Bioinspired fully physically cross-linked double network hydrogels with a robust, tough and self-healing structure

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The conventional covalently cross-linked double network (DN) hydrogels with high stiffness often show low toughness and self-healing property due to the irreversible bond breakages in their networks. Therefore, scarcity of hydrogels that possess simultaneous features of stiffness, toughness, and autonomous self-healing properties at the same time remains a great challenge and seriously limits their biomedical applications. While, many natural materials acquire these features from their dynamic sacrificial bonds. Inspired by biomaterials, herein we propose a novel strategy to design stiff, tough and self-healing DN gels by substitution of both covalently cross-linked networks with strong, dynamic hydrogen bond cross-linked networks. The prepared fully physically cross-linked DN gels composed of strong agar biopolymer gel as the first network and tough polyvinyl alcohol (PVA) biopolymer gel as the second network. The DN gels demonstrated multiple-energy dissipating mechanisms with a high modulus up to 2200 kPa, toughness up to 2111 k J m^{-3}, and ability to self-heal quickly and autonomously with regaining 67% of original strength only after 10 min. The developed DN gels will open a new avenue to hydrogel research and holds high potential for diverse biomedical applications, such as scaffold, cartilage, tendon and muscle.

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1. Introduction

Self-healing ability is one of the remarkable properties of biological materials such as skin, bone and wood. Furthermore, hydrogels for biomedical applications require simultaneously high stiffness, toughness and self-healing ability to retain shape, resist fracture and heal possible created cracks, respectively. Whereas, most of the synthetic hydrogels with good self-healing performance show low stiffness and/or toughness, which limits their use in many biomedical applications, including scaffold, cartilage, blood vessel, tendon and muscle. Therefore, many works have been done to improve toughness and strength of the self-healing hydrogels, including preparation of various nanocomposite [1-5], double network (DN) [6-8] and hydrophobically associated hydrogels [7, 9-13]. However, most of the developed self-healing hydrogels still suffer from low strength and stiffness [5, 7, 10-16]. Among the developed self-healing hydrogels, DN hydrogels [6-8] exhibited relatively higher mechanical properties, which was correlated to their strong network entanglement [17]. Design of DN hydrogels are commonly based on using two chemically cross-linked networks [18], and only a few hybrid physically/chemically cross-linked DN hydrogels were recently designed by replacing covalent bonds of the first network with non-covalent bonds [14, 19-21]. For instance, Chen et al. designed a DN gel including hydrogen bond cross-linked agar as the first network, and a covalently cross-linked polyacrylamide (PAAm) as the second network [6, 22, 23]. Furthermore, other researchers have synthesized a series of hybrid ionically/covalently cross-linked DN gels using anionic polysaccharides (alginate, gellan gum and carrageenan) as the first ionically cross-linked network and PAAm as the second, covalently cross-linked network. In spite of good strength and toughness of the developed hybrid cross-linked DN gels, their autonomous self-healing is still a slow and low efficient process due to slow

chain diffusion and irreversible breakages of covalent bond in chemically cross-linked network(s) [7, 24, 25].

Therefore, designing a new generation of DN gels comprising two non-covalent associated networks is required to prepare robust and autonomous self-healing gels. Chen et al. [7] have recently designed first fully physically cross-linked DN gels comprising of hydrogen bond associated agar gel as the first network and hydrophobically associated PAAm as the second network. The developed DN gels exhibited high-energy dissipation and extensibility. However, these hydrogels were relatively soft with tensile strength of 267 kPa, and also their self-healing efficiency and speed were relatively low (≈40% recovery of initial strength after 24 h at room temperature) [26].

Many natural materials gain their high strength and toughness from dynamic sacrificial bonds and hidden length [27, 28]. Since, the dynamic sacrificial bonds break and re-form dynamically before the fracture of the main molecular backbone, therefore, giving a ''self-healing'' property to materials. For instance, random coil PEVK (Pro-Glu-Val-Lys) domains of Titin (the largest known protein), are believed to reversibly unfold by breakage of sacrificial hydrogen bonds to permit extension of the muscle [29]. Herein, inspired by toughening and healing mechanisms of biological materials, we propose a novel strategy to design stiff, tough DN gels with self-healing ability by substitution of both covalently cross-linked networks with strong, dynamic hydrogen bond cross-linked networks. Moreover, different from the network structures of hybrid cross-linked and chemically cross-linked DN gels that the second network remains intact during loading, here both the networks of Agar/polyvinyl alcohol (PVA) DN gel can participate in energy dissipation during the deformation process. The second PVA network helps to bear force as the first agar network does, resulting in a DN gel with high toughness. We expect that the ductile and tough (not soft) PVA as the

second network will provide an additional platform to dissipate energy, and heal the broken network structure.

To the best of our knowledge, this is the first report for the preparation of biopolymer-based DN gels with neutral physically cross-linked networks, demonstrating strong mechanical properties and fast, efficient self-healing behavior using a simple one-pot method.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA Mowiol 28−99, $M_W\sim145000$ g/mol and degree of hydrolysis >99%) was obtained from Aldrich. Agar powder (with gel strength of 750 ± 50 g/cm^2 and melting point of 85 ± 5 ℃) was purchased from Scharlau, Spain.

2.2. Preparation of Agar/PVA DN gels

Briefly, a homogeneous solution of PVA was first obtained by dissolving desired amount of PVA in 100 ml distilled water at ~95 °C under vigorous stirring for nearly 2h; the flask was sealed with plastic film in the whole process to prevent water loss. Subsequently, a predetermined amount of the agar powder was added to the stirring solution of PVA. After 30 min, the obtained clear solution was poured into 5 ml syringes to obtain cylindrical shape specimens. By gradually cooling down the solution to room temperature, agar formed gel at 30–40 °C. Afterward, through a freezing/thawing (F-T) cycle (freezing at −10 °C for 1 h followed by thawing for 2 h at room temperature) a large number of crystallites were generated in PVA. The PVA SN (single network) gel was prepared with the same procedure, except no agar was added. The sealed samples were kept at refrigerator (at 5-10 °C) until conducting experimental works. Total concentration of Agar/PVA in

water was kept constant at 22 wt%, and DN gels were prepared with different proportions of agar and PVA; DN gels were designated as Agar-x/PVA-y, where x and y indicate the weight percentage of agar and PVA in the total amount of the Agar/PVA hydrogel, respectively (e.g. Agar-1/PVA-21 stands for Agar/PVA DN gel containing 1 wt% agar and 21 wt% PVA).

2.3. Characterization

For the spectroscopic studies, the dried samples were milled and mixed with dried KBr powder to make pellets. The Fourier transform infrared spectroscopy, FTIR (Perkin Elmer Spectrum 1) analysis was conducted with the subtraction of KBr background to investigate possible molecular interactions between PVA and agar interpenetrating networks, as well as the crystallization of PVA. For microscopic investigation, the frozen hydrogels in liquid nitrogen were fractured, freeze-dried and gold sputtered. Cross-sectional micrographs were taken using scanning electron microscopy, SEM (MIRA3 FEG-SEM, Tescan). The mechanical properties of cylindrical hydrogel samples (diameter of 1 cm and length of 6 cm) were determined using a Zwick Roell test machine with 1 kN load cell and crosshead speed of 10 mm/min. For reproducibility, at least 6 samples were measured for each gel, and the results were averaged.

3. Results and discussion

3.1. Design and preparation of Agar/PVA DN gels

Compared with synthetic materials, natural materials are gaining increasing interest because of their high biocompatibility and biodegradability without toxic by-products. Completely different from other chemically cross-linked and hybrid cross-linked DN gels, Agar/PVA DN gels in the present study were prepared by a

green and one-pot method using water as solvent, without using any chemical cross-linkers, organic surfactants, monomers and initiators. Fig. 1 schematically shows the procedure of preparing physically cross-linked Agar/PVA DN gels using a simple solution blending method. First, agar and PVA were dissolved in hot water and formed linear random coil macromolecules [6, 30] (Fig. 1 (a)). Then, the resulting solution was cooled down to room temperature; a coil-to helix transition occurred in agar allowing the formation of first network via hydrogen bond-associated agar helix bundles [6, 22, 30] (Fig.1 (b)). Once the first agar network formed, the agar gel and PVA in the same pot were subjected to a freezing-thawing (F-T) cycle to form the second physically cross-linked network of PVA via the formation of large numbers of crystallites [31-35] (Fig. 1 (c)). Interestingly, both the agar and PVA networks were cross-linked with strong, dynamic hydrogen bonding associations, but with different configurations, i.e. helix bundles and crystallites, respectively.
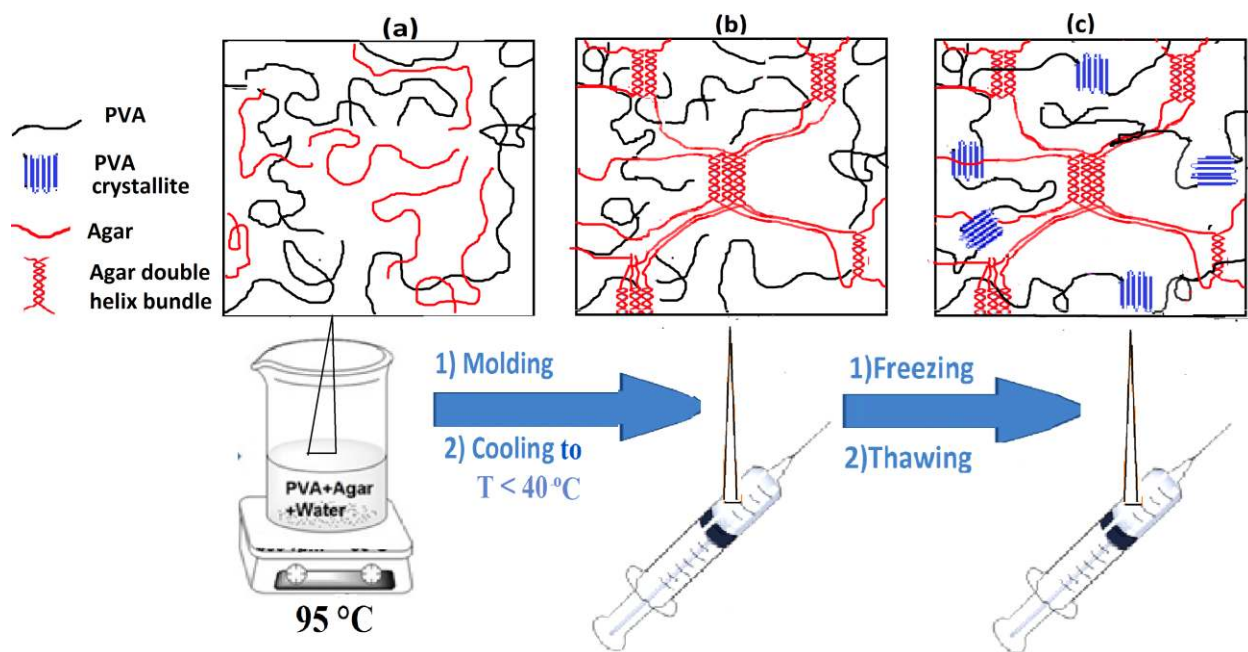

Fig. 1 Schematic illustration of the preparation process and the networks formation of Agar/PVA DN gels.

Fig. 2 (a) shows FTIR spectra of agar, PVA and Agar-1/PVA-21 DN gels before and after the freezing-thawing cycle. The broad and strong absorption at 3100–3700 cm^{-1} is attributed to the symmetrical stretching of –OH groups in PVA and agar [36, 37]. Also, the –OH stretching peak of PVA is shifted to a lower wavenumber with incorporation of agar, which can be correlated to the intermolecular hydrogen bond interactions between hydroxyl groups on the PVA and agar molecular chains [38], as shown schematically in Fig. 2 (b).

Furthermore, comparison of FTIR spectra of samples before and after the freezing-thawing cycle in Fig. 2 (a) reveals that the intensity of the band at 1140 cm^{-1} is increased after the freezing-thawing process. According to the literature [36, 39, 40], this band is mainly originating from the symmetric stretching of C–C or stretching vibration of C-O in the crystalline regions of PVA, and the intensity of this peak increases with increasing the degree of crystallinity of PVA. Therefore, these results exhibit that the crystallinity of PVA and Agar/PVA was increased after the freezing-thawing process.
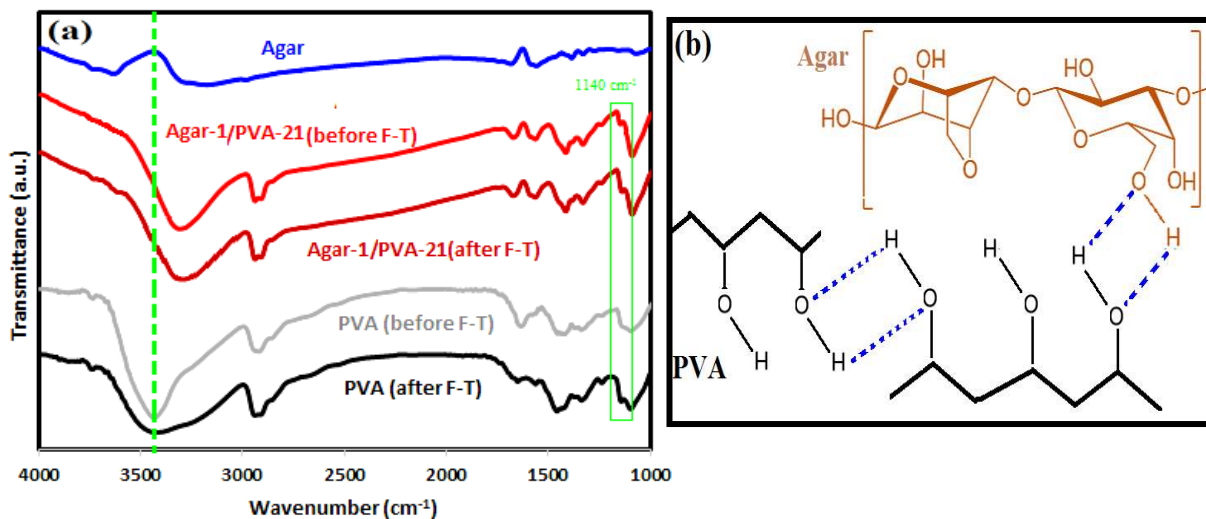
Fig. 2 (a) FTIR spectra of agar, PVA and Agar-1/PVA-21 DN gel before and after the freezing-thawing (F-T) cycle, (b) scheme of the intermolecular hydrogen bond interactions between PVA molecular chains and agar.
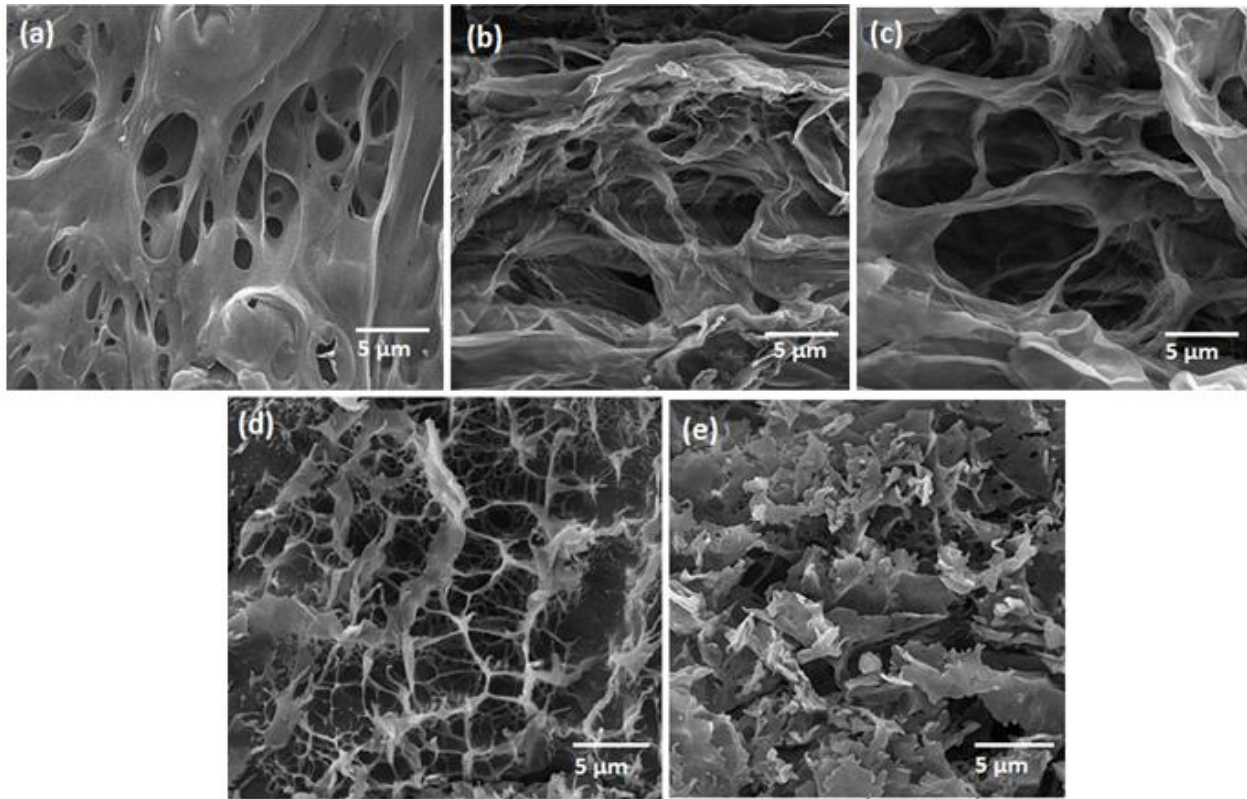
Fig. 3 The cross-sectional SEM micrographs of (a) PVA SN (single network) gel, (b) Agar-1/PVA-21, (c) Agar-3/PVA-19, (d) Agar-5/PVA-17 and (e) Agar-8/PVA-14 DN gels.

3.2. Morphological observation

Representative cross-section micrographs of samples are shown in Fig. 3. Physically cross-linked PVA SN gel exhibits pores with diameters less than 5 µm, along with smooth and thick pore walls (Fig. 3 (a)). It can be clearly seen from Figs. 3 (b) and (c) that the pore diameters are increased to 5–10 µm for Agar-1/PVA-21 and Agar-3/PVA-19 DN gels. Interestingly, further increasing agar content led to more irregular morphology with thinner pore walls and cobweb-like fiber networks inside the pores in Agar-5/PVA-17 DN gel (Fig. 3 (d)). Finally, the pores are mostly filled with agar during the freezing-thawing process in Agar-8/PVA-14 DN gel. Zhang et al. [35] also observed similar morphology changes in freeze-thawed carrageenan/PVA gels with increasing carrageenan concentration.
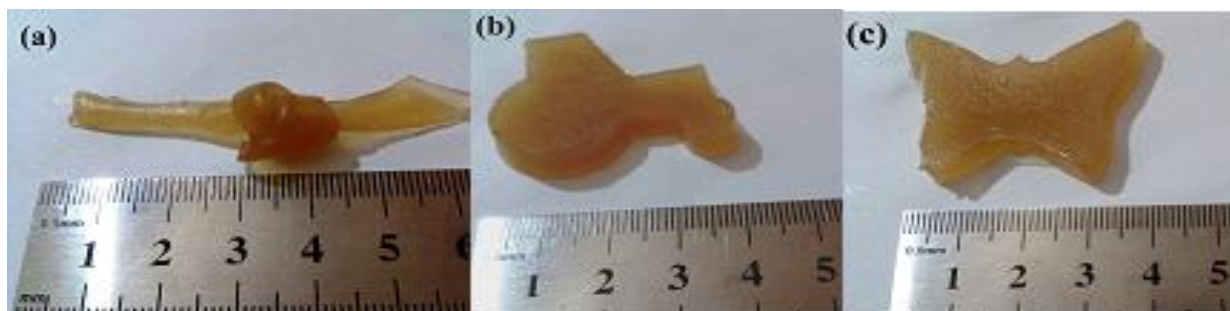
Fig. 4 Agar-1/PVA-21 DN gel showing (a) strong and flexible mechanical properties, (b) and (c) free-shapeability.

They correlated these morphological changes to the entanglement of rigid carrageenan molecules with PVA chains, and consequently confining the PVA chains during the freezing-thawing process.

3.3. Mechanical properties of Agar/PVA DN gels

Fig. 4 shows that Agar/PVA DN gel is strong and flexible, as it can be knotted (Fig. 4 (a)). Also, this fully dynamically cross-linked DN gel demonstrated good free-shapeability, as it can be cast into various complex shapes with fine details (Figs. 4 (b) and (c)), requiring for many biomedical applications such as artificial tissues (cartilages, tendons, and muscles) with specific geometrical shapes to achieve their biologically mimicking functions.

The Young's modulus (E), tensile strength (σ_f), strain (ε_f) and toughness (W) of PVA SN gel (physically cross-linked single network) and Agar/PVA DN gels (physically cross-linked double networks) are compared in Fig. 5. PVA SN gel exhibited good extensibility (ε_f of 367%), but relatively low modulus, strength and toughness (E of 124 kPa, σ_f of 464 kPa, and W of 844 kJ m^{-3}). However, by adding a small amount of agar (1 wt%), Agar/PVA DN gel achieved relatively higher mechanical properties (E of 221 kPa, σ_f of 817 kPa, ε_f of 390%, and W of 1700 kJ m^{-3}). Interestingly, the E, σ_f and W of Agar-1/PVA-21 DN gel simultaneously increased to ≈180, ≈176 and ≈200% of those of PVA SN gel.
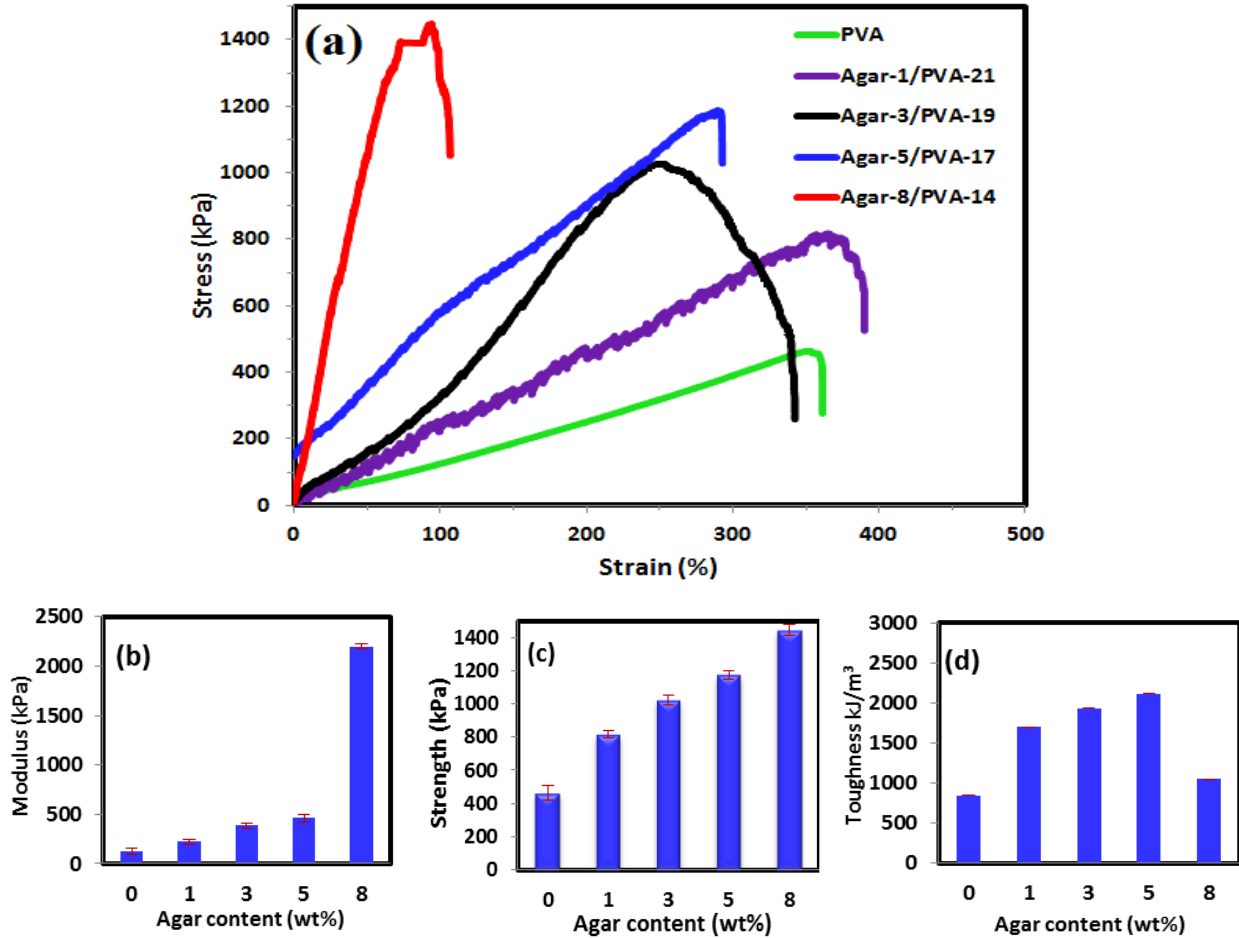
Fig. 5 (a) Typical tensile stress−strain curves of Agar/PVA DN gels containing various agar concentrations. Effect of agar concentrations on the (b) Young's modulus, (c) tensile strength and (d) toughness of Agar/PVA DN gels.

Furthermore, the strain of DN gel slightly increased with including 1 wt% agar, whereas further increases in the agar content led to decrease of that which might be attributed to the enhanced cross-link density and chain entanglements at high agar concentrations. Also, as it can be seen in Fig. 5, the mechanical properties of gels have strong dependence on agar concentration. The increase of agar content from 1 to 8 wt%, led to noticeable enhancement in tensile strength and elastic modulus, as Agar-8/PVA-14 DN gel achieved a maximum strength of 1423 kPa and modulus of 2200 kPa, which are ≈3 and ≈18 times higher than those of PVA SN gel, respectively. Surprisingly, the obtained strength and modulus for fully physically

cross-linked Agar/PVA DN gels are comparable to those reported for hybrid cross-linked DN gels [6, 8, 18, 41], but higher than those of Agar/PAAm [23], Alginate/PAAm [14, 42], Carrageenan/PAAm [43] and Gellan gum/PAAm [44] hybrid cross-linked DN gels. Fig. 5 (d) also shows that the toughness of DN gels also depended strongly on agar concentration, and it increased proportionally to agar concentration. At 1 wt% of agar, toughness was almost doubled from 845 to 1700 kJ m^{-3}. The gels achieved a maximal W of 2111 kJ m^{-3} at 5 wt% of agar, which is comparable to that of hybrid cross-linked DN gels [42, 44].

As the balanced mechanical properties observed at a small agar content of 1 w%, unless otherwise stated, below we mainly focused on Agar-1/PVA-21 DN gel prepared at agar concentration of 1 wt%.

3.4. Toughening and stiffening mechanisms of Agar/PVA DN gels

Recent studies have shown that the incorporation of various polysaccharides (alginate, gellan gum, carrageenan, and agar) [6, 14, 41, 45, 46] and also PVA [33] as a first (physical and reversible) network into an irreversible second covalent network can significantly enhance the mechanical properties of DN gels, implying that toughening of covalent gels with physically cross-linked gels is a general phenomenon. Our novel design strategy is demonstrated to use a strong, tough agar gel as the first physically cross-linked network, and a ductile, tough PVA gel as the second physically cross-linked network (instead of chemically cross-linked soft networks such as PAAm) for fabrication of a new type of stiff, tough, fully physically cross-linked DN gel.

Current toughening mechanisms of DN gels are mainly based on chemically cross-linked DN gels. For chemically cross-linked DN gels, the toughening mechanisms are mostly based on permanent rupturing of the first network into small clusters during deformation and consequently protecting and toughening the second

chemically cross-linked network [47]. Therefore, the second-network in DN gels often remains intact. While, in order to design a tough hydrogel, it is necessary to embed multiple toughening mechanisms into the hydrogel to dissipate a significant amount of mechanical energy during the deformation process [48]. In contrast to the network structures of hybrid cross-linked and chemically cross-linked DN gels, here we proposed a novel DN gel that both of its networks are participating in energy dissipation, resulting in a tough DN gel. As shown schematically in Fig. 6, the second PVA network helps to bear the applied force as the first agar network does; instead of the fracturing of first network into separated clusters, here the agar molecular chains are progressively pulled out from the aggregated helical bundles retaining continuous network of agar during the entire process of stretching [7] (Fig. 6). Meanwhile, hidden lengths of the amorphous regions between crystallites of PVA are expanded along with the rotation of crystalline lamellae to orient perpendicular to the stretching direction [31]. Further stretching of DN gel leads to lamellar breakup (unzipping of crystallites) of PVA [32, 49] and converting the lamellar structure of crystallites to the microfibrils [31, 32] yielding a DN gel with high toughness (Fig. 6).

On the other hand, PVA SN gels alone are ductile and do not have appropriate stiffness due to inadequate density of crystallites. However, when the stiff agar interpenetrates into the PVA network to build up a strong three-dimensional network via helical bundles, the first agar network not only enhances toughness, but also increases the modulus of DN gel. With increasing agar concentration from 1 to 8 wt%, the density of physically cross-linked network of agar gel increases, which is revealed in exponentially enhancement in the modulus of DN gels (Fig. 5 (b)), implying that the stiffness of first network is important in designing robust DN gels.
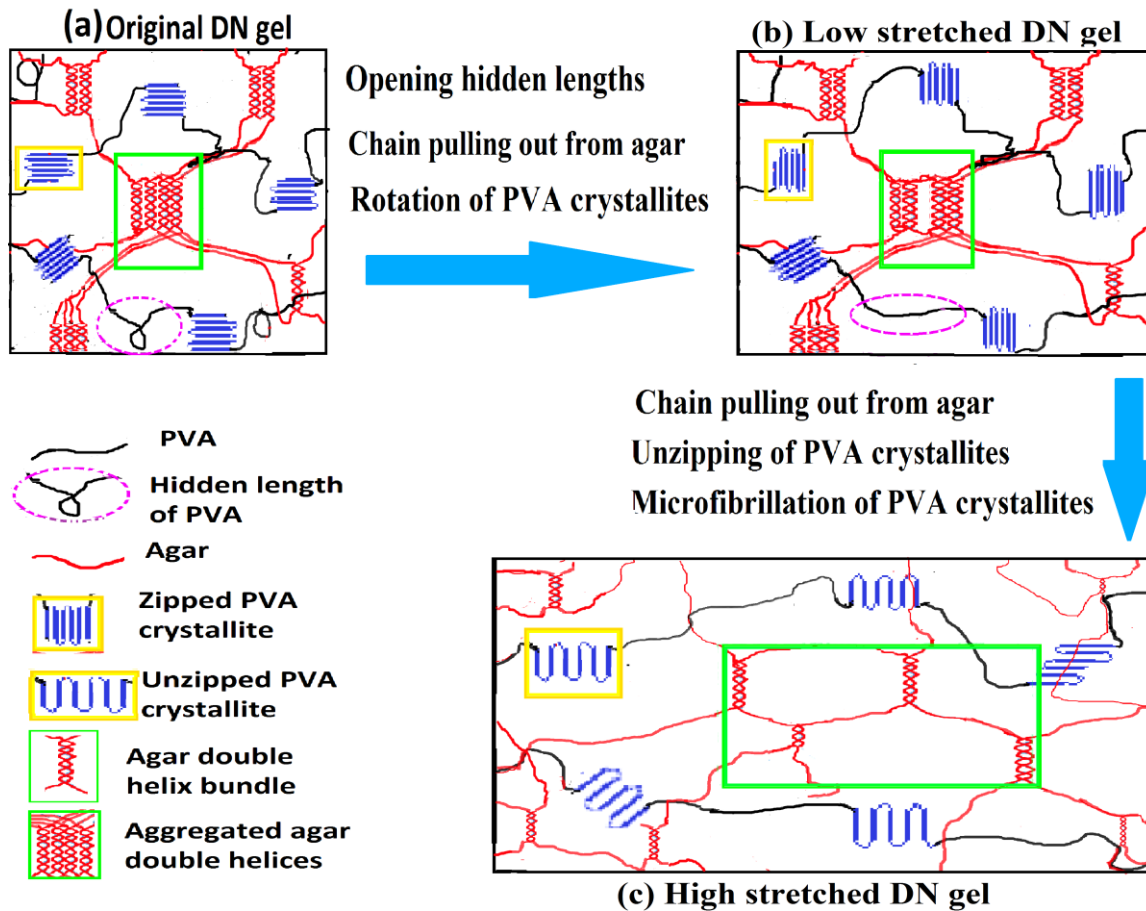
Fig. 6 Schematic illustration of (a) original, (b) low stretched and (c) high stretched Agar/PVA DN gel structure.
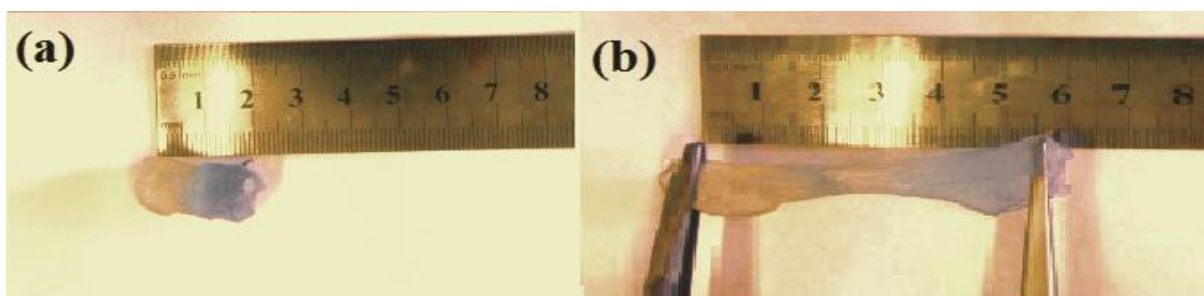
**Fig. 7** Photographs demonstrating the self-healing property of Agar-1/PVA-21 DN gel; two virgin specimens (one of them was colored with methylene blue for clarity) were cut with a razor blade, and then the cut fresh surfaces of two halves brought into contact rapidly. After 10 min healing, (a) they merge into a single piece at room temperature without any stimulus, and (b) it can be stretched to about 250% strain.

It should be noted that the stiffness and toughness are negatively correlated in chemically cross-linked gels. However, the inverse relation between these two mechanical properties no longer holds true in the fabricated Agar/PVA DN gels. As shown in Figs. 5 (b) and (d), both stiffness and toughness of Agar/PVA DN gels enhanced with increasing the agar concentration. This phenomenon can likely attributed to simultaneous stiffening and toughening effects of the first agar network in the designed DN gels.

3.5. Self-healing of PVA and Agar/PVA DN gels

In addition to simultaneous enhancement of stiffness and toughness, fully physically cross-linked Agar/PVA DN gels showed extraordinary self-healing performance at room temperature even in the absence of external stimuli or healing agent. This phenomenon is shown in Fig. 7. Two virgin cylindrical gels (one of them was colored with methylene blue for clarity of the interface) were cut with a razor blade, and then the cut fresh surfaces of two halves brought into contact rapidly within a plastic syringe. After 10 min healing, they merged into a single piece hydrogel at room temperature (Fig. 7 (a)). The self-healed hydrogel could stretch up to ~2.5 times of its original length (Fig. 7 (b)).

Moreover, self-healing property of gels was quantitatively evaluated with conducting tensile tests on the original and self-healed samples. The fracture stress recovery percentages of the self-healed gels were determined and defined as self-healing efficiency.
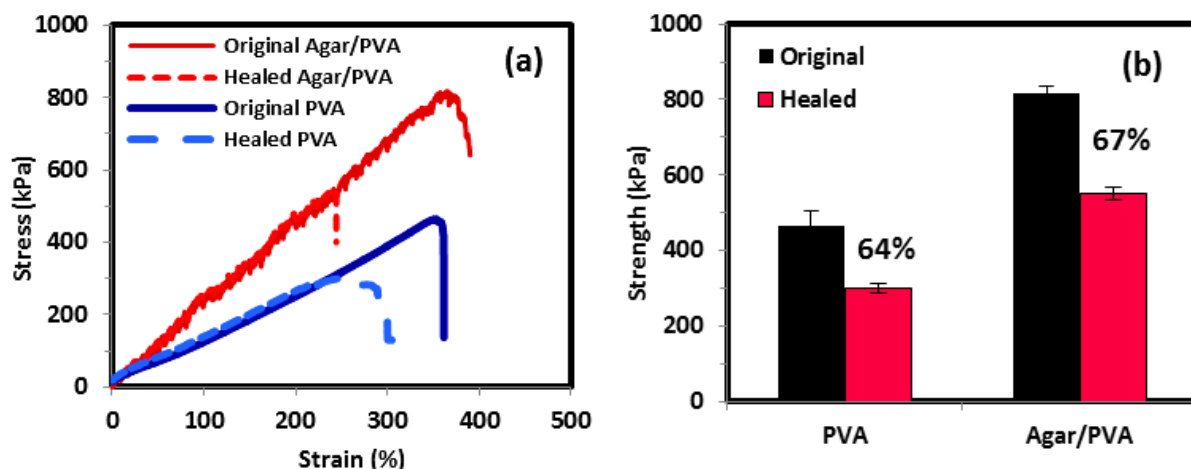
Fig. 8 (a) Stress-strain curves of the original and self-healed PVA and Agar-1/PVA-21 gels at room temperature for 10 min, and (b) comparison of tensile strength of original and healed hydrogels. Numbers denote the healing efficiency of samples.

Stress−strain curves of the virgin and healed samples are shown in Fig. 8 (a). It can be seen from Fig. 8 (b) that more than half of the self-healing process of gels occurred within 10 min. As the tensile strength of healed Agar/PVA DN gel was already up to an impressive ~551 kPa after only 10 min self-healing process, this is ~67% of the strength of original uncut DN gel. To our knowledge, as far as autonomously self-healed hydrogels are concerned, the recovered fracture stress of ~551 kPa is the highest value reported up to now. More impressively, this recovered fracture stress of the healed Agar-1/PVA DN-21 gel is even higher than that of virgin PVA SN gel (~464 kPa). Further extending the healing time and temperature did not significantly improve the healing level of DN gel (data not shown).

These results reveal that the existence of dynamic cross-links created by reversible hydrogen bonds has a crucial role in a quick and efficient self-healing performance of materials. The autonomous self-healing ability of DN gel is accomplished by the re-formation of physically cross-linked network at the interface by the diffusion of

PVA chains across the interface of two cut surfaces and physical entanglements of polymer chains, and their subsequent inter-chain hydrogen bond interactions [34]. As unlike many other reported DN gels which are mostly based on chemically cross-linked network(s) [14, 19-21, 47], dynamically cross-linked Agar-1/PVA-21 DN gel can autonomously and quickly restore most of its strength without consuming extra energy or cut surface treatment.

In Table 1, we further compared the healed strength (i.e. maximum tensile strength achieved after the autonomous healing process without any external stimuli at room temperature) of hydrogels reported in the literature, as function of their corresponding tensile strength of the original uncut specimens. It can be clearly seen that only a few successful autonomous self-healing hydrogels have been developed until now, and most of them are based on hydrophobically associated [7, 9-13], nanocomposite [1-5] and DN [6-8] hydrogels. It is worth noting that the autonomous healing of the most developed hydrogels is a very slow process, which commonly accomplished within 12-48 h at room temperature. On the other hand, the self-healing hydrogels mostly require cut surface treatment with healing agent and/or elevated temperature to exhibit efficient healing at short time. For instance, Okay et al. [12] observed a maximum healing efficiency of 30% after 30 min for hydrophobically modified poly(acrylic acid) (PAAc) at room temperature. While, a high healing efficiency of 75% achieved when the cut surfaces were treated with surfactants at 80 °C due to increased solubility of hydrophobic moieties in aqueous solutions along with enhanced chain mobility on the two cut surfaces indicating that re-formation of the hydrophobic associations is confined by low solubility of the hydrophobes.

Table 1

Comparison of the original strength, healed strength, healing efficiency and healing time of hydrogels reported in the literature.

Gel Type	Original Strength (kPa)	Healed Strength[a] (kPa)	Healing Efficiency (%)	Healing Time
P(NIPAm-co-AM)[b]/clay [5]	56	50	90	48 h
HPAAc[c]/CTA [12]	200	60	30	30 min
Agar/HPAAm[d] DN gel [7]	267	109	40	24 h
PAAm/graphene oxide (GO) [2]	350	315	90	24 h
PVA/PEG[e] hybrid cross-linked DN gel [8]	630	410	68	48 h
PVA SN gel (current work)	464	294	64	10 min
Agar-1/PVA-21 DN gel (current work)	845	551	67	10 min

[a]Maximum tensile strength achieved after the autonomous healing process without any external stimuli at room temperature, [b]poly(N-isopropylacrylamide-co-acrylamide), [c]hydrophobically modified poly(acrylic acid) (PAAc) chains with cetyltrimethylammonium, [d]hydrophobically associated PAAm and [e]poly(ethylene glycol).

Moreover, Table 1 shows that most of the prepared hydrogels with good self-healing property display low original and recovered strengths (less than 300 kPa), which limits their use in many biomedical applications. Among them, self-healing double network hydrogels demonstrated relatively high mechanical properties [18, 47]. Agar/hydrophobically associated PAAm (HPAAm) DN gels [7] displayed ≈40% recovery of initial strength after 24 h at room temperature, which was less than that of corresponding neat HPAAm (50% recovery). This again shows that re-formation of the hydrophobic associations is a slow process at room temperature, and also the presence of hydrophilic agar in DN gel reduced the self-healing efficiency of HPAAm, probably due to decreased hydrophobic interactions of HPAAm in cut surfaces. Most recently, Zhao et al. [8] constructed a shape memory and self-healing hybrid cross-linked DN hydrogel with a chemically cross-linked

poly(ethylene glycol) (PEG) interpenetrated by physically cross-linked PVA, which demonstrated relatively high tensile strength of 630 kPa, and self-healing efficiencies of 21 and 68% after 1 and 48 h at room temperature, respectively. The slow self-healing process of this hybrid cross-linked DN gel can be attributed to the presence of chemically cross-inked PEG, which decreases the number of H-bonds and physical links at the interface, and also enhances irreversible covalent bond breakages. Whereas, our designed fully physically cross-linked DN gel demonstrated not only simultaneous high stiffness and toughness, but also rapid self-healing at room temperature. Furthermore, as seen in Table 1, this mechanically strong self-healable hydrogel can regain a fracture stress of ~551 kPa, which is the highest autonomous healed strength that reported so far.

4. Conclusions

In this work, we developed a nontoxic, simple and one-pot method to design stiff, tough and free-shapeable DN gels displaying fast, efficient autonomous healing by substitution of both the covalently cross-linked networks with strong, dynamic hydrogen bond cross-linked networks. This new design strategy is demonstrated to construct a fully physically cross-linked DN gel composed of a first network formed via the strong hydrogen bond-associated agar helix bundles, and a second network built up through the ductile, tough PVA gel cross-linked with the formation of a large numbers of crystallites.

Agar/PVA DN gels demonstrated high mechanical strength up to 1445 kPa and toughness up to 2111 k J m^{-3}, which are comparable to those of conventional chemically cross-linked DN gels and higher than hybrid cross-linked DN gels. More importantly, increasing the modulus of conventional chemically cross-linked hydrogels usually leads to a reduction in their toughness. Whereas, the stiffness and toughness of Agar/PVA DN gels simultaneously increased as agar

concentration increased. This phenomenon can likely attributed to simultaneous stiffening and toughening effects of the first agar network in the designed DN gels. Furthermore, almost all of the current generated self-healing hydrogels with good self-healing property display low strength and stiffness, which limits their use in many biomedical applications. Whereas, our designed fully physically cross-linked DN gels demonstrated not only simultaneous high stiffness and toughness, but also rapid self-healing as well as high strength recovery at room temperature due to their reversible cross-linked network structures. As, these strong self-healable DN gels could autonomously and quickly restore most of their strength (as high as ~551 kPa) only after 10 min healing process without assistance of extra energy, cut surface treatment or healing agents.

The combination of strong mechanical properties, free-shapeability and rapid self-healing ability of the developed DN gels, along with their easy, green and one-pot preparation from the biopolymers, will open a new avenue to gel research and make the materials have diverse applications in biomedical fields.

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