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# Super-tough and thermo-healable hydrogel – promising for shape-memory absorbent fiber

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Recoverable hydrogels with high stretch and toughness have been synthesized by one-step radical polymerization. They consist of covalently crosslinked polyacrylamide (PAAm) and ionically crosslinked carrageenan. Such double network (DN) hydrogels can be stretched beyond 20 times its initial length, and their fracture energy reached a high value of  $\sim 9500 \text{ J/m}^2$ . By comparing hydrogel tensile properties at different temperatures, the contribution of ionic network to the toughness was quantitatively clarified in percentage for the first time. The stretched hydrogels were completely healed by short treatment at a mild temperature. Through drying at stretch, they were also transformed into stiff absorbent fibers that still preserved their shape memory of wet state.

## 1. Introduction

Hydrogels, pervading nature and technology, are highly customizable as three-dimensional networks of hydrophilic polymer chains. Based on their flexible synthesis techniques and soft physical characteristics, hydrogels have been the interesting material of choice for many biological and clinical applications. They serve as scaffolds for tissue regeneration, carriers for drugs and proteins, and adhesives or barriers at tissue and material interfaces.<sup>1-5</sup> However, most synthetic hydrogels are very weak, and much more brittle than natural hydrogels such as cartilage and tendons.<sup>6,7</sup> Their application scope is severely limited by their poor mechanical properties, particularly the application in engineering area. In textile engineering, hydrogels have been manufactured into well-known absorbent fibers.<sup>8,9</sup> The existing absorbent fibers are only used as staples in hygiene application, due to their poor toughness in tension and compression. They cannot be woven or knitted into an independent textile that survives frequent stretches and pressures in wet state. In order to obtain strong absorbent fibers, hydrogels have been engineered onto other fiber surfaces.<sup>10-12</sup> However, these composite fibers usually lose several advantages of hydrogels, such as flexibility and transparency. Here, we present a tough and shape-memory absorbent fiber from 100% hydrogel with surprising durability against tension and compression, benefiting from a new generation of hydrogel with double-network (DN) structures.

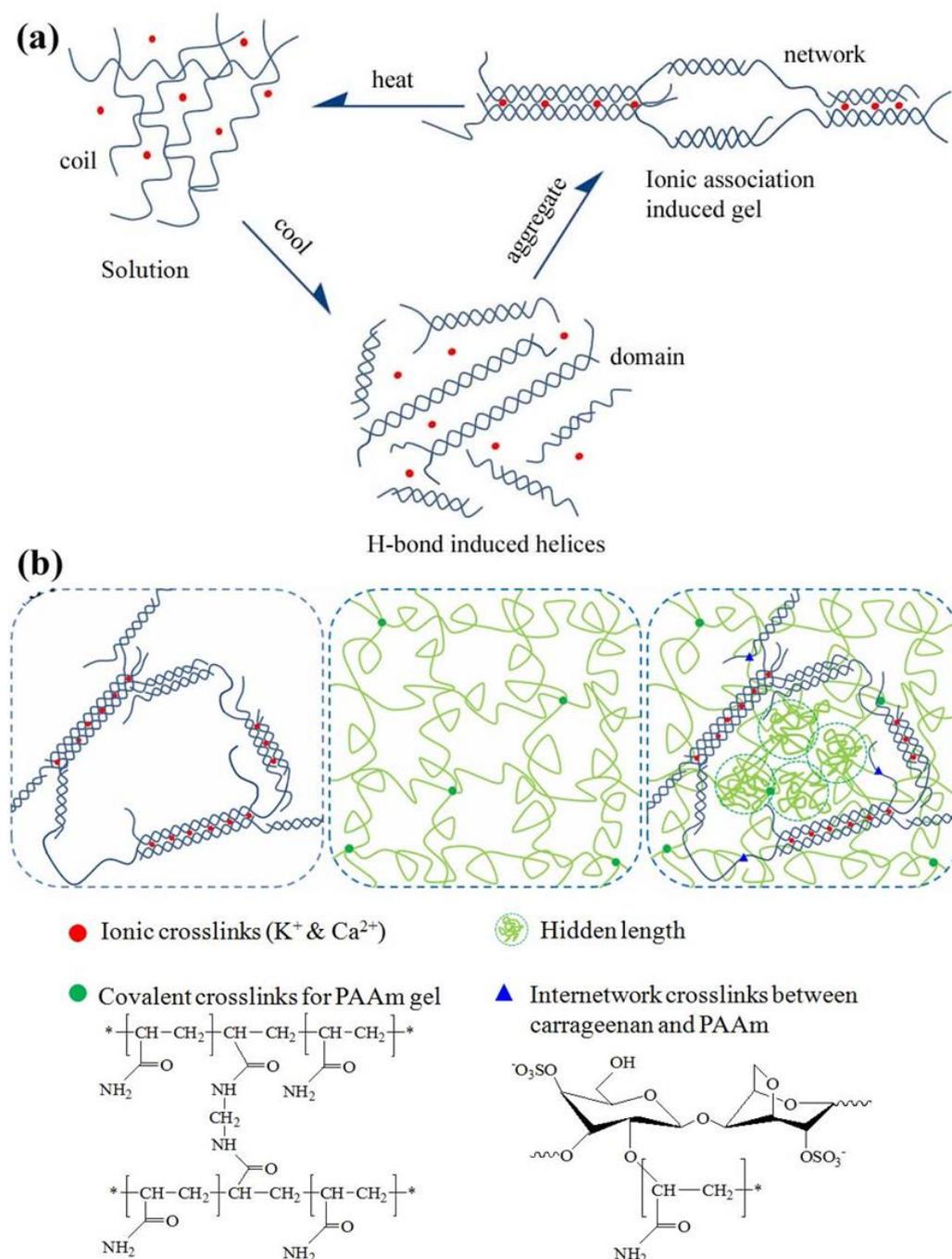
A common single-network hydrogel has poor cooperation between polymer chains in its whole volume, because of the inhomogeneity of its crosslink network structure. It usually begins to break at the weakest link and shows a poor mechanical property.<sup>13,14</sup> With a DN structure, hydrogel mechanical properties can be improved, which degree depends on the synergism between the two networks.<sup>15-21</sup> For example, combination of two covalent networks with much different

crosslink densities improved the hydrogel fracture energy up to  $300 \text{ J/m}^2$ ,<sup>15</sup> interpenetration of a covalent network and an ionic network showed fracture energy of  $\sim 9,000 \text{ J/m}^2$ .<sup>19-21</sup> The latter is superior to the early systems by presenting much higher toughness and also recoverability. However, the recovery of reported DN system needs a significant period at a rather high temperature of  $80 \text{ }^\circ\text{C}$ . To develop a more versatile and practical DN system, we tried another smart natural polymer - carrageenan. Carrageenans are a family of linear sulfated polysaccharides extracted from red seaweeds. They are made up of repeating galactose and 3, 6-anhydrogalactose units, both sulfated and nonsulfated. Three types of carrageenans have been commercialized with their sulfate groups in different amounts (molecular structures are shown in ESI Fig. S1): Kappa-carrageenan (KC) has only one sulfate per disaccharide; Iota-carrageenan (IC) has two sulfates per disaccharide; Lambda-carrageenan (LC) is more highly sulfated.<sup>22</sup> Both KC and IC solutions form melttable gels, which melting temperature varies with the concentrations of themselves and existing cations (e.g.,  $\text{K}^+$  and  $\text{Ca}^{2+}$ ).<sup>23,24</sup> Being different from alginate that directly gels with  $\text{Ca}^{2+}$ , carrageenan crosslinks through ionic association between cations and double helix units that formed at a sharp temperature (Fig. 1a). For the salt-free IC solution of 5.0 wt%, its sol-gel transition occurs at  $35 \text{ }^\circ\text{C}$ .<sup>23</sup> With 0.2 M KCl added, the IC solution of 1.0 wt% and 2.5 wt% concentrations show higher sol-gel temperature of  $54$  and  $60 \text{ }^\circ\text{C}$ , respectively. This property enables the IC hydrogel to heal quickly at mild temperatures below  $70 \text{ }^\circ\text{C}$ . Through combining this ionic network with a covalent network of PAAm, a more flexible hydrogel system can be created, which completely heals at a mild temperature and preserves its memory even after being dried into stiff fibers. Such fibers dried from that hydrogel may be assembled into smart medical textiles for wound dressing application.

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**Fig. 1** The schematic illustrations of hydrogel network structures: a) reversible gelling mechanism of carrageenan; b) pure carrageenan gel, pure PAAm gel, and carrageenan / PAAm DN gel.

## 2. Materials and methods

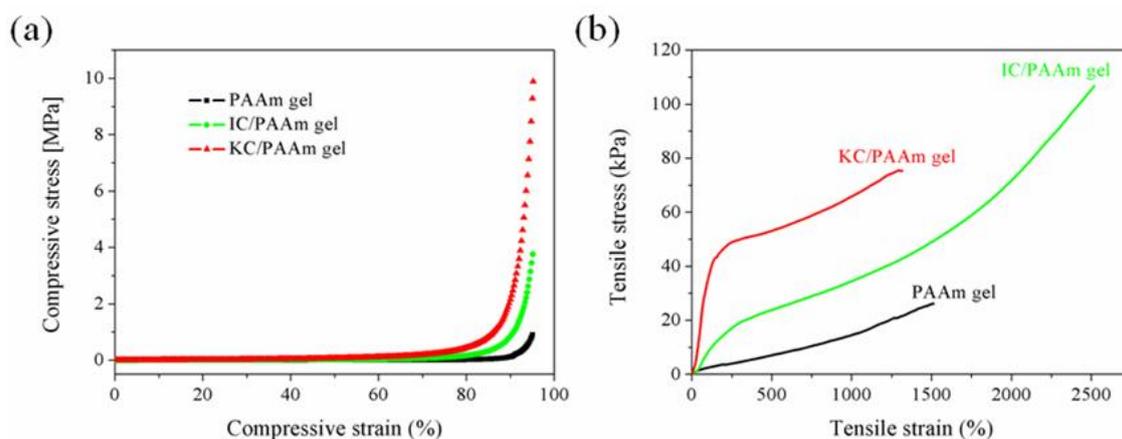
### 2.1 Materials

Two types of carrageenans were purchased from Sigma-Aldrich Co.: Iota-carrageenan (IC, 4.48 wt%  $K^+$  and 2.68 wt%  $Ca^{2+}$  tested by ICP) and kappa-carrageenan (KC, 14.57 wt%  $K^+$ , 5.50 wt%  $Ca^{2+}$  tested by ICP). Acrylamide (AAm), potassium

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**Fig. 2** Compression (a) and stretch (b) performances of PAAm gel, KC / PAAm DN gel, and IC / PAAm DN gel.

peroxydisulfate (KPS), and N, N-methylenbisacrylamide (MBA) were also purchased from Sigma-Aldrich Co. and used as received.

## 2.2 Synthesis of hydrogels

The DN hydrogel was synthesized by one-step radical polymerization in an aqueous solution of carrageenan and acrylamide (AAm), where water content was fixed at 86.0 wt%. Typically, designated amounts of carrageenan and acrylamide were dissolved in deionized water at 70 °C under continuous magnetic stirring. Then, predefined amounts of KPS and MBA were added under stirring. The obtained mixture was quickly poured into a polystyrene petri dish ( $\Phi$  55 mm  $\times$  10 mm) and tightly sealed to avoid water evaporation. The sealed dish was put into an oven at 70 °C for 6 hours, then stored at 25 °C before further treatments and tests. Similarly, cylindrical hydrogel strands were obtained by replacing the petri dish with plastic tubes of preferred diameters.

## 2.3 Characterizations

Tensile properties were measured by the Instron 4411 testing machine (USA) with a 5.0 N load cell at a strain rate of 50.0 mm/min and at room temperature without special notation. The starting distance between two clamps was set as 10.0 mm. The rectangle samples for the tensile test were cut into 2.5  $\times$  8.0  $\times$  30 mm<sup>3</sup>. Apparent values of tensile strain at break (%), tensile stress at break (kPa), Young's modulus (kPa) and fracture energy (J/m<sup>2</sup>) were recorded from the instrument. The fracture energy (J/m<sup>2</sup>) is the integral of stress (N/m<sup>2</sup>) over the extension distance (m). The same instrument was also used to measure hydrogel compression property at a rate of 10 mm/min. For each sample, at least 6 specimens were tested and taken average to obtain reliable results, although only a single curve of typical specimen was demonstrated in some figures. In order to investigate the gel's energy dissipation mechanism, the specimen was also treated by successive and progressive stretches: it was stretched to 2 times

and released in the 1st cycle, then stretched to 3 times and released in the 2nd cycle... many more cycles were applied to the same specimen. In each loading and unloading cycle, the hysteresis loop was assessed to analyze the energy dissipation of gel samples. All dry fiber samples were well conditioned in a standard room (T = 25 °C, RH = 60%) before the tensile test. FTIR spectra were measured on a PerkinElmer spectrum 100 spectrometer with an ATR accessory.

## 3. Results and discussion

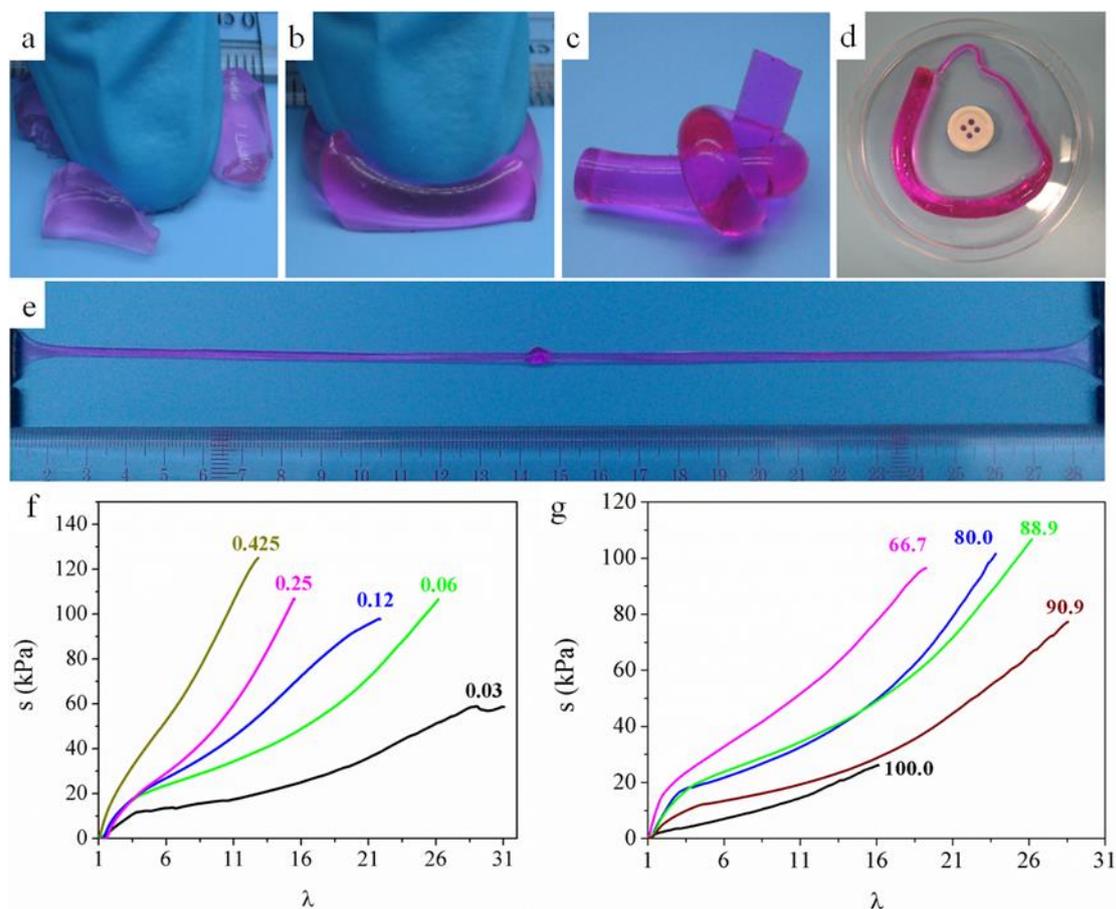
The DN hydrogels were synthesized via a sequential network formation technique: the covalent PAAm network was formed through the radical polymerization at 70 °C while the ionic carrageenan network was formed through double helix association with cations upon cooling (Fig. 1b). A representative composition consists of carrageenan and AAm in a mass ratio of 1/8, with 0.06 wt% MBA and 0.6 wt% KPS (both based on AAm amount). Both KC and IC were prepared into DN hydrogels respectively. For comparison, pure carrageenan gels and PAAm gels were also prepared respectively, using the same component concentrations in the DN hydrogel.

These new DN hydrogels demonstrate surprisingly high toughness under both compression and tension. As shown in Fig. 2a, when the hydrogels are compressed to only 5% of original thickness, the DN hydrogels (KC / PAAm and IC / PAAm) retain integrity very well. After unloading, they almost completely recover their shapes in a few seconds. In comparison, the pure PAAm hydrogel is difficult to recover even after a long storing. Its compression strength 0.95 MPa is much lower than those of DN hydrogels (9.9 and 4.0 MPa). Pure KC and IC hydrogels are easily broken into fragments under a modest pressure below 5 kPa, which are not shown in Fig. 2a. Both KC and IC also remarkably enhance the tensile strength of PAAm hydrogel: from 26 kPa up to 75 and 107 kPa, respectively (Fig. 2b). In comparison, KC endows the hydrogel higher modulus of 40.8

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**Fig. 3** In comparison to pure IC gel (a), the IC / PAAm DN gel shows extraordinary mechanical properties: b) pressing DN gel; c) knotting; d) skinning through a narrow hole; e) knotting & stretching; and stretching performances of IC / PAAm DN gels: f) varying ratio of MBA / AAm; g) varying ratio of AAm / (AAm and IC) (wt%).

5 kPa but lower stretchability of 1300%, while IC creates a tougher hydrogel with total fracture energy of  $\sim 9500$  J/m<sup>2</sup>. Since a tough hydrogel with high stretchability is preferred for fiber manufacturing, only IC / PAAm DN hydrogel system is further discussed in detail in following sections.

10 The enhanced toughness of IC / PAAm hydrogel against compression is visually demonstrated in Fig. 3a and 3b. Its high flexibility and stretchability are also directly observed by knotting and extending a strand synthesized in a tube template (Fig. 3c and 3e). To confirm its outstanding toughness against both  
15 compression and tension, a thick hydrogel strand ( $d = 10.05$  mm) is successfully led through a much narrower buttonhole ( $d = 2.23$  mm) (Fig. 3d and supplemental video S1). After going through the tiny hole, this hydrogel strand quickly recovers in size. No obvious necking or plastic deformation is observed during the stretch. Its thinning and extension ability is much higher than all  
20 existing rubber materials, indicating great engineering potential in special textiles.

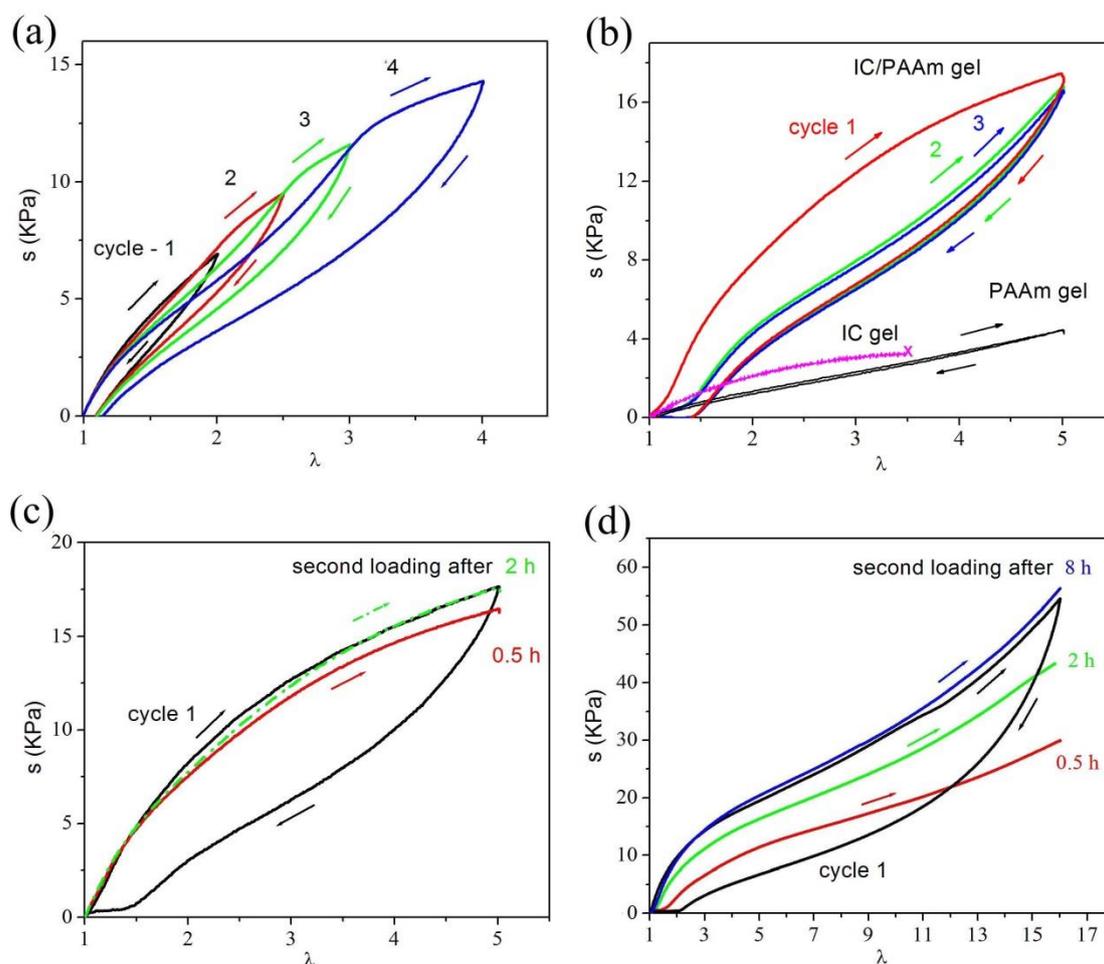
The IC / PAAm hydrogel system is further analyzed in detail

on the effect of composition. As the amount of MBA increases, the stiffness and brittleness of the hydrogel increase monotonically (Fig. 3f) (see Table S1 for detail results). The highest fracture energy is obtained at an intermediate MBA content of 0.06%, which corresponds to the optimum crosslink density of PAAm network. For the IC network, the cross-linker cations ( $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ ) were used at their original concentrations of commercial products without any variations. The DN hydrogel's Young's modulus decreases with the increasing AAm proportion (Fig. 3g). At about 89 wt% AAm composition (based on dry weight), its tensile stress at break and fracture energy reached  
35 maximum values of 26.2 times (26.2 x) and  $\sim 9500$  J/m<sup>2</sup>. This optimal IC / PAAm hydrogel does not show obvious strain rate dependence as shown in Table S1. It should be noted that the DN hydrogel of 66.7 wt% AAm composition shows obvious cracks and necking upon stretch (shown in Fig. S2). Because the  
40 hydrogel contains too much IC and produces many cracks upon stretch, the PAAm chains cannot bridge all the cracks right at their beginning stage, resulting in visible cracks and simultaneous

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**Fig. 4** Repeated stretch performance of IC / PAAm DN gels at progressive stretches lower than 5 (a) and at a constant stretch 5 together with pure 2.0 wt% IC gel and 12.0 wt% PAAm gel (b); thermal treatment effect on following stretches of the specimen with a stretch 5 (c) and 16 (d).

necking on the specimen. However, this specimen still extends over 18 x before failure, being longer than that of pure PAAm gel. This observation indicates that the carrageenan takes the lead in fracture or acts as a sacrificial bond while PAAm retains the hydrogel as a whole till the end.

Many natural materials have such sacrificial bonds that break before the main structural framework (often the covalent chain) is broken, and also hidden length that is a part of molecular chain constrained from stretching by the sacrificial bond.<sup>25</sup> These sacrificial bonds are weaker than common covalent bonds, but create an energy dissipation mechanism by breaking themselves instead of the main framework and thus greatly increase the toughness of host matrix. Several sacrificial bonds are reported as ionic link, hydrogen bond, and organo-metallic bond.<sup>26</sup> For our DN hydrogels, cation-mediated (Ca<sup>2+</sup>, K<sup>+</sup>) ionic crosslinks between carrageenan helices serve as sacrificial bonds (shown in Fig. 1b), increase stiffness and toughness of hydrogels through energy dissipation. Due to the constraint of carrageenan network,

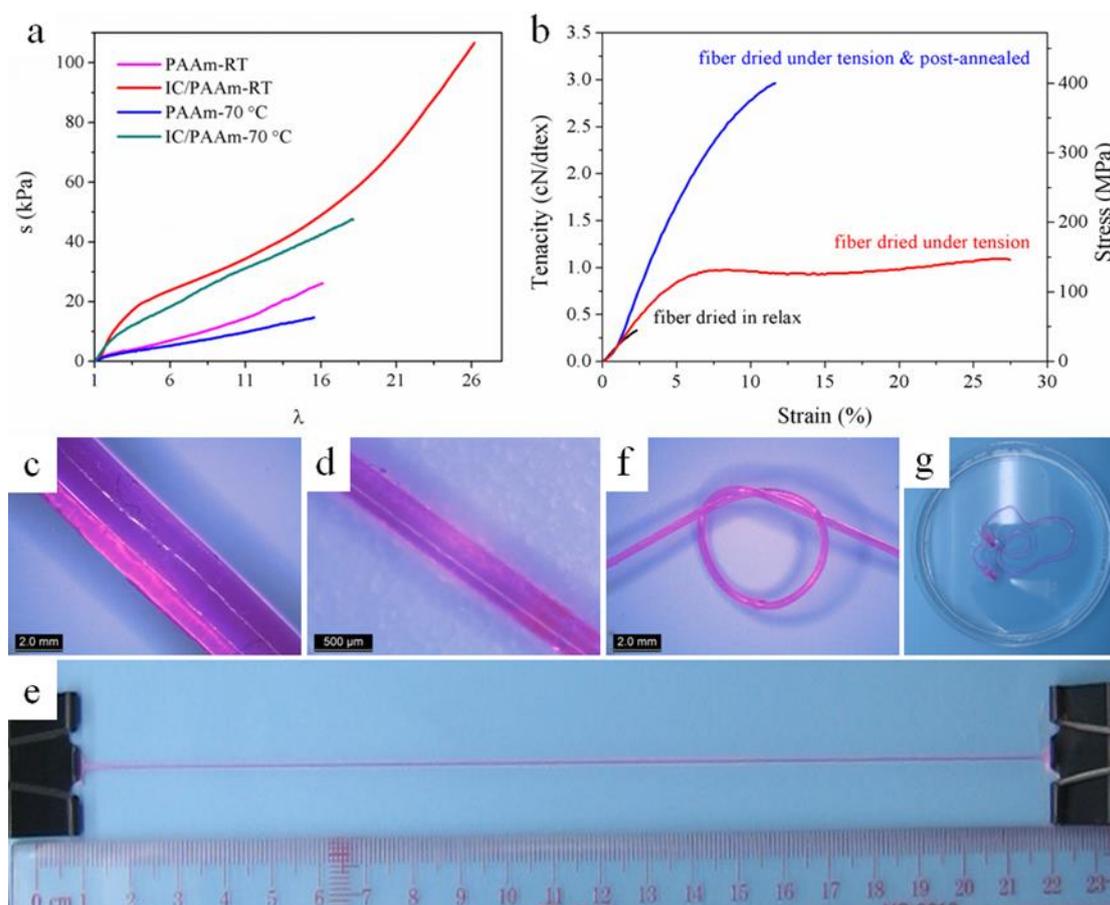
the hidden length of PAAm chain allows ultra-extension of the hydrogel before failure (Fig. 1b). Concretely speaking, a large portion of the “brittle” carrageenan network gradually unzips as the stretch increases, and avoids the stress concentration on the PAAm host matrix, thus retains the PAAm network intact over a super stretch.

To observe the energy dissipation mechanism in detail, successive cyclic tensile tests are conducted on the optimal DN hydrogel, with increasing end stretch  $\lambda_{\max}$  from 2 up to 4. The area between the loading and unloading curves indicates effective energy dissipation like the behaviour of alginate-PAAm DN hydrogels (Fig. 4a).<sup>19</sup> This dissipation area increases with the end stretch, suggesting that unzipping between IC chains became more serious at higher stretch. Comparing the loading curves of all cycles, the difference between adjacent tension paths also increases with the end stretch, which shows the trend of damage degree in each preceding stretch.<sup>27,28</sup> Furthermore, the additional stretch section in each loading curve almost coincides with the

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**Fig. 5** Stretching performances of hydrogels at different temperatures (a) and fibers transformed from the DN hydrogel (b); photos of fibers: c) as-synthesized wet DN gel fiber; d) wet DN gel fiber stretched to ~ 15 x and dried at 25 °C; e) highly stretched and dried gel fiber; f) dried gel fiber in a knot; g) recovering gel fiber in water.

5 loading curve of a normal hydrogel specimen.

Upon a higher stretch up to 5, the DN gel exhibits a clear  
 10 decrement in modulus in the following tensile curve, which is not  
 observed for the stretch below 4 (Fig. 4b). It indicates that the  
 structural change at a high stretch is irrecoverable in a short time  
 and serious enough to affect specimen modulus. At the same stretch,  
 the pure PAAm hydrogel shows negligible hysteresis and fully recovers  
 15 its length after unloading, behaving as an elastic material. Therefore,  
 the change in DN hydrogel is mainly caused by the unzipping of  
 adjacent IC helices while the PAAm network remains intact. The  
 second and the third loading cycles of DN hydrogel show much less  
 20 hysteresis and follow the same path, indicating that the little  
 hysteresis in 2nd cycle is compensated by a quick recover in  
 structure before the 3rd cycle. No further damage happens in these  
 following cycles, since their unloading paths coincide with that of  
 25 the first cycle. Similar pattern is observed in more successive  
 cycles (Fig. S3). Since the DN gel's modulus lowers to the level of  
 pure PAAm gel after the 1<sup>st</sup> stretch to 5, we assume that the IC  
 30 network completely breaks at a

specific cross-section and loses its reinforcing function at that  
 25 section. This assumed critical stretch (3 ~ 5) of IC network in  
 DN gel is supported by the experimental failure stretch of pure IC  
 gel (3.5 at a concentration of 2.0 wt%, Fig. 4b). This weakening  
 phenomenon was reported in another hydrogel composed of two  
 30 covalent networks: a stiff and brittle network together with a soft  
 and ductile network.<sup>29</sup> In that DN hydrogel, hysteresis occurred  
 in the first cycle due to the irreversible fracture of covalent bonds  
 in the brittle network.<sup>30</sup> After the first cycle of even a short  
 stretch, that DN hydrogel became much weaker and could not  
 35 recover. In contrast, our DN hydrogel is recoverable.

Compared to covalent hydrogels, physically crosslinked  
 hydrogels (such as carrageenan and agar hydrogels) undergo the  
 sol-gel transition at a proper temperature, thus are thermo-  
 reversible. As introduced previously, carrageenan gels through  
 40 ionic association of double helix units and melts at a mild  
 temperature below 70 °C, being much different from alginate  
 that directly gels with Ca<sup>2+</sup>. This property enables the IC  
 network to heal quickly at mild temperatures below 70 °C. To show the

recovery property of this DN hydrogel, we sealed a stretched then relaxed sample in a polyethylene bag, and stored it at 70 °C for a prescribed time (hydrogel samples are shown in Fig. S4) and then measured its tensile property again. As shown in Fig. 4c, second drawing curve recovers and becomes closer to the original curve. This specimen with a stretch 5 recovers ideally within 2 hours, during which the IC network dissociates upon heating and reforms upon cooling while the intact PAAm network preserves the specimen shape memory. Pronounced hysteresis of the DN hydrogel is further demonstrated by applying larger stretches (Fig. S5). For the specimen stretched up to 16 x, its structural damage is also successfully healed gradually (Fig. 4d). After storing at 70 °C for 8 hours, its tensile curve closely follows the first cycle, showing a complete recovery. While for the alginate-PAAm hybrid hydrogels stretched to only 7 x, the work on reloading recovers to only 74% after storing for 1 day at 80 °C.<sup>19</sup>

Moreover, previous researches reported that some vinyl monomers, e.g. AAm or acrylic acid, could be easily grafted onto carrageenan backbone during polymerization (Fig. 1b and Fig. S6).<sup>31-33</sup> This grafting is beneficial for networks to cooperatively share the stress in deformation. Its ability to dissipate stress is better than that of random chain entanglement.<sup>34,35</sup> To clarify the contributions of various existing links to hydrogel toughness, the IC / PAAm DN hydrogel is strained at 70 °C, where IC network is dissociated into free random chains. Its failure strain and modulus obviously decrease to 1710% and 6.0 kPa, which are still higher than that of pure PAAm hydrogel (1475% and 1.5 kPa) (Fig. 5a, Table S1). The temperature increment leads to a reduction in modulus and strength of pure PAAm gel too, while the decrease in failure strain is ignorable (from 1512% down to 1475%). Therefore, the random coil of IC and the grafting link between IC and PAAm also contribute to the toughness of DN hydrogel, although their contributions are not as significant as that of IC physical network. By observing the change in fracture energy, the latter contributes about 2 times of the former. This is the first report to quantitatively evaluate the toughness contributions from physical network and random coil in the same covalent network.

The high stretchability of such hydrogels allows significant orientation of polymer chains that counts essentially for a fiber's tenacity. The newly developed gel spinning technique produces much stronger textile fibers than common wet and melt spinning approaches, mainly due to a higher orientation degree resulted from high stretches in a physical gel state.<sup>36</sup> Our DN hydrogel strand (d = 3.34 mm) is dried under a stretch of 15 at room temperature, producing a flexible and transparent fiber (d = 0.33 mm) that is easily knotted (Fig. 5c-g). This highly stretched dry fiber still preserves the shape memory and quickly shrinks back upon wetting (Fig. 5g, video S2). Its tenacity reaches 1.10 cN/dTex (Fig. 5b, Table S2). In contrast, the fiber obtained by drying relaxed hydrogel is much weaker with a low tenacity 0.33 cN/dTex. When the fiber dried under a stretch is further heated at 60 °C for 1 hour, a higher tenacity of 2.96 cN/dTex is obtained, being as strong as common acrylic fiber applied in textiles. In comparison with the absorbent fibers available in market,<sup>37</sup> our DN gel fiber is tougher and smarter with a shape-memory property (Fig. S7). It may find potential applications in wound dressing and other medical textiles.

## 4. Conclusions

In this work, we succeeded in creating a highly stretchable and tough hydrogel from the physically cross-linked IC and the covalently cross-linked PAAm. Its fracture energy reached a high value of ~9500 J/m<sup>2</sup>. This DN hydrogel is healable by short treatment at 70 °C. Upon stretching and drying, a tough absorbent fiber with shape-memory property was obtained from the DN hydrogel strand. It would be a good candidate for advanced medical textiles and smart engineering fibers.

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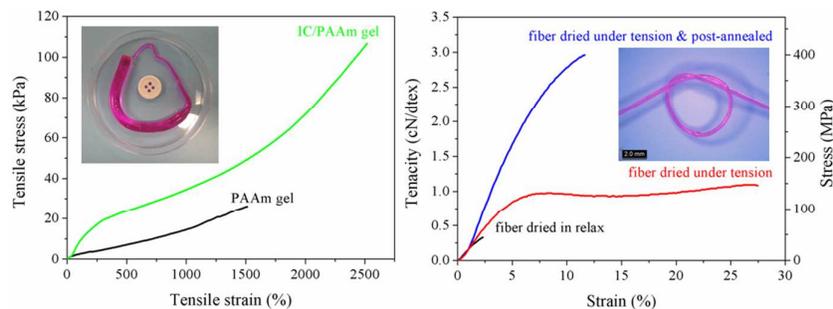
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- <sup>b</sup> Polymers and Composites Division, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences. 519 Zhuangshi Road, Zhenhai District, Ningbo 315201, China.
- † Electronic Supplementary Information (ESI) available: Molecular structures of carrageenans; Stable cracks in a stretched DN hydrogel; Successive loading / unloading cycles of PAAm and DN hydrogels; Recovery of stretched DN hydrogel by heating; Loading / unloading cycles of DN hydrogels at various end stretches; FTIR spectra of dried IC, PAAm, and IC / PAAm DN hydrogels; Recovery of DN hydrogel fiber after drying, rewetting and heating; Tables listing tensile properties of PAAm gels, IC / PAAm gels, and the absorbent fibers dried from DN gels; Movies of the DN gel fiber led through a buttonhole and the DN gel fiber recovered by wetting after drying. See DOI: 10.1039/b000000x/
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## Super-tough and thermo-healable hydrogel – promising for shape-memory absorbent fiber

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**Super-tough and highly squeezable hydrogel** by one-step polymerization shows ultra extendability and healability and leads to a shape-memory absorbent fiber.

**Keyword:** hydrogel, toughness, thermal healability, shape memory, absorbent fiber