and the fracture energy of the DN gel was observed, which is in agreement with the models (Figure 3).



Figure 2 Yielding, necking, and hysteresis of a DN gel.

So, the toughness of DN gels is a consequence of the internal fracture of the brittle network to dissipate significant amounts of energy under large deformation and the elasticity of the second

network to maintain their original configurations after the deformation. Because of this mechanism, a large damaged zone of the first network, several hundred micrometers in thickness, is formed at the crack tip of these materials. Energy is dissipated as the first network is broken into small fragments within this zone, so that the fracture energy of the double network is enormously larger than that of either of the corresponding single networks. Thus, the covalent bond of the brittle first network serves as true "sacrificial bond", a phrase initially used to describe the fracture mechanism of bones[8, 9].



Figure 3 Relationship between fracture energy (G) of DN gel and the thickness of the yielding zone (h).

The high fracture energy of the toughening DN gel can be quantitatively expressed in terms of the energy gain by an intense factor  $h/\xi$  due to the fragmentation of the rigid PAMPS into clusters of size  $\xi$  in the yielding zone with a thickness *h*, as shown in Figure 4. For a typical tough DN gel, the cluster size  $\xi$  is estimated as ~100 nm from the hysteresis of the tensile curves. On the other hand, *h* is observed as ~100 µm. This gives an intense factor of ~1000. From the tear test, the fracture energy for the DN gel, PAMPS gel (rigid), and PAAm (soft) were 100~1000 J/m<sup>2</sup>, ~1 J/m<sup>2</sup>, and ~10 J/m<sup>2</sup>, respectively. These results confirm the validity of the relation

 $G_{DN} = G_{Soft} + (h/\xi)G_{Rigid}.$ 

The fragmentation of PAMPS into clusters with a size  $\xi$  in the order of 100 nm is considered to be related to the heterogeneous structure of the chemically cross-linked PAMPS gel [10].

Figure 4 Toughening mechanism of DN gel.

Tough materials generally possess mechanisms to dissipate substantial mechanical energy. Comparing with other tough materials having non-covalent bonds to dissipate energy, the covalent sacrificial bond of brittle networks has advantages of high bond energy, and weak dependence of the stiffness and toughness on temperature and deformation rate. The disadvantage is that once the brittle network is broken, it is not reversible, which leads to negligible fatigue resistance. To solve this problem, some recent works have replaced the covalent bonds with non-covalent bonds to allow the fractured bond to be re-formed in hydrogels[11-13]. Studies along these lines have successfully produced tough hydrogels with partial or full self-recovery after internal rupture.

The double network concept naturally suggests a more general strategy for designing tough soft materials: incorporating, on purpose, a mechanically fragile structure to toughen the material as a whole. This strategy gives more freedom in the molecular design, not limited to double or multiple network systems but also applies to single network system as long as it has sacrificial bond to dissipate energy and can retain original configurations of the material after large deformation. This strategy has been proved effective using ionic bonds in hydrogels[12-13]. One further goal is to develop tough soft materials with anisotropic mechanical performance resembling to skins, cartilages, muscle, and tendons. Using self-assembly molecules, such as lipid molecules, rod-like macromolecules, block copolymers, to build anisotropic energy dissipation structure would be a strategy. This possibility is demonstrated by a fully anisotropic hydrogels consisting of layered lipid membranes entrapped in the matrix of neutral network[14]. The integrations and interactions of different mechanisms for dissipating energy and maintaining elasticity are essential to the design of tough soft materials. In a recent review, a matrix that combines various mechanisms is constructed to guide the design of next-generation tough hydrogels[15].

Conceptually, the double network principle is general for toughening the elastomers materials, as long as the contrasting network structure is formed. However, applying this double network concept to the non-hydrated elastomers is usually not easy. One difficulty is the how to form the

contrasting double network structure using non-hydrated polymers. In the case of hydrogels, the contrasting structure is synthesized by a two-step sequential network formation process, using polyelectrolyte as the first network and neutral polymer as the second network. The polyelectrolyte brings two effects by its high osmotic pressure: it stretches the first network into stiff state, and makes this primary network in dilute concentration. As no polyelectrolyte effect can be used, it is difficult to form the contrasting structure in elastomers. Another difficulty is the limited combinations of the polymer networks that are mixable in the absence of solvent. Recently, Creton et al have synthesized double and triple network elastomers that having much improved toughness comparing with the single network elastomer[16].

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