Tough physical double network hydrogels based on amphiphilic tri-block copolymers

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Hydrogels, consisting of polymer networks and water, resemble biological tissues. Thus, hydrogels have drawn great attention as synthetic equivalents for a variety of applications in biological systems.[1-3] However, real-world use of conventional hydrogels has been limited by their poor mechanical properties. Recently, a number of approaches have been developed to create hydrogels with excellent mechanical performance. Among them, double network hydrogels (DN gels) which consist of a brittle polyelectrolyte first network and a flexible neutral second network stand out because they exhibit high toughness as well as high Young's Modulus (10^5-10^6 Pa).[4] These properties gives DN gels great potential in load-bearing applications.

The high toughness of DN gels comes from the internal facture of covalent bonds in the brittle first network which dissipates significant energy.[5-7] Due to this mechanism however, DN

gels show permanent internal damage that leads to poor fatigue resistance. One possible method to remedy these shortcomings is by applying recoverable physical bonds as sacrificial bonds. In recent work, partially or completely recoverable tough hydrogels were successfully synthesized by using ionic bonds as recoverable sacrificial bonds.[8-12] However, ionic bonds are unstable in saline conditions, which limits the suitability of these materials in some physiological and mechanical applications.[9] In the recent work, hybrid hydrogels, which apply covalent bonds to maintain elasticity and use crystallites as recoverable sacrificial physical cross-links, showed very high strength and toughness together with recoverability and high stability in saline solution. [13] Applying other physical bonds, such as hydrophobic associations and hydrogen bonds, is another possible way to remedy the limitations of ionic cross-linked tough gels. However, for most tough and recoverable hydrogels based on hydrophobic associations or hydrogen bonds, the tensile fracture stresses of can barely exceed ~MPa.[14-18]

In this work, we designed a novel physical, double network (DN) hydrogel that is tough, stiff, and recoverable. As the first network, an amphiphilic tri-block copolymer was employed to form a physical hydrogel (B gel) which is cross-linked by strong hydrophobic association. The amphiphilic tri-block copolymer consists of the hydrophobic end-blocks of poly(butyl methacrylate) (PBMA) and hydrophilic mid-block of poly(methacrylic acid) (PMAA), PBMA-b-PMAA-b-PBMA, with the weight-average degree of polymerization of 134-273-129. Subsequently, linear polyacrylamide (PAAm) was used as the second network. The amide groups on PAAm are able to form hydrogen bonds with the carboxylic acid groups on the hydrophilic mid-block (PMAA). The hydrogen bonds between the first and second network act as sacrificial bonds for energy dissipation. Such DN gels, having no chemical cross-linking, are named as B-DN gels. Schematics of the structures of the block copolymer single network gel (B gel) and double network gel (B-DN gel) are shown in **Scheme 1**.

The modulus and fracture energy of the B-DN gels are tunable by altering the AAm concentration of the second network (Figure S1, Table S1).The gel synthesized with an AAm concentration of 3 M, referred to as B-DN3, with ~42% water content, exhibits the highest fracture energy of ~3000 J/m^2, and an elastic modulus, fracture stress, and fracture strain of ~2 MPa, ~10 MPa, and ~600%, respectively, while possessing self-healing and self-recovery abilities. Different from other DN gels that show yielding or strain softening, this gel shows an unusual, linear stress-strain curve up to the fracture strain of 600%. The B-DN gels developed here exhibit high mechanical performance similar to cartilage, yet contain no permanent covalent cross-links or ionic associations, distinguishing them from traditional DN gels and other tough physical hydrogels.

To verify the structure of the block-copolymer gel, Small Angle X-Ray Scattering, SAXS, was performed. **Figure 1a** shows the SAXS profiles for the B gel and B-DN3 gel. For the B gel, the SAXS profile shows 4 peaks at a low scattering vector, q. However, the ratios of the scattering peak positons (q_m, m = 1, 2, 3, 4) to the maximum scattering peak positon (q_1) do not obey any known ratios of ordered block copolymer structures. Even without any ordered structure, randomly distributed domains of nearly identical size will also give rise to several broad scattering peaks.[19] Some studies of tri-block copolymer gels in a mid-block selective solvent have revealed disordered structures of spherical domains of end-blocks, and the SAXS profiles of the gels were well fitted by the Percus-Yevick hard sphere model.[20, 21] The SAXS profile in our study was also fitted by the Percus-Yevick hard sphere model, and it well describes the peak positions when taking into consideration a Gaussian distribution of domain sizes (Figure S2). Thus, we consider that the hydrophobic blocks associate into randomly distributed, spherical domains, and these domains serve as the cross-links in the B gel.

We can further use the SAXS results to calculate the functionality (f) of the hydrophobic domains. From the q_1 value (q=0.201 nm^{-1}) of the first peak that corresponds to the structure factor, the average inter-domain distance, d, was calculated as $d = 2\pi/q_1 = 31.2$ nm and the polymer chains per hydrophobic domain, f, was calculated as $f = 33$ (Supporting information)[22]. This demonstrates that the hydrophobic domains exhibit a high degree of functionality. For the B-DN3 gel, only the peak at the lowest scattering vector, q_1, remained, and the peak position slightly shifts to a higher q value ($q = 0.224$ nm^{-1}), indicating a decrease of the distance between hydrophobic domains. For the broadening and disappearance of the peaks at high scattering vector, several factors, such as shape deformation and surface roughness of the domains, as well as size distribution of the domains may play a role. The results suggest that the surface of the hydrophobic domains was blurred by the adsorption of PAAm chains. Due to the formation of hydrogen bonds between the first and the second network, the volume of the B-DN3 gel shrunk by a factor of 0.60 ($V_{B\text{-}DN\,gel}/V_{B\,gel}$) in comparison with the B gel. As the inter-domain distance of the B-DN gel was estimated as 28.0 nm, the inter-domain distance changes as $1 - d_{B\text{-}DN\,gel}/d_{B\,gel} = 0.11$, which is very close to, but slightly smaller than that estimated volume change ($1 - (V_{B\text{-}DN\,gel}/V_{B\,gel})^{1/3} = 0.16$), assuming affine deformation. Therefore the macroscopic size change of the hydrogels closely follows that of the microscopic size change.

Formation of hydrogen bonds between PAAm and PMAA is vital to provide sacrificial bonds. To verify the formation of hydrogen bonds between the PAAm and PMAA, we compared the hydrogen bond stability of different pairs comprised of PAAm, PMAA, and water from calculation of final heat of hydrogen bonding formation using the PM7 semi-empirical molecular orbital method by MOPAC 2007 (Supporting Information). The result shows that the hydrogen bonding between the amide group of PAAm and carboxylic acid group of PMAA is the most stable in aqueous conditions (Table S2). Formation of hydrogen bonds

between PAAm and PMAA in the B gel should cause a peak shift in the IR spectrum. The FT-IR spectra of the B gel, PAAm and B-DN3 gel is shown in Figure 1b. As the stretching resonance bands of the hydrogen donors (N-H, O-H) are overlapped by the stretching resonance bands of water, the shifting of the stretching resonance bands of carbonyl groups (C=O) which are the electron donors, was studied. The carbonyl stretching resonances for PAAm and B gel are observed at 1669.8 cm^{-1} and 1724.0 cm^{-1}, respectively. For the B-DN3 gel, two distinct absorption peaks are observed at 1673.9 cm^{-1} and 1721.1 cm^{-1}, which are attributed to the stretching resonances of carbonyl group from PAAm and the B gel, respectively. Compared to the FT-IR spectra of the B gel, in the B-DN3 gel the absorption peak corresponding to carbonyl stretching resonance shows a red shift, indicating the formation of the C=O···H-N hydrogen bond between PMAA and PAAm. The absorption peak corresponding to carbonyl stretching resonance of the amide group shows an improper blue shift. We consider that this occurs because after the formation of the hydrogen bond, the electron density was averaged and the p-π conjugation effect of the amide group is decreased. In conclusion, there is substantial evidence that hydrogen bonding occurs between the PAAm and PMAA.

Dynamic mechanical studies can be used as a tool to clarify the strength of the dynamic bonds within the hydrogel system.[9] The dynamic mechanical measurements show that the dynamic modulus of the B gel follows time-temperature superposition, and the B gel exhibits elasticity as the shear storage modulus, G', shows a weak frequency dependence and low loss factor, $tan\delta$, over a large frequency range, as shown in Figure 2a. The constructed master curve of $tan\delta$ increased with the decrease of frequency and reached a top at ~7 × 10^{-6} rad/s, corresponding to the relaxation time of $1/(7 × 10^{-6}$ rad/s$) \simeq 10^5$ s. This justifies that the hydrophobic domains have a relaxation time longer than 10^5 s, which is sufficiently long to act as strong bonds. The Arrhenius plot for the shift factor of the master curve, a_T, is shown in

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Figure 2a', which gives an apparent activation energy (E_a) of ~260 kJ/mol. This high apparent activation energy (E_a) is considered to be due to the motion of the PBMA chains in the hydrophobic domains. Thus, over an ordinary time scale, the hydrophobic associations act like permanent bonds.

At room temperature, the B-DN3 gel exhibits viscoelasticity. As shown in Figure 2b and 2b', at moderate to high frequencies the shear storage modulus, G', shows an obvious frequency dependence with a high $tan\delta$ value, indicating that the B-DN3 gel is more viscoelastic than the B gel. The constructed master curve of $tan\delta$ shows two viscoelastic peaks at ~2.4×10^{-5} rad/s and ~20 rad/s, respectively, corresponding to relaxation times of ~4.1×10^4 s and ~5×10^{-2} s. From the Arrhenius plot of the shift factor, a_T, two apparent activation energy values (E_a) of ~254 kJ/mol and ~180 kJ/mol were obtained. This indicates the existence of two kinds of physical bonds with different bonding strengths. The bonds with a relaxation time of ~4.1×10^4 s and E_a of ~254 kJ/mol correspond well with those of the hydrophobic associations in the B gel. The bonds with a relaxation time of ~5×10^{-2} s and E_a of ~180 kJ/mol should therefore be attributed to the hydrogen bonds between the mid-block (PMAA) of the first network and the PAAm second network. To confirm this, we synthesized DN gels consisting of chemically cross-linked PMAA gels as the first network and linear PAAm as the second network. In these gels, denoted as c-DN gels in this work, only hydrogen bonds between the PMAA and PAAm exist as dynamic physical bonds. The constructed master curve and Arrhenius plot of the c-DN gel is shown in Figure 2c and 2c', respectively. As shown in the figure, a relaxation time of ~5×10^{-2} s and E_a of ~179 kJ/mol were observed, which agree well with the values of the hydrogen bonds in the B-DN3 gel. Thus, it is clear that for the B-DN3 gel, hydrophobic associations, which are strong and exhibit long relaxation times, act as permanent cross-links, and hydrogen bonds, which are weak and exhibit short relaxation times, act as sacrificial bonds in the gel.

The mechanical properties of the hydrogels were determined by uniaxial tensile test and pure shear test (supporting information)[9, 23, 24]. As shown in Figure 3a, the block copolymer gel (B gel), which only contains physical cross-links from hydrophobic associations, is brittle and weak, showing an elastic modulus of 0.051 ± 0.04 MPa, fracture stress of 0.19 ± 0.04 MPa, and fracture strain of 0.97 ± 0.2 mm/mm. The fracture energy of the B gel was 63 ± 7 J/m^2 (Table S1), which is relatively tough compared to previously reported ABA block copolymer gels [25, 26], but is far less tough when compared to conventional DN gels, due to the lack of sacrificial bonds. On the other hand, the B-DN3 gel with strong physical hydrophobic associations *and* sacrificial hydrogen bonds, shows a high elastic modulus of 2.2 ± 0.2 MPa, fracture stress of 10.5 ± 1.4 MPa and fracture strain of 5.7 ± 0.7 mm/mm (Figure 3a). Different from other DN gels and other tough hydrogels that show yielding or strain softening [5-12], this gel shows an unusual linear stress-strain curve up to the fracture strain of 600%. Meanwhile, the S-S curve shows large hysteresis in cyclic tensile tests (Figure 4), and at room temperature the B-DN3 gel shows partial self-recovery properties. This indicates that there is bond rupture during stretching which dissipates energy. The linear S-S curve is possibly caused by a combined effect of strain hardening of the polymer chains and softening effects from bond breakage. Furthermore, the B-DN3 gel was very tough with a tearing energy of 2850 ± 220 J/m^2. The robust mechanical properties of the B-DN gel is demonstrated in Figure 3b and Video S1 by hanging a 1 kg weight from the gel (load bearing ability), and in Figure 3c and Video S2 by tying the gel into a knot, applying stress, and releasing to its original form (flexibility, toughness, and self-recoverability). The B-DN gels exhibit outstanding properties with both high stiffness and toughness, which is comparable to different kinds of tough hydrogels and rubbers, as well as natural skin and cartilage (Figure S6).[17-32, 13]

The structure of the first network plays an important role in the resulting mechanical

properties of the gels. The B-DN3 gel is much stronger and tougher than the c-DN gel with a chemically cross-linked first network consisting of PMAA (Figure S3). As the modulus of the B-DN3 gel is much higher than the c-DN gel at the same AAm concentration and same elastic modulus of the first network, the hydrophobic domains of the first network in the B-DN gel substantially enhance the formation of hydrogen bonds. The enhancement of hydrogen bonds by hydrophobic interaction was also applied in a very recent work by Sheiko et al., to create stiff and tough hybrid hydrogels where the hydrogen bonds act as sacrificial bonds while the chemical cross-links maintain elasticity.[33] The large amount of hydrogen bonding effectively serves as sacrificial bonds to substantially increase the strength and toughness of the B-DN gel in comparison with the c-DN gel.

To confirm the effect of the hydrogen bonds as reversible sacrificial bonds, cyclic tensile tests of the B-DN3 gel were performed. Figure 4a shows the self-resilient behavior at a strain of 100% for different waiting times between successive loading-unloading tests. Large hysteresis is observed, indicating energy dissipation during deformation due to the rupture of hydrogen bonds. Except for the first loading and unloading cycle, the gel shows quick and full recovery with a recovery efficiency of ~85% and no residual strain after a waiting time of only 5 min. Figure 4b shows the waiting time dependence of the residual strain and hysteresis ratio, which was measured as the area ratio of the second hysteresis loop to the first. This fast recovery is related to the short relaxation time of $\sim 5 \times 10^{-2}$ s of the dynamic sacrificial hydrogen bonds, which ensures the deformed chain can return to its original conformation quickly. The gel shows no further improvement in recovery efficiency at waiting times from 5 min to 50 min, representing the existing of some unrecoverable ruptured bonds.

In order to clarify if the unrecoverable behavior is due to the rupture of physical bonds with long relaxation times, such as the hydrophobic bonds, or the rupture of the covalent bonds of

the polymer chains, thermal treatment was performed. The relaxed B-DN gel after cyclic tensile testing was heated to 60°C, near the softening temperature of the B gel (70°C, Figure S4a). After being held at 60°C for 1 min, the hydrogen bonds were broken, and a long time (90 min) was required to reform the hydrogen bonds at room temperature (Figure S4b). By decreasing the temperature to 5 ^{o}C, the time for reformation of hydrogen bonds was shortened to 15 min. Thus by performing a heating-cooling process, the gel is able to be made 100% recovery with a short time of 16 min (heating for 1 min and cooling for 15 min), as shown in Figure 4a. This result confirms that the residual area in the cyclic tensile test is not due to the rupture of covalent bonds but due to the rupture of the physical bonds with long relaxation times. It is highly possible that these long relaxation time bonds are associated with the hydrophobic domains.

Due to the supramolecular nature of the B-DN gel, self-healing between two cut surfaces is expected. However, automatic self-healing at room temperature was not observed. This is likely due to the high stiffness of the gel which hinders full contact of the cut surfaces; furthermore the strong hydrophobic associations with long relaxation times are not easy to recover after being broken. As the hydrophobic associations are able to be softened by a good solvent such as DMF, the cut edges were dipped in DMF, brought in contact, heated at 60 ^{o}C for 60 min, and finally immersed in water to extract the DMF. Figure 4c and Figure 4d show the images of a healed B-DN3 gel and the tensile test of the healed and original B-DN3 gel, respectively. Due to some defects existing in the joint and the high modulus of the gel, the healing efficiency of the B-DN3 gel was not high, but the joint reformed between the cut surfaces can withstand a fracture stress up to 2.3 MPa. To our knowledge, this value is the highest reported so far for healed gels. The recovery and healing property induced by simple treatment give rise to interesting potential applications for B-DN gels, such as loading history memory components which can be repeatedly used after simple treatment.

In summary, this work demonstrates supramolecular double network hydrogels based on an amphiphilic tri-block copolymer that contains strong hydrophobic domains and sacrificial hydrogen bonds. This special combination of physical bonds results in high toughness, stiffness, fatigue resistance, and high mechanical performance in concentrated saline solution (Figure S5), making it a good candidate as a load bearing material. The B-DN gel design introduced here provides a platform for developing new, tough physical hydrogels.

Experimental Section

Formation of B gel: The amphiphilic tri-block copolymer poly (butyl methacrylate)-b-poly(methacrylic acid)-b-poly(butyl methacrylate) with the target degree of polymerization of 109-221-109 was synthesuzed by Otsuka Chemical Co., Ltd., Japan. The measured weight-average molecular weight of the obtained block polymer is 60,800 with M_w/M_n of 1.34, the molar ratios of each block are 25%-51%-24%, and the weight-average degree of polymerization of each unit of the block copolymer is calculated as 134, 273 and 129, respectively. A solution of 20% (*w/w*) triblock copolymer/N,N-dimethylformamide was poured into a rectangular mold with dimensions of 80 mm × 80 mm × 1.5 mm, and gelation was induced by spraying water vapor on the surface of the solution for several minutes, during which time the hydrophobic PBMA chains gathered to form solvent-swollen end block domains due to the increase of the solvent interaction parameter-χ of the end blocks.[25] Then, the as-prepared weak gel was immersed in water for 3 days and the water was changed several times. The B gel obtained has a water content of 82-83 wt%.

Synthesis of B-DN gel: The B gel was immersed in the second network precursor solution containing the prescribed concentrations (*M*) of acrylamide (AAm) as monomer, and 2-oxoglutaric acid (0.02 mol% relative to the monomer) as photo-initiator for 3 days. After that,

the sample was irradiated with 365 nm UV (~4 mW/cm^2) for 7 h to synthesize PAAm within

the B gel. The as-prepared B-DN gel was immersed in purified water for 4 days to reach

equilibrium. After equilibrium the B-DN gels have a water content of 45 wt%-60 wt%. The

B-DN gels synthesized from n M AAm solution were named as B-DNn. The water content

and mechanical properties of the samples prepared in this study are summarized in Table S1.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Figures

Scheme 1. Structure of block copolymer gel (B gel), the synthesis procedure of the double network gel (B-DN gel), and the structure of B-DN gel with hydrogen bonds.
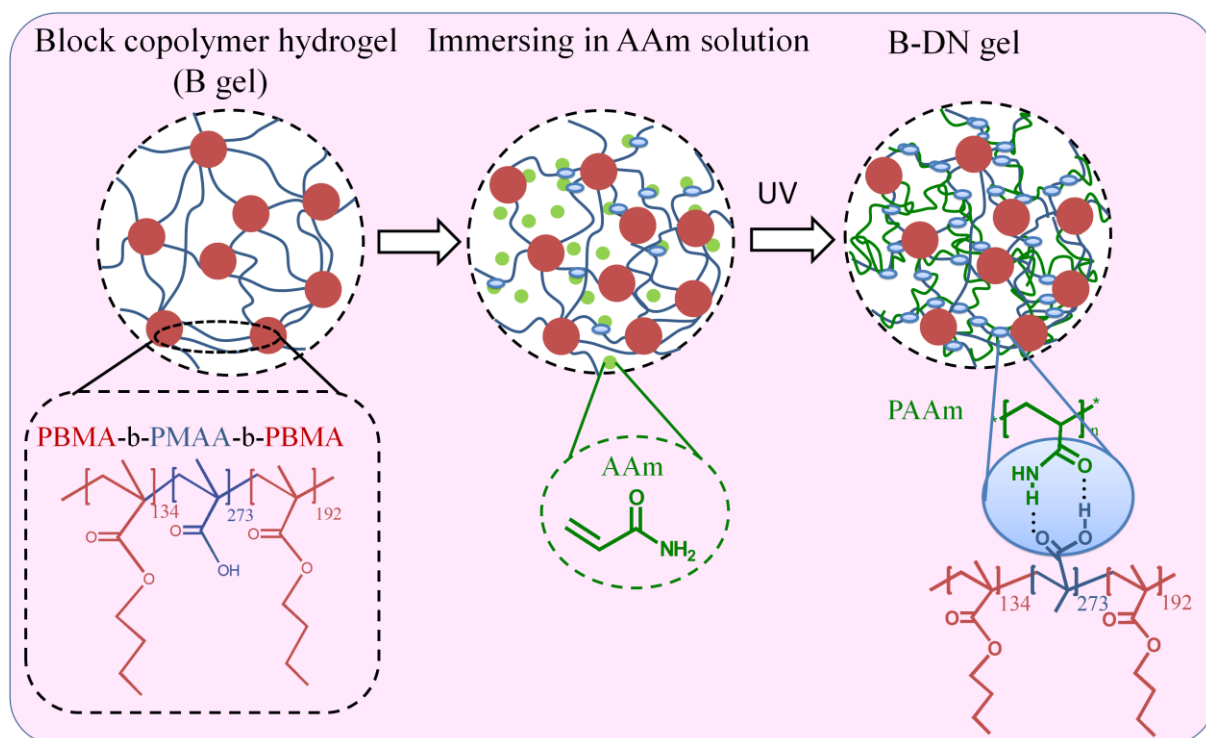
Figure 1. Structure characterization of gels: a) SAXS profiles of B gel and B-DN3 gel. b) FT-IR spectra of B gel, PAAm solution and B-DN3 gel.
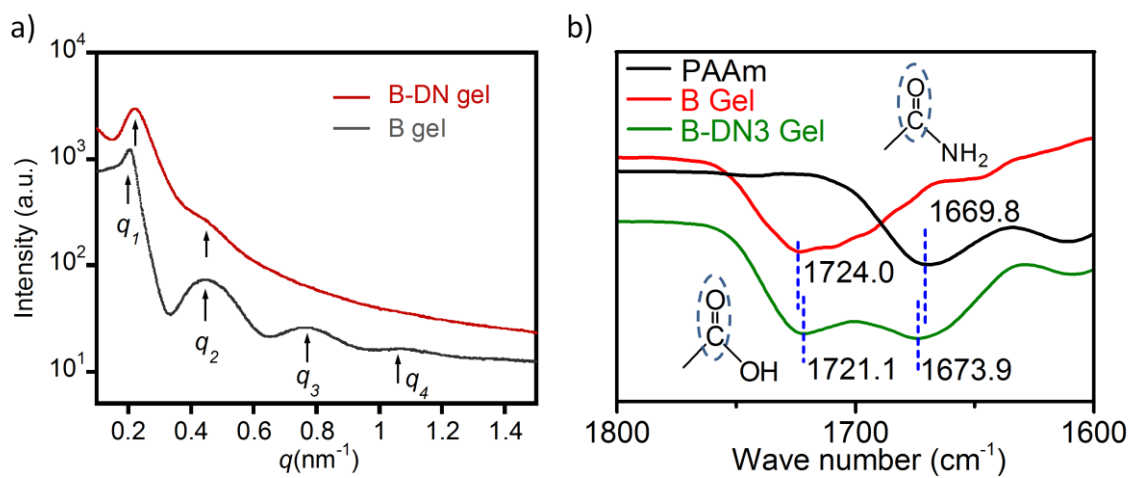
Figure 2. Dynamic mechanical behaviors of the gels: a, b, c) Frequency (ω) dependence of the storage modulus G', loss modulus G'', and loss factor $tan\delta$ of B gel, B-DN3 gel, c- DN gel, respectively; the corresponded temperature for each color is shown in figure a. a', b', c') Arrhenius plot for the shift factors of the B gel, B-DN3 gel, c-DN gel, respectively. The apparent activation energy values E_a shown in the figures were calculated from the slope of the curves. The c-DN gel (water content: 45% ± 1%) of the similar water content with B-DN3 gel (water content: 44% ± 2%) was used. In figure c and c': for the c-DN gel, the average partial chain length N of PMAA network is 75, and 3 M AAm solution was used to form the second network.
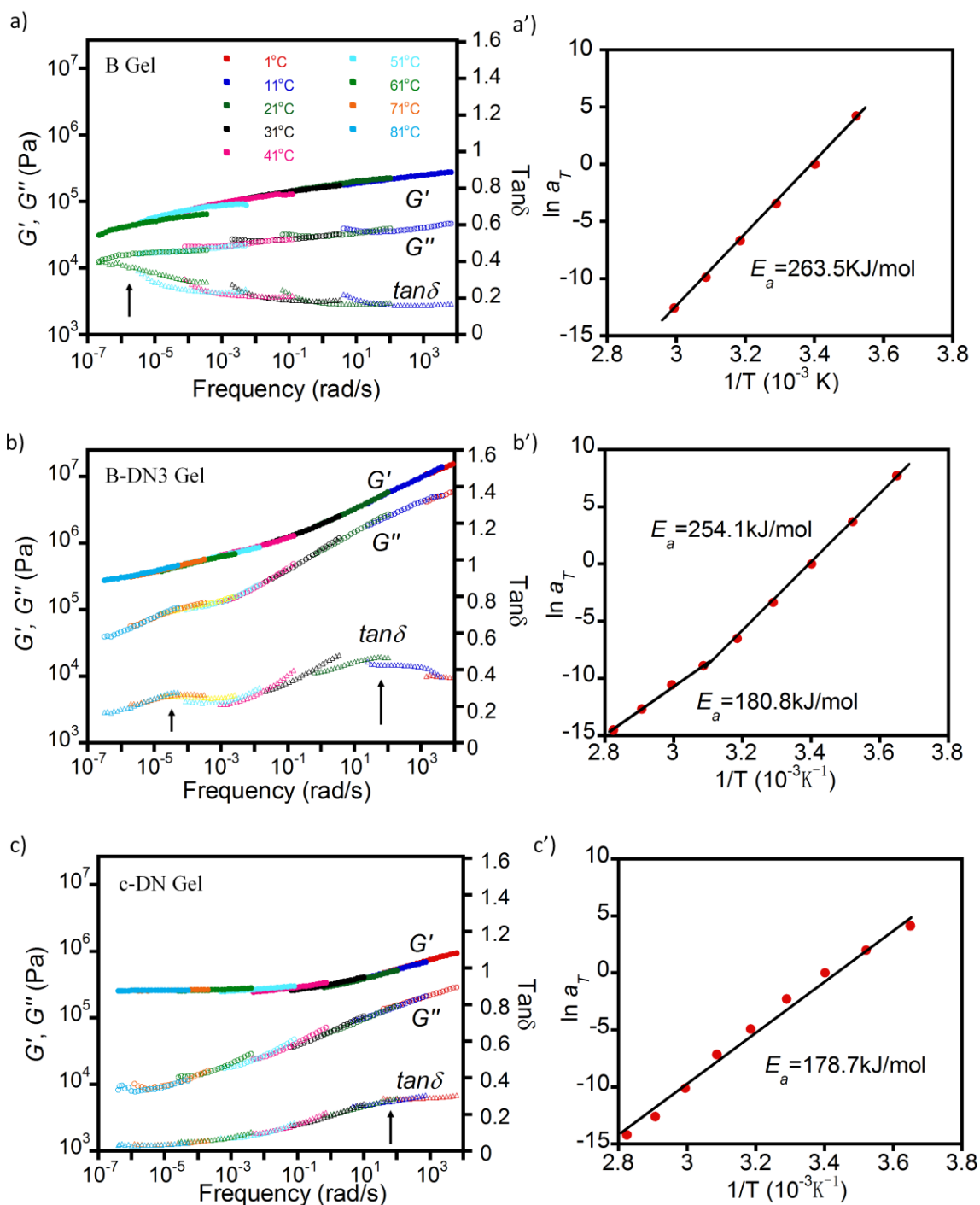
Figure 3. Mechanical performance of B-DN3 gel: a) Tensile stress-strain curve of B-DN3 and B gel. b, c) Images to demonstrate the high strength and toughness of B-DN3 gel, and the sample size in (b) is 2cm × 4cm × 0.1cm with a 1 cm hole in diameter.
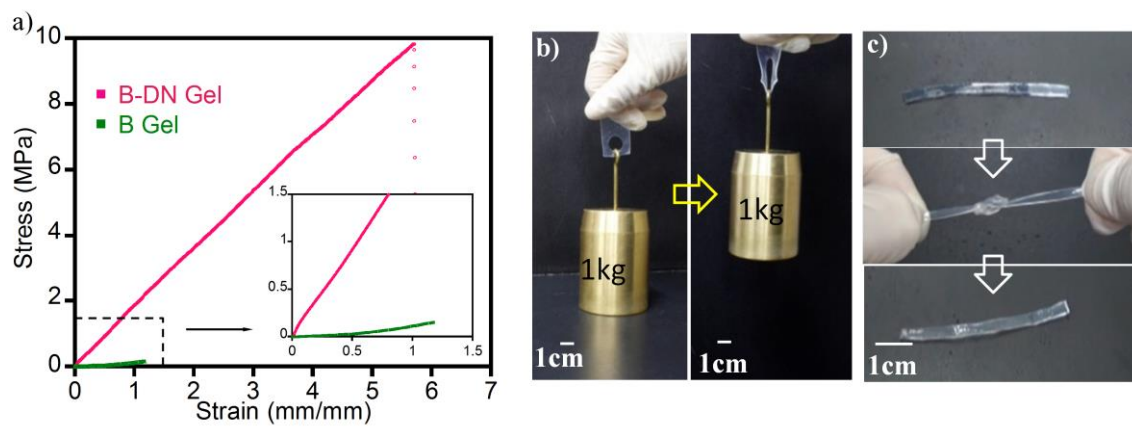
Figure 4. Self-recovery properties of B-DN3 gel: a) Cyclic tensile loading-unloading curves for different waiting times between two successive measurements, and the cyclic stress-strain curve of the loaded sample after heating-cooling treatment at 60 $^{\circ}$C for 1 min and at 5 $^{\circ}$C for 15 min. b) Waiting time dependence of hysteresis ratio (the area ratio of the second hysteresis loop to the first) and the residual strain. c) Images demonstrating partial self-healing of the sample: the healed dumbbell-shaped sample with width and thickness of 0.2 cm × 0.1 cm easily holds a weight of 100 g. d) Stress-strain curves of virgin and healed sample.