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ARTICLE TYPE

Shape Healable Tough Hydrogel

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Abstract

In this work, the physically broken tough agar/poly(dimethylacrylamide) double network hydrogel was healed by a two-step process using silica nanoparticle solution and thermal treatment. Not only the shape of the hydrogel can be integrated again, its mechanical properties of the healed hydrogel can achieve a very high recovery rate (64.1% of tensile strength) and the interface between two parts disappeared. This tough, mechanical-recoverable and shape-healable hydrogel is a suitable candidate for future tissue substitution due to its high mechanical properties and repairing mechanism.

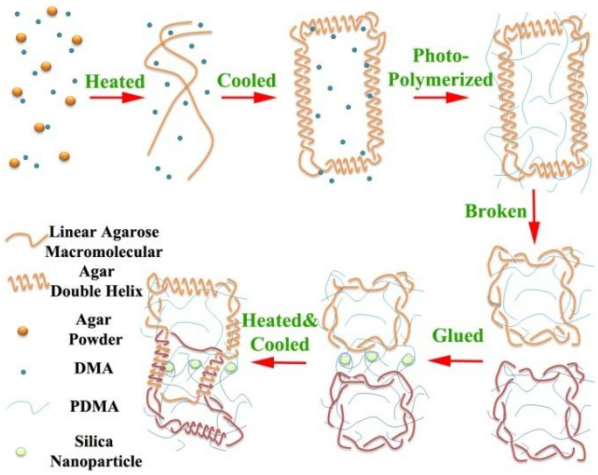
1. Introduction

Hydrogels are the combination of three-dimensional hydrophilic polymer networks and large amounts of water. They are formed by crosslinking polymer chains through covalent bonds, hydrogen bonding, Van der Waals interactions, or physical entanglements[1]. Due to their unique viscoelastic properties, hydrogels have been widely used as scaffolds in tissue engineering[2], carriers for drug delivery,[3] and superabsorbent in disposable products.[4] Astounding academic studies have been performed to study and develop multifunctional hydrogel in broad applications areas.[5] Unfortunately, rare hydrogels applications can be made because of their poor mechanical properties.[6]

In recent years, tremendous efforts have been made to develop double network hydrogels (DN gels) due to their excellent mechanical properties and easy fabrication process.[7] DN gels are produced by arranging inter/intra-molecular interactions to form two networks. The first network strengths the hydrogel while the second network integrates it. During stress, the first network absorbs the energy while the second network keeps the hydrogel unbroken.[8] Although DN gels can suffer >99% compressive strain without breaking and some special polymers, like the thermo-reversible sol-gel polysaccharides, have been used to recover their mechanical properties after stress[7a], the DN gels can break under strong tensile and shear forces which makes the DN gel difficult to be used in the practical and clinic applications, for example the cartilage substitute. Under hard athletic conditions, the tears in the natural cartilages, like meniscus, are easy to happen. Since the mechanical properties of current hydrogels are still not comparable with the natural cartilage,[9] the cartilages substitute made by hydrogels are vulnerable. Due to the unique structure of each cartilage and the high expense for surgery to replace the broken substitute, a tough hydrogel is able to heal itself repeatedly and sustain damage repeatedly, is the urgent target for hydrogel clinic applications.[10]

Self-healing hydrogels with the ability to repair themselves after damage are emerging as an interesting class of smart materials. Various hydrogels[11], such as chitosan[12], poly(vinyl alcohol)[13], poly(ethylene glycol)[14], and hybrid hydrogels[15], are developed to possess the self-healability via sol-gel transition.[16] With the help of the nanoparticles, such as graphene oxide, silica nanoparticles, and nanodiamond, more self-healable hydrogels have been developed recently.[17] For example, Rose et al. reported a rapid, simple and efficient way to recombine the gels and biological tissues through applying nanosilica solution as adhesives,[18] which is enticing for crowded emerging medical applications such as tissue engineering and surgery. However, the limit still exists that their mechanic properties are unsatisfactory. Tough and shape and mechanical properties recoverable hydrogels have not been developed till now.

Herein, a novel agar/poly(dimethylacrylamide) (PDMA) double network hydrogel was developed. With the help of silica nanoparticles which efficiently connect two piece of PDMA hydrogels,[18] the breakage of agar/PDMA double network hydrogel can be rejoined under 90 ^{o}C temperature heating (as shown in Scheme 1). 64.1% of tensile stress can be restored. To our best knowledge, this is the first time a tough DN gel was reported, which shows strong mechanical properties, facile and rapid healablility, and high remaining mechanical performance.



Scheme 1, Preparation of thermal-repaired and recoverable Agar/PDMA double network hydrogels

2. Experimental section

2.1 Materials

The agar, silica ludox TM-50 solution, N,N'-dimethylacrylamide (DMA), Irgacure 2959, and N,N'- methylenebis (acrylamide) (MBAA) were purchased from Sigma Aldrich.

2.2 Sample Preparation

The hydrogel was fabricated with double network structure using agar for the first network polymer and poly(dimethylacrylamide) (PDMA) for the second network polymer. In order to investigate the mechanical properties from different formulation, 5 sets of gels with 5 different formulations were fabricated. These formulations are listed in Table 1. Because it is the agar network enduring the majority of stress, high agar concentration is preferred. However, the viscosity of the solution would be too high for injection when too many agar powder is added. In that case, the agar concentration is fixed at 300 mg for 15 ml water. Because the second network should be elastic with low crosslinking density, the concentration of the crosslinker and initiator to the monomer is fixed at low level in this work as seen in Table 1. The ratio of the first network and the second network in DN gel system is investigated for the first to unveil their influence on DN gels' mechanical performance.

The DN gel preparation process is described here. Firstly, all the materials were added into 15 ml DI water according to the formulation in Table 1. After bubbling this mixture for 15 minutes with nitrogen gas, it is placed in an oil bath. The mixture turned into transparent liquid after about 10 min of heating at 90^{o}C. This phenomenon indicates the agar powder become soluble. Then, the transparent liquid was injected into a cylinder mold (r=5mm, h= 5mm) for compression test and a dog-bone mold for tensile test. The agar solution turns into gel when the temperature decreasing when agar form helix structure and crosslinked. After the injection, the gelation of the agar took 12 h in the refrigerator. Then the second network, PDMA, was cured by 1 hr UV irradiation to polymerize DMA by free radical reaction. A set of injection mold was fabricated to produce meniscus shape hydrogel using a 3D printer (FORTUS 250mc, STRATASYS).

Table 1. The formulations of gels

Sample	Agar(mg)	DMA(ml)	MBAA(mg)	Irgacure(mg)
$DN_{2.4}$	300	3.7	1.6	80.5
$DN_{3.0}$	300	4.6	2.4	100.6
$DN_{4.0}$	300	6.2	2.7	134.2
$DN_{4.6}$	300	7.1	3.1	154.3
$DN_{5.6}$	300	8.6	3.7	187.8

2.3 Characterization

The tensile and compressive tests were implanted by a commercial test machine (SHMADZU, AGS-X) with a 10 mm/min head to head speed for tensile and 10% strain per minute for compression. The agar gel is sol-gel thermoreversible. In order to determine the melting temperature of agar gel (T_M), Differential Scanning Calorimetric (DSC, TA Q20) is used.[19] Measurements were performed from 40 ^{o}C to 100 ^{o}C with a heating rate of 2 ^{o}C/min.

2.4 Healing Process

The two step healing of hydrogel was implanted by gluing the cylinder and dog-bone gels, which were cut into halves previously. Because the stable hydrogen bond can easily form between the carbonyl groups on the PDMA and silanol on the silica, silica solution can be used to glue PDMA hydrogel through physical crosslinking. In this work, the pure silica solution (TM-50, 50wt% silica in water) was used as the glue. The agar gel turns from gel to solution when it is heated above its melting temperature. Inspired by this phenomenon, the agar network can be reorganized through heat treatment. When the gel is heated above its melting temperature, the agar become sol and the diffusion of agar between contacted DN gels is accelerated.

Three kinds of healing processes were used: glued, heated, and heated & glued. The glued gels were attached at the cut cross section after wetting with the silica solution. The heated gels were attached at the cut cross section and sealed in a vial for 10 min at 70 ^{O}C The glued & heated gels were firstly glued and then heated with 10 min intermission. All the shape healed gels were kept for 3 days before testing.

A meniscus shaped gel was injecting molded and cut into halves to simulate the tearing. It was then glued & heated at the cross section to simulate the shape healing process.

3 Results and Discussions

3.1 Thermal healing temperature

In order to determine the thermal healing temperature, the T_M of agar in the agar/PDMA double network hydrogel is determined by the DSC. As seen in the Fig. 1, the peak around ~67 ^{o}C is identified as T_M.

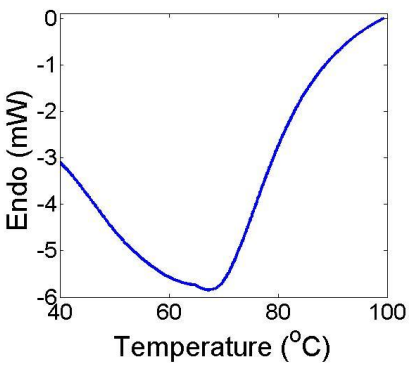


Fig.1. T_M of agar in the agar/PDMA double network hydrogel determined by DSC.

3.2 Compressive Test

The optimized formulation was investigated by the compressive test. The gels with five different DMA concentrations were compressed. Because the unbroken of all the gels, the nominal stress σ_{nom} increased continuously with the increasing strain (Fig. 2 (a)). In order to obtain the fracture of the internal structure of gels, the corresponding σ_{true}-ε plots were used (Fig. 2 (b)). The true compressive ($\sigma_{true}=\lambda\ \sigma_{nom}$) is calculated by force per cross-sectional area. The λ is the deformation ratio ($\lambda = h/h_0$, h_0 is the original thickness of cylinder gel, h is its current thickness). The strain (ε) is calculated as $\varepsilon=100\%\times(h_0-h)/h_0$. The maxima strain in the σ_{true}-ε plots indicates the failure strain (ε_f) where the gel specimens fail. The corresponding σ_{nom} with the ε_f is used as the fracture strength (σ_f) for gel specimen. The toughness of the gel specimen is the integration of σ_{nom} and ε until the ε_f. The toughness is defined as:

$$U = \frac{\int_0^{\varepsilon_f} F\, ds}{\pi R^2}$$

where$F$ is the loading, ε_f is the facture stress, and s is the displacement to the corresponding strain.

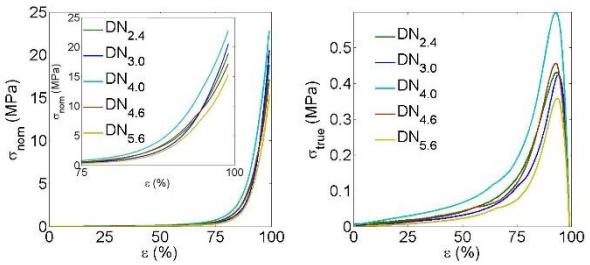


Fig.2.Compressiveresults of DN gels with different formulations: (a) strain vs. nominal stress plot and (b) strain vs. true stress plot.

Because the DN gel is so elastic that it returns to its original shape even after 99% strain compression. Therefore, the nominal stress increases continuously when the strain increasing. However, the corresponding true stress can reach its maxima when the contacting area is considered. The maxima of the true stress indicates the onset of failure in the gel specimen. The corresponding nominal stress and the strain with the onset of failure are the fracture stress and strain representing the maximum performance of the DN gel.

As seen in Fig. 2(a), the hydrogels kept integrated after 99% compression. As seen in Fig. 2(b), the fractures of the DN gels with different formulations fall in the range of 90% to 99% of strain. These results indicate that the agar network is homogeneously dispersed with in the PDMA network to support the hydrogel.

As seen in the Table 2, similar ε_f were achieved by all samples. The maximum σ_f and U were presented by $DN_{4.0}$ sample. The mechanical properties of the hydrogel mainly depend on its crosslinking density. The addition of the low crosslinked PDMA network diluted the concentration of the densely crosslinked agar network as well as the overall crosslinking density of the DN gel[20]. As a result, the mechanical properties of the DN gel with increasing PDMA concentration decreased, like the trend of $DN_{4.0}$, $DN_{4.6}$ and $DN_{5.0}$. However, the higher concentration of second network polymer in the hydrogel can also result in the better mechanical performances due to the additional osmotic pressure[21]. The trend of $DN_{2.4}$, $DN_{3.0}$, and $DN_{4.0}$ represents this effect[21-22] that the second network exerts additional osmotic pressure to toughen the DN gel. In that case, the concentration of the agar and PDMA in DN gel is required to be optimized to balance the crosslinking density and additional osmotic pressure. The $DN_{4.0}$ sample presented the optimization of the benefits from both networks and achieved the best mechanical performance.

Table 2. The compressive results of DN gels with different formulations

Sample	ε_f (%)	σ_f (MPa)	U (kJ/m^3)
$DN_{2.4}$	94.1 ± 1.0	7.3 ± 0.3	1011 ± 98
$DN_{3.0}$	95.0 ± 0.7	8.5 ± 0.5	999 ± 128
$DN_{4.0}$	93.9 ± 0.9	9.8 ± 0.6	1385 ± 169
$DN_{4.6}$	94.3 ± 0.6	7.9 ± 0.8	1057 ± 189
$DN_{5.6}$	94.6 ± 0.5	6.6 ± 0.3	597 ± 75

3.3 Healing Process

In order to investigate the healing process influencing the healed gels, stretching and tensile tests were implemented. The diffusion at the cut cross-section is essential. In this work, it is firstly investigated by stretching of the gels healed by different methods as seen in Fig. 3. The failure of a material generally involves two sequential process: initial fracture formation (nucleation) and following fracture propagation (growth). The different failure behaviors of gels with different healing treatments indicate their different network structures. All the specimens failed at the interface because the diffusion of the polymers at the interface cannot achieve as homogeneous as other unbroken parts. For the Glued specimens, the failure growth rapidly into fracture after the nucleation formed. This is because only the PDMA network is healed. Because the agar in the DN gel performs the pull out mechanism during stretching[7g, 23], very little stretched agar was observed at the interface for the Glued specimens which indicated the diffusion of agar at the interface is poor without special treatment. Different from the Glued specimens, the Heated specimens did not fail immediately after the nucleation. Instead, the entire interface broke into halves at small strain due to the poor integration of PDMA and the agar network was pulled out which restricted the growth of the failure. The Glued & Heated specimens with integrated PDMA and agar networks performed the best elongations in all specimens. The interface stayed connecting after the nucleation because the integrated double networks restrained the growth of the fracture. In order to investigate the structures and diffusion at the interface with more details, tensile tests was implemented. All dogbone specimens were cut at the middle and healed by different methods. The healing strength and elongation were measured to analyze the healing ratio.

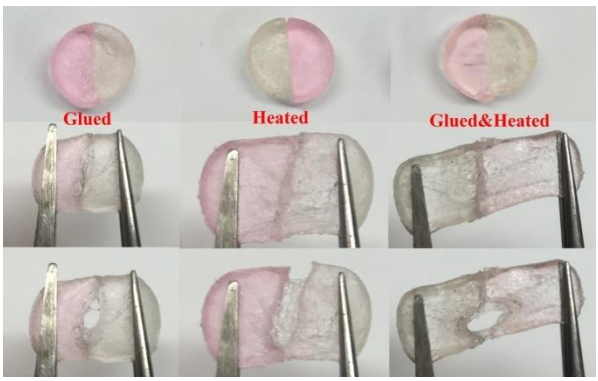


Fig. 3. The stretching of the hydrogels with different healing process.

As seen in Fig. 4, the healed strengths are not as strong as the original fracture strength. Although Heated gel present almost half of the mechanical properties as the Origin gel which is far better than the Glued gel, the Glued & Heated gel achieved ~ 65% mechanical properties in strength and toughness of the Origin gel. These results are similar like the stretching results that the diffusion of the agar network is the key to improve healing. However, it is the interaction at the cross-section to prevent the nucleate and prevent the fracture growing. A two-step healing process is necessary for double network hydrogel.

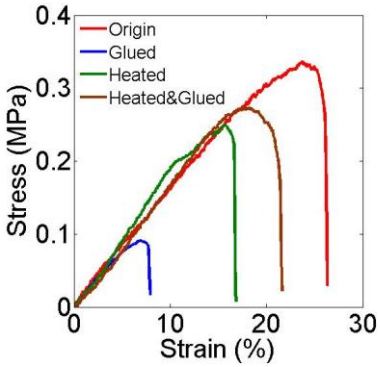


Fig. 4. The tensile results of gels with different healing processes.

Table 3. The tensile results of gels with different healing processes.

Samples	Strain (%)	Strength (kPa)	Toughness (kJ/m^2)
Origin	26.3 ± 2.9	337 ± 47	104 ± 26
Glued	7.9 ± 0.8	91 ± 14	7 ± 1
Heated	16.8±1.7	168 ± 57	47 ± 8
Heated & Glued	21.6 ± 0.2	216 ± 21	65 ± 1

As shown in Fig. 5, an artificial cartilage (meniscus) was fabricated to simulate the restoration of cartilage broken. A transparent agar/PDMA double network hydrogel was inject molded into meniscus shape (Fig. 5(a)). After serious tear, the meniscus was broken into two pieces (Fig. 5(b)). The silica nanoparticles were used to glue the breaking point firstly. However, the interface can still be clearly found (Fig. 5(c)). After heating, the interface between the two pieces can be barely seen which indicated that not only the glued PDMA hydrogel was involved in the healing process but also the agar network was reconnected during the Heat Treatment (Fig. 5(d)). Adapting particle surface chemistry of nanosilica provides a strong particle adsorption on gel surface by improving specific interaction such as hydrogen bonding, which can effectively recombine the PDMA gel.[6a, 24] Under heating, the thermo-reversible sol-gel polysaccharide agar clusters can refold and transform into linear conformation for better diffusion, and on a subsequent cooling, the agar reforms a double-helix structure and aggregates into helical bundles, which regenerate the agar cross-linked network, leading to hydrogel reconnection at broken interface.[7a]

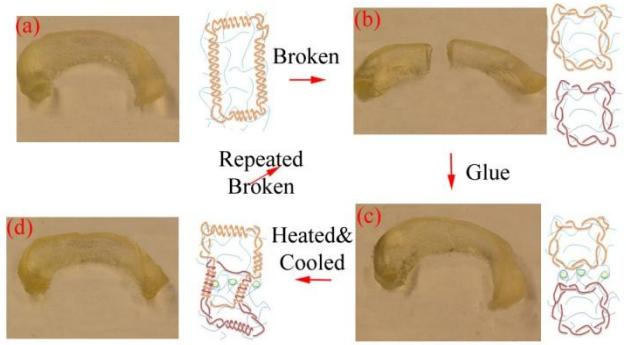


Fig. 5. Thermal healing of meniscus shaped gel.

4 Conclusions

In this work, a shape-healable and tough hydrogel was fabricated. Because there are two networks producing a double network gel, a two-step process was proposed. Silica solution was used to integrate the structure of the hydrogel first. After that, heating above the melting temperature of agar gel was performed to make strong connection. The silica glue of the poly(dimethylacrylamide) makes sure the connection of the agar at interface and the heating accelerates the diffusion of agar network. The healed gel presents ~64% of its original tensile strength and toughness and there were no interface can be found. This tough and healable hydrogel structure is the perfect candidate for feasible repairable substitutions for tissue engineering applications.

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Notes

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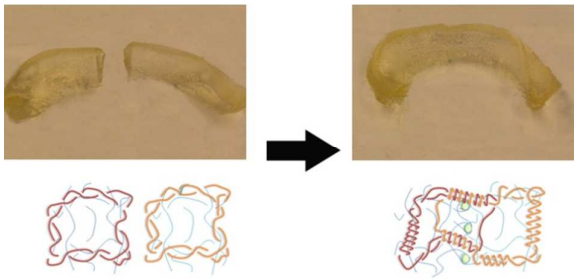
Graphical Abstract



The artificial meniscus made by double network hydrogel was recovered by a two-step healing process.