



Feature article

Super tough double network hydrogels and their application as biomaterials

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ABSTRACT

The double network (DN) technique, developed by authors' group, provides an innovative and universal pass way to fabricate hydrogels with super high toughness comparable to rubbers. The excellent mechanical performances of DN hydrogels originate from the specific combination of two networks with contrasting structures. The first brittle network serves as sacrificial bonds, which breaks into small clusters to efficiently disperse the stress around the crack tip into the surrounding damage zone, while the second ductile polymer chains act as hidden length, which extends extensively to sustain large deformation. Based on the principle of DN hydrogel, the author's group recently has developed several novel systems and techniques, which has greatly expanded the practical accessibility of DN technique for practical use. The DN principle and the DN gel have already attracted much attention in the soft matter community. Inspired by the DN principle, many research groups have also designed and developed some innovative hydrogels with large enhancement in their mechanical strength and toughness. Some tough hydrogels fabricated by the DN technique also exhibit good biocompatibility and low friction resistance with promising prospective in industrial and medicine fields, especially for load-bearing artificial soft tissues such as artificial cartilage. In this feature article, we address the major concept and toughening mechanism of DN gel, then we describe some recent novel hydrogel systems based on the DN concept, and finally the applicability of DN gel as soft biomaterials is discussed.

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1. Introduction

Hydrogels, which are soft and wet materials, usually composed of three-dimensional polymer network structure and large amount of water (50–99%) inside the network structure and have potential applications in many fields. Beside their wide variety of applicability such as drug delivery system, superabsorbents, microfluidics, and contact lenses in the materials science domain, they have become extensively attractive in tissue engineering because of their stimuli responsive property [1–19]. However, most of the synthetic hydrogel suffered from a lack of mechanical strength compared with the hydrogel-like bio-tissues such as cartilage, tendon, muscle, and blood vessel [20]. These load-bearing soft tissues exhibit excellent mechanical performances, for example, cartilage tissue possesses high toughness, shock absorbing, low sliding friction [21]. Seeking artificial tissues (excellent soft, wet, and tough hydrogel material) as a replacement of damaged ones has been a challenging task for material scientists.

Over past 10 years, several hydrogels with excellent mechanical performance have been successfully developed [22–26]. Soft and

highly extensible gels with a relatively homogeneous network structure are developed by using sliding cross-linkers (slide ring, SR, gel) [22], or by using two kinds of tetrahedron-like macromonomers (tetra-PEG gel) [23]. These gels exhibit an ideal elastic deformation. On the other hand, high modulus and high toughness gels with composite structures are developed by combining clay with polymer (nanocomposite, NC, gel) [24], or by combining a rigid and brittle network with a soft and ductile network (double network, DN, gel) [25,26]. The former one has shown effective improvement of mechanical strength while the latter one (DN gel, which was developed by author's group) has exhibited the highest fracture toughness.

The double network (DN) gels possess interpenetrating polymer network (IPN) structure where the properties of two networks existing in sharp contrast such as network density, rigidity, molecular weight, cross-linking density etc. They are generally synthesized via a two-step sequential free-radical polymerization process in which a high relative molecular mass neutral 2nd polymer network is incorporated within a swollen heterogeneous polyelectrolyte 1st network [25]. The mechanical properties of DN gels prepared from many different polymer pairs were shown to be much better than that of the individual components. Under an optimized structure, the DN gels, containing about 90 wt% water,

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possess hardness (elastic modulus of 0.1–1.0 MPa), strength (failure tensile stress 1–10 MPa, strain 1000–2000%; failure compressive stress 20–60 MPa, strain 90–95%), and toughness (tearing fracture energy of 100–4400 J·m⁻²) [26–34]. These excellent mechanical performances had never been realized before in synthetic hydrogels, and are comparable to and even exceed some soft load-bearing tissues [21].

Enhancement in mechanical strength by the double network concept has been observed in some other works of authors' group as well as other groups. Combination of bacterial cellulose (BC) with neutral polymers, such as gelatin, or synthetic polymers also exhibits an enhanced mechanical performance [35,36]. Similarly, based on the DN principle, the authors' group have developed several novel systems with enhanced mechanical property and techniques such as void-DN gel [37], microgel-reinforced particle DN gel [38], liquid crystalline DN gel [39], ultrathin DN gel [40], bilayer incorporated tough gel [41,42], free-shaped tough DN gel [43], bonding of one gel to another gel or solid substrate [44], etc. that should greatly expand the diversity of DN principle. Inspiring with the DN concept, other groups have also developed some novel interpenetrating polymer network (IPN) systems such as poly(ethylene glycol)/poly(acrylic acid) (PEG/PAAc) [45–47], poly(etherurethane)/poly(methyl-methacrylate) (PEU/PMMA) [48], agarose/poly(ethylene glycol) diacrylate [49]. The IPN systems are developed from two different polymers with similar properties. As, in principle, DN gel also possesses IPN structure and above mentioned IPN systems were developed by applying DN concept, all the IPN gel systems are defined as DN gel in this article. Some other DN gel systems such as the modified hyaluronan/poly(N,N'-dimethylacrylamide) (PHA/PDMAAm) [50], jellyfish/polyacrylamide (JF/PAAm) [51] have also been reported by other research groups. Recently, Zhang et al. synthesized DN hydrogel from two biocompatible polymers [52]. These entire DN systems exhibit enhanced mechanical strength and toughness much better than that of the individual components and most of them possess fracture stress and toughness in the order similar to the soft bio-tissues.

In this feature article, we first address the main concept of tough DN gel, including the method of preparation, structure, mechanical feature and the toughening mechanism. Then, we discuss how the DN concept helps to develop above mentioned novel DN gel systems by the authors' group as well as other groups. Finally we discuss the applicability of those synthetic hydrogels as biomaterials, *i.e.*, as a replacement of natural cartilage or others.

2. A short review of double network (DN) gel

2.1. Method of preparation

The DN gels are generally synthesized via a two-step sequential free-radical polymerization process [25]. In the first step, a hydrogel composed of tightly cross-linked network structure of rigid and brittle polyelectrolyte is formed. This brittle gel is subsequently swelled in an aqueous solution of a neutral monomer and then the monomer is polymerized to form a loosely cross-linked, flexible network inside the first brittle gel. The obtained hydrogel so-called DN hydrogel is immersed in water again to reach the equilibrium swelling state.

2.2. Structure

The DN gels are comprised of two independently cross-linked networks. An optimal combination has been found when the first network is a rigid polyelectrolyte and the second one is a flexible neutral polymer. The optimum feature of two kinds of polymers with strong contrast structure are; (a) rigid and brittle polymer as

the first network, such as polyelectrolyte; soft and ductile polymer as the second network, such as neutral polymer, (b) the molar concentration of the second network is 20–30 times the first network, and (c) the first network is tightly while the second network is loosely cross-linked, which requires a very high molecular weight of the second polymer [26,27]. In a word, the delicate balance between a suitable brittleness of the first network and a ductility of the second network is preserved to obtain the anomalous DN structure of the hydrogel. We should note here that the strong contrast properties of the two networks in DN gels make them quite different from the conventional interpenetrating polymer network (IPN) gels. It is found that the dramatic increase in the mechanical strength of the DN gels occurs above the region where linear PAAm chains are entangled with each other and the entanglement between the second component PAAm plays an important role of the toughening mechanism of DN gels [27]. The high strength of DN gels is due to a synergistic effect of the binary structure rather than a linear combination of two component networks, like the conventional IPN or fiber-reinforced hydrogels [53].

2.3. Mechanical feature

So far, the DN gels synthesized with poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) polyelectrolyte as the first network and polyacrylamide (PAAm) neutral polymer as the second network stands out with unusual properties and serves as the system for further studies. At an optimal composition, the PAMPS/PAAm DN gels show excellent mechanical performance, although they include ~90 wt% of water. The compressive fracture stress of the DN gels achieves several dozens of MPa, which is comparable to that of cartilage. In addition, the tearing energy reaches up to 4400 J/m², which is several thousand times of that of single network PAMPS and PAAm hydrogels [27–31,34]. During the tensile test, tough DN gels usually show remarkable necking phenomenon, as shown in Fig. 1a. Narrowed zones appear in the sample at a certain strain, $\epsilon \sim 2$ mm/mm, and grow up to with further elongation [26,28,54,55]. In the stress-strain curve, yielding occurs and a plateau region appears during the neck zone propagation, which is insensitive to strain rate. After the necking, the gel becomes very soft with an elastic modulus approximately 1/10 of that before the elongation test [56]. It was confirmed that the first PAMPS network breaks into small clusters even at several percent of strain because of the intrinsic fragile properties of PAMPS single network hydrogel. These clusters play a role of physical cross-linker of long flexible PAAm chains (second PAAm network is loosely cross-linked). The fragmentation during the elongation involves dissipation, which is reflected in the hysteresis of the second loading curve (Fig. 1a) [26,55,57]. The necking phenomenon can be regarded as a damage accumulation of the first network; on the strongly stretched region, the gels transform into a very soft one by breaking the first network into small clusters (Fig. 1b). Both the fragmentation of PAMPS network and chain-pulling process of flexible PAAm chains from the clusters dissipate energy, endowing the DN gel with toughness. However, the former is predominant in the case of the DN gel, which is the reason why the mechanical behaviors (strength and toughness) are hardly influenced by the strain rate [26,28,32,56]. Besides the tensile test, tearing test as a measurement of the fracture energy is applied to qualify the mechanical strength of the DN gels (Fig. 2a) [30,32,55]. The tearing energy T of PAMPS/PAAm DN gels ranges from 10² to 10³ J/m² [34,55], which is 100–1000 times larger than that of single network PAAm gels (~10 J/m²) or PAMPS gels (~0.1 J/m²) with the similar polymer concentrations to those of DN gels. It should be noted here that the tearing energy T , defined as the energy required for

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