Double-Network Hydrogels with Extremely High Mechanical Strength

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Double-Network Hydrogels with Extremely High Mechanical Strength**

By *Jian Ping Gong*,* *Yoshinori Katsuyama*, *Takayuki Kurokawa*, and *Yoshihito Osada*

Gel scientists are facing challenges in providing synthetic connective tissues that serve a predominantly biomechanical role in the body, such as articular cartilage, semilunar cartilage, tendons, and ligaments. However, in order to replace the natural tissues with hydrogels, a number of significant engineering questions should be addressed, such as the

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provision of low surface friction and wear, a suitable elastic modulus, and high mechanical strength, both in vivo and in vitro. For instance, an articular cartilage that is a gel containing 70 % water exhibits little wear under a loading as high as several to a hundred megapascals and millions of cycles with a wide range of sliding velocity.[1] Our recent study shows that if a gel has free dangling polymer chains on its surface, its frictional coefficient becomes as low as 10^{-4}.[2] From this viewpoint, gels have a high potential as an artificial articular cartilage. Although poly(vinyl alcohol), PVA, hydrogel has been found to be mechanically strong and serves as a candidate for artificial articular cartilage,[3,4] most hydrogels derived from either natural or synthetic sources suffer from lack of mechanical strength. We report a general method of obtaining very strong hydrogels by inducing a double-network (DN) structure for various combinations of hydrophilic polymers. These DN hydrogels, containing 60–90 % water, exhibit a fracture strength as high as a few to several tens of megapascals and show high wear resistance due to their extremely low coefficient of friction. These gels might open new era of soft and wet materials as substitutes for articular cartilage and other tissues.

Hereafter, the DN gels are referred to as P_1-x_1-y_1/P_2-x_2-y_2, where P_i, x_i, and y_i (i = 1,2) are the abbreviated polymer name, molar monomer concentration, and the crosslinker concentration in mol-% with respect to the monomer for the ith network, respectively. The DN hydrogels with an optimized network structure can sustain a compressive pressure as high as several tens of megapascals. This is in stark contrast to most common hydrogels with a single network, which are easily broken either by pressing with a finger or pulling with the hands. As shown in Figure 1, for example, the PAMPS-1-4/PAAm-2-0.1 DN gel is so tough that it is resistant to slicing with a cutter, despite containing 90 wt.-% water. Here, PAMPS stands for poly(2-acrylamido-2-methylpropanesulfon-
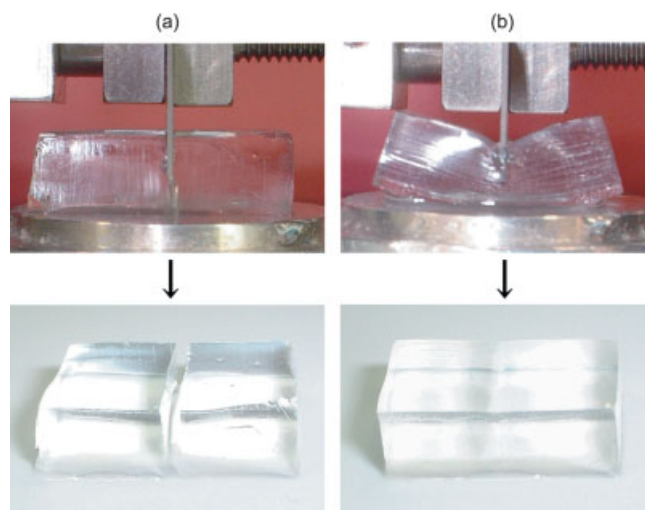

Fig. 1. Pictures demonstrating the strength of a DN hydrogel that resists slicing with a cutter. The PAMPS-1-4 SN gel is easily sliced at a stress of 0.2 MPa (a), while the PAMPS-1-4/PAAm-1-0.1 DN gel resists even at a stress of 25 MPa with a strain as great as 80 % (b). Water content of the PMPS SN gel is 90 wt.-% and that of the PAMPS/PAAm DN gel 88 wt.-%.

ic acid) and PAAm for poly(acrylamide). The high-strength DN gel showed a good reproducibility.

Figure 2 shows a typical stress–stain curve of a PAMPS-1-4/PAAm-2-0.1 DN gel under compression. PAMPS-1-4 and PAAm-2-0.1 single-network (SN) gels break at stresses of 0.4
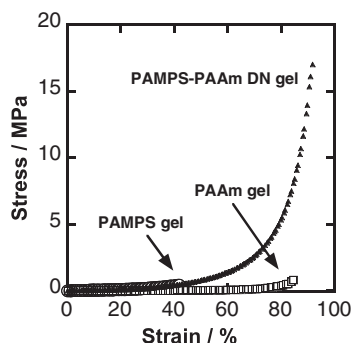

Fig. 2. Stress–strain curves for hydrogels under uniaxial compression. Circles: PAMPS-1-4 SN gel (water content: 90 wt.-%); squares: PAAm-2-0.1 SN gel (water content: 90 wt.-%); triangles: PAMPS-1-4/PAAm-2-0.1 DN gel (water content: 90 wt.-%).

and 0.8 MPa, respectively, while PAMPS-1-4/PAAm-2-0.1 DN gel sustains a stress of 17.2 MPa, which is more than 20 times that sustained by the component SN gels. The fracture strain of the DN gel is $\lambda = 92\%$, which is much higher than that of both the PAMPS SN gel ($\lambda = 41\%$) and the PAAm SN gel ($\lambda = 84\%$). The stress–strain curve of the DN gel overlaps with that of PAMPS SN gel at small strains, suggesting that the first network contributes to increasing the elastic stress and the second one to the strain. Figure 3 demonstrates how the DN gel sustains a high compression while the PAMPS SN gel breaks down easily.[5] The stretching efficiency of the DN gels is also much greater than that of the component SN gels: the DN sample can sustain up to $\lambda = 75\%$ stretching and breaks at a stress of 0.68 MPa, while the PAMPS SN gel breaks at only $\lambda = 6\%$ and a stress of 0.05 MPa.

Our systematic study of the surface friction shows that the surface friction of hydrogels does not conform to Amonton–Coulomb's law, and exhibits very low frictional coefficients when the two gel surfaces have a repulsive interaction with each other. For example, when two pieces of negatively charged polyelectrolyte gels are allowed to slide over each other, the friction coefficient is as low as 10^{-3}, which is on the same order as that of a cartilage.[6–9] Prompted by the unique attributes of the hydrogels, we attempted to investigate the wear properties of the DN gel against an aluminum pin using a pin-and-flat wear tester, and found that the PAMPS-1-4/PAAm-2-0.1 gel containing 90% water shows a wear rate of 3×10^{-7} mm³/Nm, measured at a sliding velocity of 0.05 m/s under a load of 4.7 N (compressive stress of 0.1 MPa) for a sliding distance of 50 km. This pin wear rate is of the same order as an ultra-high molecular weight polyethylene (UHMWPE, GRU 1050, Kyosera Co.) control.

We should emphasize that two structural parameters are crucial for obtaining these mechanically strong gels. One is
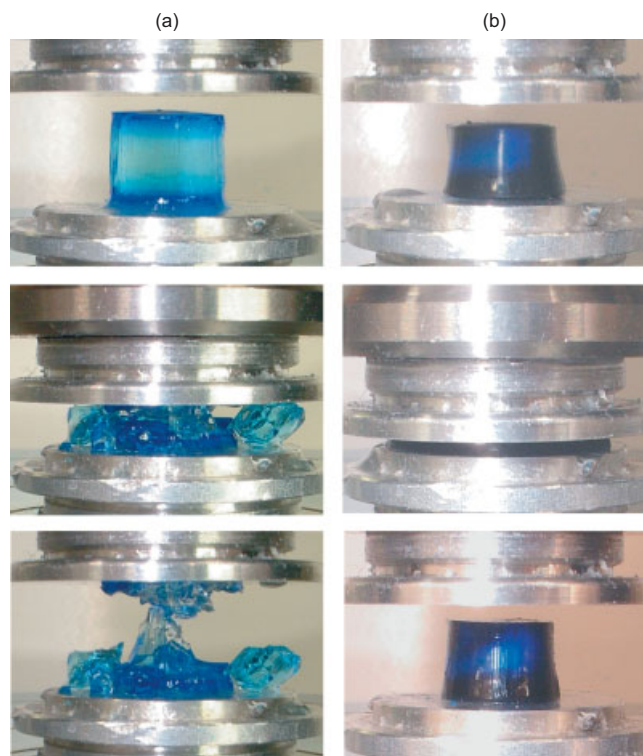

Fig. 3. Photographs demonstrating how a DN gel sustains a high compression. a) PAMPS-1-4 SN gel, b) PAMPS-1-4/PAAm-2-0.1 DN gel. Fracture stress: PAMPS SN gel, 0.4 MPa, PAMPS/PAAm DN gel, 17.2 MPa.

the molar ratio of the first to the second network, and the other is their crosslinking density. Figure 4 shows the effect of molar ratio of the second network to the first network on the fracture stress for PAMPS/PAAm DN gel. It is seen that a dramatic enhancement in the mechanical strength of the gel is obtained only when the molar ratio of the second network to the first network is in the range of several to a few tens. This is in strong contrast with conventional interprenetrated network (IPN) hydrogels, which do not exhibit any substantial improvement in mechanical strength.[10]
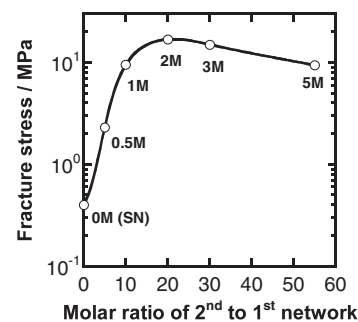

Fig. 4. Effect of the molar ratio of the second network to the first network on the mechanical strength of the PAMPS-4-1/PAAm-x_2-0.1 DN gels. The different composition ratios of the second network to the first were obtained by immersing the first network gel in solutions of the monomer constituting the second network with various concentrations. Numbers on the curve denote the value of x_2, the monomer concentration at which the second network was polymerized. The value at zero molar ratio is for the SN gel.

We also found that the crosslinking density for the first and second networks is critical for a dramatic increase in the mechanical strength of DN gels. A notable increase in the mechanical strength occurs when the first network is highly crosslinked and the second one is loosely crosslinked. If we keep the crosslinking density of the first network constant at approximately 4 mol-% and change that of the second network systematically from 0 to 0.1, 0.5, 1.0, and 2.0 mol-%, all the PAMPS/PAAm DN gels show a similar elastic modulus, regardless of the crosslinking density of the second network. However, the highest fracture strength and strain are obtained when the second network has a crosslinking density of 0–0.1 mol-%. Incorporation of a second polymer with a higher crosslinking density results in substantial lowering of the mechanical strength of the DN gel.

Use of the DN structure to obtain high-strength hydrogels is effective for a wide variety of network combinations, when the networks have appropriate structures, that is, a high molar ratio of the first network to the second network, with the first network highly crosslinked and the second network loosely crosslinked. Some examples are summarized in Table 1. DN gel consisting of poly(acrylic acid) (PAA) and PAAm shows a fracture stress 21 times higher than that of the PAA SN gel. The mechanical strength of the copolymer gel composed of AMPS and 2,2,2-trifluoroethyl acrylate (TFEA) (molar ratio of AMPS to TFEA is 3:1), P(AMPS-co-TFEA), increases 700 times when PAAm is incorporated as the second network. It should be noted that biocompatible and mechanically strong DN gels can be obtained by suitable combinations of natural with synthetic polymers. For example, one can use collagen or agarose as the first network and biocompatible synthetic polymers such as poly(2-hydroxyethyl methacrylate) (HEMA)

and poly(N,N′-dimethyl acrylamide) (PDMAAm) as the second network. The latter are used as soft contact lenses. The results, showing a dramatic enhancement in the mechanical strength, are summarized in Table 1. These biocompatible hydrogels have great potential as biomedical materials.

Since the polymers constituting the DN gels are miscible in water, as confirmed by light scattering, and have no specific interaction with each other, as elucidated by NMR, the dramatic increase in the mechanical strength is due neither to phase separation nor to molecular interaction between the two networks. Furthermore, the described experimental results show that the increased mechanical strength of the DN is not simply attributable to an increase in the chemical crosslinkage or physical entanglement between the two networks because DN gels with a loosely crosslinked second network exhibit the most prominent increase in the mechanical strength. We assume that the presence of appropriate fluidity (viscosity) to effectively dissipate the stress by the second network is crucial to enhance the strength. The highly crosslinked first network has a relatively high Young's modulus due to its high crosslinking density but is rather brittle. For example, PAMPS SN gel fractures into many small pieces under a compression of 0.4 MPa, suggesting that cracks develop easily in the gel (Fig. 3a). Similar brittle fracturing behaviors are observed for PAMPS/PAAm DN gels whenever the crosslinking density of the second network is higher than 1 mol-%. However, if the crosslinking density of the second network is 0.1 mol-%, which is the optimized condition, the gel can sustain up to 17 MPa compression and show only one or two large cracks at breaking. We have observed the process of compression in situ using optical interference, and found notable birefringence under a certain strain for the DN gels prepared at off-optimized conditions. This indicates that the mechanical stress applied is localized without effective dissipation. However, the DN gel prepared at the optimized condition shows very weak birefringence, which indicates that the mechanical stress is effectively and isotropically dissipated. This suggests that the loosely crosslinked second network effectively absorbs the crack energy by deforming the network conformation and/or sliding the physical entanglement points along the chains to prevent the crack growing to a macroscopic level. In other words, the increased mechanical strength of DN gels is largely attributable to the effective relaxation of locally applied stress and dissipation of the crack energy through combinations of two networks with different structure and densities.

Table 1. Compressive properties of hydrogels at room temperature.

First network	Second network	Water content [wt.-%]	Fracture stress σ_{max} [MPa]	Fracture strain λ_{max} [%]	$\sigma_{max}^{DN}/\sigma_{max}^{SN}$
PAMPS-1-4 [a]	–	92	0.4	41	–
	PAMPS-2.2-0.1	93	3.0	80	7.5
	PAA-1-0.1	92	2.3	75	5.8
	PAAm-2-0.1	90	17.2	92	43
PAMPS-1-8	–	98	0.006 [b]	0.13 [b]	–
	TFEA-1-0.1	52	1.6 [b]	4.9 [b]	267
PAA-1-4	–	99	0.1	65	–
	PAA-1-0.1	95	0.7	77	7.0
	PAAm-1-0.1	89	2.1	95	21
PAAm-1-1	–	93	0.7	98	–
	PAAm-1-0.1	92	5.4	92	7.7
P(AMPS-co-TFEA)-1-4	–	98	0.03	73	–
	AAm-1-0.1	93	21.0	97	700
Collagen [c]	–	93	0.26	52	–
	PDMAAm-1-0.1	87	2.9	53	11
Agarose [c]	–	96	0.02	20	–
	HEMA-2.5-0.1	66	2.4	87	120
Bacteria cellulose	–	–	–	–	–
	Gelatin	78	3.7	37	31 [d]

[a] P-x-y: P, x, and y denote the abbreviated polymer name, molar monomer concentration, and the crosslinker concentration in mol-% with respect to the monomer, respectively. [b] Stretching properties. [c] Physically crosslinked gel prepared from 2 wt.-% solution. [d] Relative to gelatin SN gel.

It should be emphasized that, although the high-strength DN gel has some similarities with regard to the preparation process to IPNs, it is different in concept. IPN structure is usually induced to combine various properties of each component material, such as adhesion to cells, water-absorbing ability, biocompatibility, biodegradability, etc.; these IPN hydrogels do not exhibit any notable improvement in mechanical strength in comparison to their original single-network structure.[10] The DN gel differs also from a fiber-reinforced hydrogel, which consists of a mechanically tough "dry" component (hydrophobic plastics) and mechanically weak "wet" component (hydrophilic gel), in that the mechanical properties of the composite are basically determined by the tough "dry" component while the hydrophilic component behaves as a water absorber, playing practically no role in improving the mechanical strength.[11] The high strength of the DN gels is not due to a linear combination of two component networks, like the common IPN or fiber-reinforced hydrogels, but due to a nonlinear effect of the binary structure. Although both of the two individual networks are mechanically weak, that is, the first one is stiff and brittle and the second soft and ductile, their combined DN gels are stiff but not brittle, ductile but not soft.

Experimental

DN hydrogels were synthesized by a (two-step) sequential network formation technique. For example, the first network of the PAMPS-1-4/PAAm-2-0.1 DN gel was synthesized from an aqueous solution of 1 M 2-acrylamido-2-methylpropanesulfonic acid (AMPS) containing 4 mol-% crosslinking agent, N,N′-methylenebisacrylamide (MBAA), and 0.1 mol-% initiator, 2-oxoglutaric acid, in a reaction cell consisting of a pair of glass plates with 2 mm spacing. This gel (first network) was then immersed in an aqueous solution of 2 M acrylamide (AAm), containing 0.1 mol-% MBAA and 0.1 mol-% 2-oxoglutaric acid, for one day until equilibrium was reached. The second network was subsequently synthesized in the presence of the first network. The gel thus prepared consists of two polymer networks entangled with each other. Details of the sample preparation are described in [2].

The compressive stress–strain measurements were performed on water-swollen gels using a tensile-compressive tester (Tensilon RTC-1310A, Orientec Co.). The cylindrical gel sample of 9 mm diameter and 4 mm thickness was set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate of 0.1 %/min. A tensile tester (Tensilon RTC-1150A, Orientec Co.) was used to carry out uniaxial stretching on specimens of 50 mm length, 5 mm breadth, and 3 mm height at a strain rate of 10 %/min. The strain λ under compression (or stretching) is defined as the change in the thickness (or length) relative to the freestanding thickness (or length) of the specimen. Details are described in [12].

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Enantioselective Discrimination of D- and L-Phenylalanine by Chiral Polyaniline Thin Films**

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Polyaniline is unique in the conjugated polymer family in that it undergoes a non-redox reversible doping/de-doping process based on simple acid/base chemistry.[1] Doping of polyaniline with a strong acid preferentially protonates the imine nitrogens, leading to an increase in conductivity from the insulating to the metallic regime.[2] The positive charge created along the backbone by protonation is counter-balanced by negatively charged counter-ions created from the doping acid, which causes a physical rearrangement of the polyaniline chains to accommodate them. The counter-ions make very important contributions to the properties of polyaniline through their interactions with the polymer backbone and/or their effects on the packing and orientation of polymer chains. Counter-ions can be used to improve solubility, processability, and conductivity by using functionalized protonic acids.[3–7] Wallace and co-workers[8,9] and Havinga et al.[10] demonstrated that chiral counter-ions can induce optical activity in achiral polyaniline. The polyaniline backbone is believed to adopt a helical conformation in the presence of chiral dopants.[10]

Inspired by our previous experience in gas and liquid separations using polyaniline,[11,12] we suggested the possibility of using chiral polyaniline for enantiomeric recognition.[13] The key concept is that the chiral chain conformations induced by the dopants are retained[14] when the dopants are removed from solid films,[13,15] thus creating a novel chiral polymer capable of recognizing a single enantiomer of an amino acid (Fig. 1). Here, we present visual, circular dichroism (CD), and

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