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Fracture of the Physically Cross-Linked First Network in Hybrid Double Network Hydrogels

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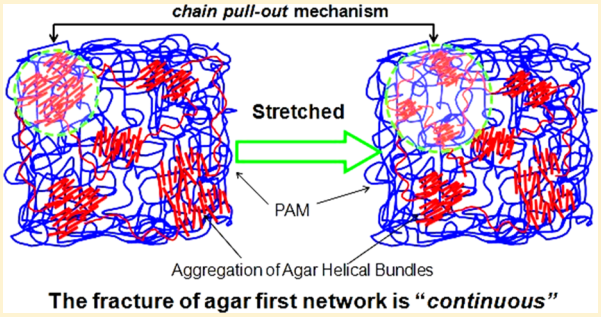
ABSTRACT: Fundamental understanding of the fracture process and toughening mechanisms of double network (DN) hydrogels is critical for rational design of the next generation of tough DN gels with desirable mechanical properties. However, current knowledge of DN gels from synthesis methods to toughening mechanisms mainly comes from chemically cross-linked DN gels. Little is known about hybrid physically chemically cross-linked DN gels. Herein, we synthesize tough DN hydrogels by combining two types of cross-linked polymer networks: a physically cross-linked first network of agar and a covalently cross-linked second network of polyacrylamide (PAM). The resulting Agar/PAM DN gels achieved high toughness of 500−1000 J/m^2. More importantly, we reveal several differences and similarities between hybrid Agar/PAM DN gels and chemically linked PAMPS/PAM DN gels. First, different from the nearly velocity-independent mechanical properties in chemically linked DN gels, hybrid Agar/PAM DN gels show velocity-dependent fracture behaviors and toughness. Second, successive cyclic loading−unloading tests indicate the continuous fracture of the first agar network, instead of a phase transition from continuous to discontinuous in chemically linked DN gels. Third, Agar/PAM DN gels exhibit different yielding and necking behaviors from chemically linked DN gels, including much lower yielding stress/strain, no stable necking platform, and simultaneous necking. We thus propose a chain pulling-out model to interpret the continuous fracture process of the first agar network and associated energy dissipation mechanism for hybrid Agar/PAM DN gels. This work strives to provide a better fundamental understanding of structure−property relationship of DN gels, which help to develop new DN gels with desirable properties.



1. INTRODUCTION

Hydrogels as "soft-wet" materials, which adsorb a large amount of water in three-dimensional polymeric network, possess many unique properties in a single material matrix such as stimuli responsiveness, high stretchability, shock adsorbing, low sliding friction, and/or swelling/deswelling. Integration of these unique properties has made the hydrogels being commercially used for waste treatment,[1,2] agriculture and food chemistry,[3−6] environmental engineering,[7,8] and superabsorbents[9−11] as well as being served as model systems that support and develop a wide range of fundamental research in photochemistry,[12,13] medicine,[14,15] and tissue engineering.[16−18] However, many hydrogels are generally mechanically weak and brittle, which greatly limit their extensive uses for the applications where the mechanically properties are not highly concerned. The poor mechanical properties of these hydrogels are largely attributed to inefficient energy dissipation in heterogeneous network structures.[19,20]

Significant efforts have been devoted to develop highly tough hydrogels with improved mechanical properties, including nanocomposite hydrogels,[21] hydrophobically modified hydrogels,[22] ionically cross-linked hydrogels,[23] hydrogen bonding or dipole−dipole enhanced hydrogels,[24,25] and double network hydrogels.[26] Among them, double network (DN) hydrogels exhibit extremely high strength (fracture tensile stress of 1−10 MPa and strain of 1000−2000%) and toughness (tearing fracture energy of 10^2−10^3 J/m^2),[26,27] due to their contrasting network structures where the first, brittle polyelectrolyte network is strongly entangled and interpenetrated with the second, soft, neutral polymer network. Gong and co-workers for the first time developed a two-step sequential free-radical polymerization method to synthesize the PAMPS/PAM DN hydrogels[26] comprising poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) as the first network and polyacrylamide (PAM) as the second network. The PAMPS/PAM DN hydrogels achieved fracture toughness of 10^2−10^3 J/m^2, fracture tensile stress of 1−10 MPa, and fracture tensile strain 1000−2000%. They also proposed general design principles for the synthesis of tough chemically linked DN hydrogels:[19] (i) rigid and brittle polyelectrolyte as the first network, while soft

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and ductile neutral polymer as the second network; (ii) the molar concentration of the second network is 20−50 times the first network; and (iii) the first network is tightly while the second network is loosely cross-linked to achieve strong asymmetric gel structure. Based on the design principles, different tough chemically linked DN hydrogels were developed using the two- or multiple-step polymerization methods, including microgel-reinforced DN gel,[28] void DN gel,[29] inverse DN gel,[30] jellyfish DN gel,[31] liquid crystalline DN gel,[32] lamellar bilayers DN gel,[33] and other DN gels.[19,20,26−29,32−36]

Almost all DN hydrogels are chemically cross-linked in both networks; thus, these chemically linked DN gels appear to show some similar toughening behaviors. Upon deformation, the first, rigid, and brittle polyelectrolyte network fractures into small clusters, which act as sliding cross-linkers of the second network to enhance the resistance against the crack propagation by forming a large damage zone (soften area) at crack tips.[19,27] More importantly, the internal fracture process of the first network is thought to be critical for toughness enhancement because relatively large damage zones formed in the first network allow for more accumulated damage before macroscopic crack propagation occurs throughout whole networks. Gong et al.[37] found a continuous−discontinuous structural transition of PAMPS network during the internal fracture process of PAMPS/PAM DN gels, and such structural transition of the first PAMPS network led to the higher internal fracture efficiency of 85% as compared to 59−67% for vulcanized rubbers. Spink et al.[38] independently reported that the fracture toughness of PNVP/PAAc DN gels appeared to be positively correlated with the toughness of the first network. However, all these findings from synthesis methods, design principles, to toughening models are solely derived from chemically linked DN gels, which may not be applied to hybrid physically chemically linked DN gels. Additionally, due to permanent bond breakage at high strain, chemically linked DN gels are lack of ability to recover efficiently from damages resulting in the reduced toughness.

Only a few physically chemically linked DN gels with a combination of noncovalent and covalent linkings were developed very recently.[36,39,40] We developed a new, simple, "one-pot" method to synthesize a new type of hybrid physically chemically cross-linked agar/polyacrylamide (Agar/PAM) DN hydrogel, consisting of two interpenetrating networks of a hydrogen-bond linked Agar network and a covalently cross-linked PAM network.[41] The hybrid physically chemically linked Agar/PAM DN hydrogels exhibited highly mechanical properties of stiffness (elastic modulus of 123 kPa), strength (failure compression stress of 38 MPa and failure tensile stress of 1.0 MPa), and dissipated energy (9 MJ/m^3), excellent extensibility (15−20 times longer relative to its initial length), and a unique free-shapeable property (formation of many complex geometrical shapes). Similar to other physically cross-linked polymers including $(SIS)_p$-type multiblock copoymers,[42] Agar/PAM DN gels could also recover its mechanical properties upon temperature stimuli. In our previous study, the cyclic loading−unloading strain−stress data have shown that Agar/PAM DN gels were able to recover 65% of energy loss that represents a toughness recovery and 90% of elastic modulus that represents a stiffness recovery at 100 °C within 10 min. This finding clearly indicates that the temperature-responsive sol-to-gel transition is responsible for the recovery property of Agar/PAM gels; i.e., the agar network can be reorganized and rehealed through re-formation of the physical cross-linking points at an elevated temperature via a gel-to-sol transition. The yielding, necking, hysteresis, and softening phenomena were all observed in our Agar/PAM gels. Interestingly, Agar/PAM DN gels exhibited different yielding and necking behaviors from chemically linked PAMPS/PAM DN gels, including much lower yielding stress/strain, no stable necking platform, and simultaneous necking,[41] which cannot be well interpreted by the existing fracture mechanisms derived from the chemically linked DN gels. Along similar lines, Suo et al.[39] prepared the alginate/PAM DN gels combining a Ca^{2+} cross-linked alginate network and covalently cross-linked PAM network, which achieve remarkable fracture toughness of ∼9000 J/m^2 and stretch ability of beyond 20 times longer than their initial lengths. Panhuis et al.[35,36,40] also developed a series of ionic−covalent gellan gum/PAM, gellan gum/epoxy−amine, and carrageenan/epoxy−amine DN gels using a "one-pot" method. They found that all hybrid gels displayed the improved mechanical properties. Suo et al.[39] have suggested a synergy effect between ionically and covalent cross-linked networks on the enhancement of mechanical properties; however, the fracture details of hybrid physically chemically linked DN gels and their correlation with underlying mechanical properties still remain poorly understood.

In this work, we studied the toughness and internal fracture process of Agar/PAM DN gels using tearing tests and cyclic tensile tests. Unlike chemically cross-linked DN gels that exhibit nearly velocity-independent tearing properties including yielding point, mechanical hysteresis, and even fracture energy for some gels,[19,27,34] we examined the effects of stretching rates on mechanical properties and fracture behaviors of Agar/PAM DN gels, showing velocity-dependent tearing behaviors and high tearing energy (10^2−10^3 J/m^2). Finally, we observed a continuous fracture process of the first agar network, which is completely different from a discontinuous fracture of chemically linked gels. By revealing differences and similarities between hybrid Agar/PAM DN gels and chemically linked PAMPS/PAM DN gels, we proposed a chain-pulling-out model to interpret the facture process of network and the associated mechanical enhancement mechanisms. This work provides new insights into the fracture process and energy dissipation mechanisms of physically chemically linked DN gels and hopefully guides the design of the next-generation gel materials with desirable properties.

2. MATERIALS AND METHODS

2.1. Materials. All chemicals and solvents purchased were of the highest available purity, and unless otherwise stated they were used as received. Agar (gel strength of >800 g cm^{-2} and melting point of 85−95 °C) and 2-hydroxy-4′-(2-hydoxyethoxy)-2-methylpropiophenone (Irgacure 2959) were purchased from Aldrich Inc. and used as received. Acrylamide (AM) was recrystallized from acetone once. *N*,*N*′-Methylbisacrylamide (MBA) was purchased from Alfa Aesar Inc.

2.2. Preparation of DN Gels. Agar/PAM DN gels were synthesized by a one-pot method as reported in our previous work.[41] Unless otherwise stated, the optimal conditions as determined from our previous work (agar of 20 mg mL^{-1}, AM of 3.4 mol L^{-1}, MBA 0.03 mol % of AM, and UV-initiator (Irgacure 2959) 1 mol % of AM) were used to prepare Agar/PAM DN gels. Briefly, all reactants were added into a tube, and the tube was sealed under N_2 protection after three degassing cycles and then gradually heated up to 95 °C in an oil bath to dissolve the reactants in the water. The resulting solution was injected into a plastic tube (D = 9 mm) or a mold and cooled at 4 °C for 30 min to form an agar gel first. The photopolymerization reaction was carried out to form an Agar/PAM DN gel under UV light (λ = 365 nm wavelength, intensity of 8 W) for 1 h. After

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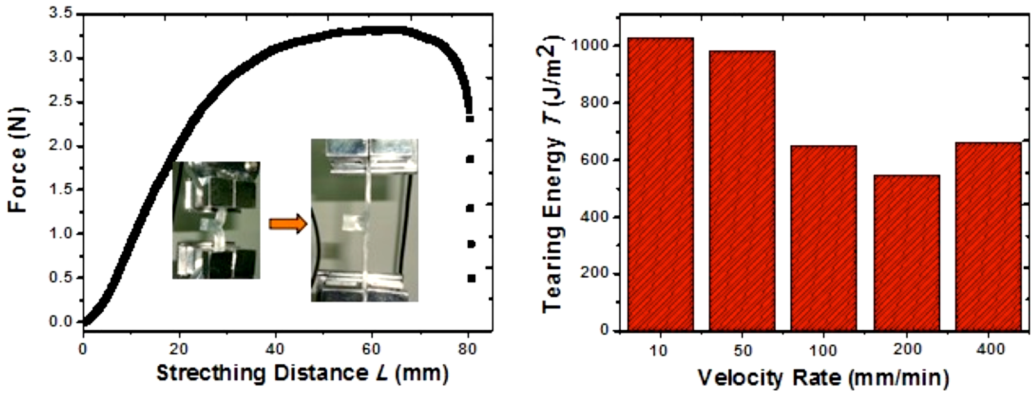

Figure 1. (a) Force−displacement curve of Agar/PAM DN gels at 50 mm/min. (b) Tearing energy of Agar/PAM DN gels as a function of crack velocities.

polymerization, gels were removed from the molds and used for mechanical tests.

2.3. Mechanical Testing. *Tearing Test.* Tearing testing was performed using commercial test machine. The gel samples were cut into a trousers shape (40 mm in length, 10 mm in width, and 10 mm in thickness) with an initial notch of 20 mm. The two arms of the samples were clamped, in which the one arm was fixed, while the other one was pulled upward at different velocity rates. The tearing energy (T) is defined as the work required to tear a unit area, as estimated by[28]

$$T = \frac{2F_{ave}}{w} \tag{1}$$

where F_{ave} is the average force of peak values during steady-state tear and w is the width of the specimen.

Tensile Test. Uniaxial tensile tests of as-prepared gels (diameter = 9 mm and length = 60 mm) were carried out using a universal tensile tester equipped with a 100 N load cell with a variety of crosshead speed of 10, 50, and 100 mm min^{-1}. For hysteresis measurement, gel specimens were first stretched to a maximum strain ε_1 and then unloaded. After returning to the original length, the specimens were reloaded and stretched to an increased maximum strain ε_2 at the same velocity rate as the first loading and unloaded again. The loading−unloading operations were repeatedly conducted on the same specimen with increased ε_3, ε_4, ..., ε_n until the specimen failed at a elongation break. ε_{max} denotes the maximum strain where the specimen experienced. The elastic modulus (E_{DN}) at each ε_{max} was calculated in the range of 5−10% strain from the loading curve. The facture energy dissipated during each loading cycle, ΔU_{hys_n}, is estimated by area between the nth loading−unloading curves. The total dissipated fracture energy from the first loading to the nth loading is calculated by

$$U_{hys,n} = \sum_{i}^{n} \Delta U_{hys,i} \tag{2}$$

The work required to fail the gel specimen at strain ε_n, W_n, is calculated by

$$W_n = U_{hys,n} + \int_0^{\varepsilon_n} \sigma_{n+1}\, d\varepsilon \tag{3}$$

Fracture ratio (ϕ_m) represents the fraction of the fractured agar chains out of the "elastically effective" agar chains that can be calculated from variation in the modulus E_{DN} of gel samples as defined by Gong et al.[37] Specifically, ϕ_m is defined as

$$\phi_m = 1 - v_e/v_{e0} \tag{4}$$

where v_e and v_{e0} (m^{-3}) denote the number density of elastically effective agar chains in the elongated and virgin DN gels, respectively. The ratio v_e/v_{e0} can be obtained from

$$v_e/v_{e0} = E_{Agar}/E_{Agar0} \tag{5}$$

where E_{Agar} and E_{Agar0} are the initial elastic moduli of agar component in prestretched and virgin DN gels, respectively. Thus, ϕ_m can be calculated by

$$\phi_m = 1 - E_{Agar}/E_{Agar0} \tag{6}$$

Since E_{Agar} can not be measured directly due to the complex structure of DN gels, we estimated E_{Agar} from the initial elastic modulus of DN gels (E_{DN}), under an assumption that the modulus of DN gels is the sum of the moduli of the two networks:

$$E_{DN} = E_{Agar} + E_{PAM} \tag{7}$$

Considering that PAM gel does not show any mechanical hysteresis in our previous work,[41] the initial elastic modulus of the PAM component, E_{PAM}, is treated as a constant during mechanical hysteresis measurements. So, E_{PAM} of DN gels is approximately close to that of PAM SN gels. The modulus of PAM SN gel was found to be 0.018 MPa in our previous work.[41] Thus, fracture fraction is reformulated by

$$\phi_m \approx 1 - (E_{DN} - 0.018)/(E_{DN0} - 0.018) \tag{8}$$

3. RESULTS AND DISCUSSION

3.1. High Toughness of Agar/PAM DN Gels. The "toughness" of hydrogels can be generally quantified by dissipated energy or tearing energy. Gong et al.[43] suggested that instead of measuring dissipated energy on an intact gel, tearing energy (T) of a notched gel can provide a better measurement for the toughness of high strength hydrogels. Figure 1a shows a tearing force curve of Agar/PAM DN gel as a function of stretching distances. Upon a steady tearing, tearing force increased rapidly as the gel was stretched to 40 mm, and then tearing force slowly approached a plateau until a breaking point of ~80 mm. Based on average tearing force (F_{ave}), Figure 1b clearly shows the dependence of tearing energy (i.e., toughness) of Agar/PAM DN gels on crack velocities. As crack velocities were less than 50 mm/min, tearing energies of Agar/PAM gels were ~1000 J/m^2, similar to those of PAMPS/PAM DN gels (10^2−10^3 J/m^2), cartilages (10^2−10^3 J/m^2), and rubbers (10^3 J/m^2).[19,27] Tearing energies, however, were significantly reduced by ~50% as crack velocity increased above 100 mm/min. The rate-dependent fracture behavior could be attributed to the physically cross-linked nature of agar first network. Single-network (SN) agar gels also showed the rate-dependent toughness.[44] In parallel, tensile tests also confirmed that Agar/PAM DN gels[41] exhibited very high

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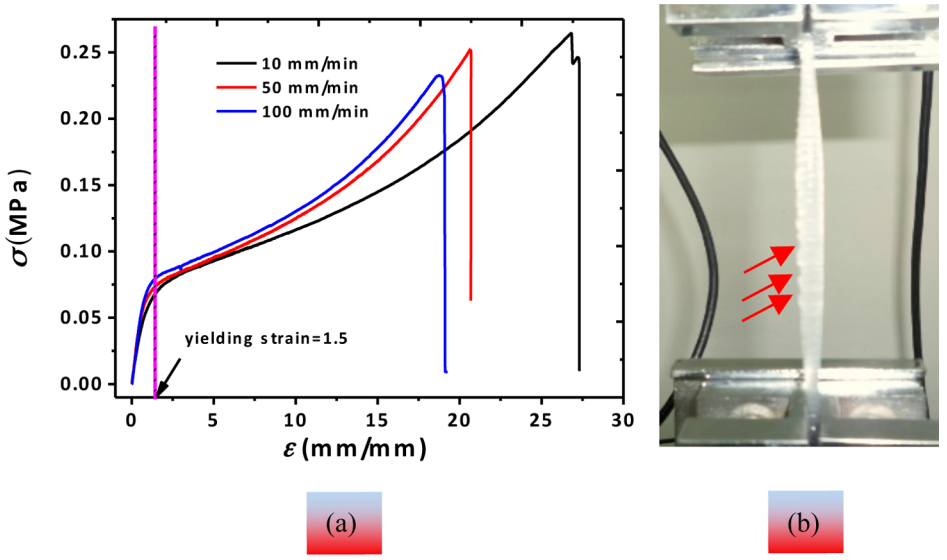

Figure 2. (a) Stress–strain curves of Agar/PAM DN gels at different stretching rates. (b) Simultaneous necking of Agar/PAM DN gels at 10 mm/min.

dissipated energy of ~10 MJ m^{-3} similar to ~14 MJ m^{-3} for PAMPS/PAM DN gels.[28]

Both Agar/PAM and Ca^{2+}-alginate/PAM DN gels consist of hybrid physically chemically linked networks, where the first networks in both gels are physically linked by noncovalent bonds. Specifically, the first agar network is physically linked by agarose helix bundles via hydrogen bonding,[41] while the first alginate network is cross-linked by Ca^{2+} ions.[39] Compared to Agar/PAM gels, the Ca^{2+}-alginate/PAM hydrogels exhibited the relatively higher toughness of ~9000 J m^{-2}, which could be due to the ionically cross-linked network of alginate gels and the interconnection between covalently cross-linked PAM and ionically cross-linked alginate through covalent bonds, as evidenced by FTIR and TGA.[39] Differently, Agar/PAM gels in the absence of chemical cross-linkers exhibited no changes in mechanical properties compared to agar SN gel, indicating no cooperative chemical reactions (covalent bonds) between agar and PAM. Similar to our observation, Gong et al.[45] also reported that *truly independent* PAMPS/PAM DN gels ("*t*-DN" gels), which did not have any covalent bond between the first and the second networks, cannot be toughened by the un-cross-linked second network. They also found that *t*-DN gels became stronger than *c*-DN gels (two networks are connected by covalent bonds) when the second network is loosely cross-linked. High toughness of Agar/PAM DN gels and *t*-DN gels suggests that covalent bonds between two networks are not necessarily essential for toughening the gels.

3.2. Rate-Dependent Tensile Properties of Agar/PAM DN Gels. Figure 2a shows typical tensile stress–strain curves of Agar/PAM DN gels at different stretching rates. Comparison of these stress–strain (σ–ε) curves revealed some interesting similarities and differences. First, all tested gels exhibited strong mechanical properties. The failure stress and strain of the gels were σ = 0.23 MPa and ε = 18.8 mm at 100 mm/min, 0.25 MPa and 20.6 mm at 50 mm/min, and 0.26 MPa and 26.8 mm at 10 mm/min, respectively, indicating that the gels stretched at the lower rate (10 mm/min) can withstand much higher stress and strain than the gels stretched at the higher rates (50 and 100 mm/min). Second, the gels exhibited a nearly same yielding strain (ε_y ~ 1.5) at different stretching rates, with almost rate-independent yielding stress. More importantly, the gels displayed different stress–strain behaviors before and after yielding. Before the yielding occurred, the stress and strain of the gels were almost independent of stretching rates, achieving σ = 0.075 MPa at ε = 1.5. After the yielding, strong dependence of stretching rates on stress and strain was observed. The gels experienced the relatively larger fracture stress and strain at low stretching rates of 10 mm/min than those at high stretching rates of 100 mm/min. Kwon et al.[44] also reported the dependence of loading rates on the fracture of agarose SN gels. However, agarose SN gels exhibited the smaller fracture stress and strain at the lower loading rates, different from our observation. This is not surprising because unlike SN gels, Agar/PAM DN gels experience an earlier softening whenever the fracture of the first agar network occurs early at the lower loading rates. Third, simultaneous necking in tensile tests was observed for all gels at different stretching rates. The virgin gel had smooth surface before deformation, but it produced a rougher surface like caterpillars upon a small strain (Figure 2b). Upon applying a small strain, our Agar/PAM DN gels exhibited multiple necking regions, while PAMPS/PAM DN gels and other chemically linked DN gels only exhibited single necking region. It can be clearly seen in Figure 2b that many necking regions (red arrows) in Agar/PAM gels were shown and separated from unnecking ones, which make the gel appearance look like "caterpillars", where the deformation of the necking regions was more apparent than that of the unnecking ones. When applying the larger strains, we directly observed the disappearance of the unnecking regions at a certain stain. Similar phenomena were also reported in Al^{3+}-alginate/PAM hydrogels and Fe^{3+}-alginate/PAM hydrogels, but not in divalent cross-linked alginate/PAM hydrogels.[46] Lining with the fact that no necking platform beyond yielding point was observed in other high strength physically linked hydrogels including PAM–Laponite gels,[47] polyampholyte gels,[23] and hydrophobically modified PAM gels,[48] simultaneous necking in our Agar/PAM DN gels and Al^{3+}/Fe^{3+}-alginate/PAM gels suggests that the fracture of the agar network is not an abrupt fracture process.

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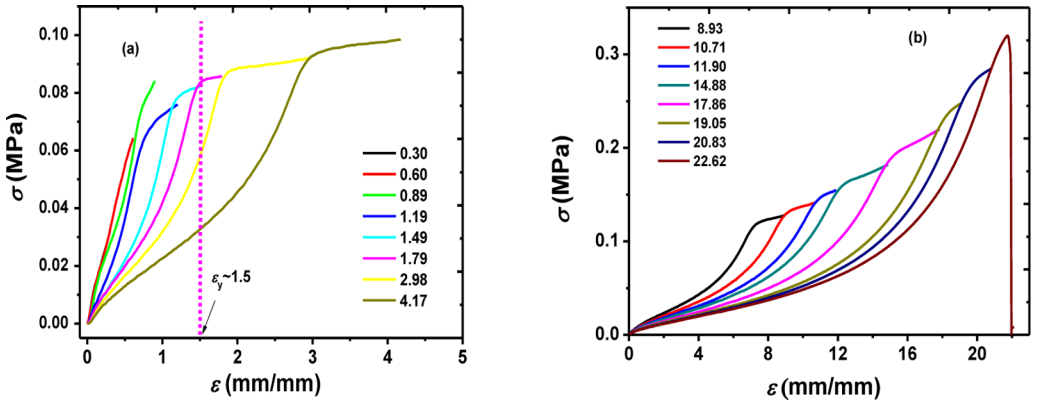

Figure 3. Successive cyclic loadings curves of Agar/PAM DN gels at a wide variety of ε_{max} from 0.30 to 22.62: (a) small strain; (b) large strain (unloading curves not shown). The stretching rate for loading and unloading cycles is 100 mm/min.

3.3. Energy Dissipation upon Cyclic Loading–Unloading Tests. A cyclic loading–unloading tensile test is a facile way to analyze the internal fracture process of DN gels,[37] and the resulting stress–strain curve is another index to assess the capability of energy dissipation and the mechanical properties of gels. Figure 3 shows the successive cyclic loading–unloading of Agar/PAM DN gels at different ε_{max}. The stress–strain curves of Agar/PAM gels showed large hysteresis before and after yielding, suggesting the occurrence of large internal facture in the first agar network upon deformation. It is notable that the hysteresis loops first appeared at ε_{max} = 0.6, indicating the internal facture of agar gel occurs at far below the yielding point. Similar tensile mechanical hysteresis occurring before a yielding point was also observed in PAMPS/PAM DN gels.[37] On the other hand, chemically linked PAMPS/PAM gels showed three distinct regions in stress–strain curves: prenecking (before yielding point), necking (stress plateau), and hardening (after necking) regions, while Agar/PAM gels display no stable necking (stress plateau), instead of simultaneous necking. It is apparent that different internal facture behaviors between chemically linked PAMPS/PAM gels and hybrid linked Agar/PAM gels may originate from different network structures and association forces.

Two facture parameters of initial elastic modulus (E_{DN}) and fracture ratio (ϕ_m) are defined to quantify the internal fracture behavior of DN gels. Figure 4a shows the E_{DN} calculated from the cyclic loading curves of DN gels at various maximum strains ε_{max}. Overall, all E_{DN} decreased with ε_{max} at different stretching rates. However, some observable differences in the E_{DN}–ε_{max} curves also indicate different facture behaviors of Agar/PAM DN gels at different stretching rates. At 100 mm/min, the E_{DN}–ε_{max} curves showed three characteristic regions: (i) a remarkable decrease of E_{DN} below yielding strain of ε_y = 1.5, (ii) a slow decrease of E_{DN} between ε_y = 1.5 and ε_{max} = ~6, and (iii) a nearly flat plateau of E_{DN} at ε_{max} > 6 until breaking point. At 50 mm/min, a similar trend of E_{DN} at three regions was also observed, but with much slower decrease of E_{DN} at the first two regions. However, different from the higher stretching rates (>50 mm/min), only two regions were observed at 10 mm/min.

ϕ_m—calculated from variation in the modulus E_{DN}—represents the fraction of the fractured chains out of the "elastically effective" chains.[37] Figure 4b shows ϕ_m of the gels as a function of ε_{max}. Consistent with Figure 4a, three regions in ϕ_m were identified. Overall, ϕ_m increased significantly with ε_{max} in the first two regions, then slowed down the increment, and

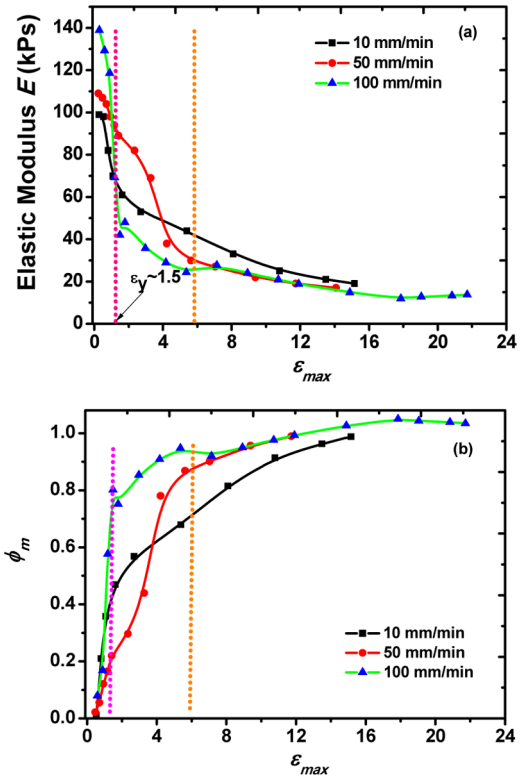

Figure 4. Internal fracture behavior of agar/PAM DN gels. Two fracture parameters of (a) initial elastic modulus (E_{DN}) and (b) fraction of fractured effective elastic agar chains (ϕ_m) in DN gels as a function of ε_{max} at different stretching rates.

finally reached to almost 100% at the end of the necking region (i.e., at ε_{max} of ~6). The final values of ϕ_m indicate that almost 100% of elastically effective chains of agars are fractured at its failure. ϕ_m also showed the dependence of stretching rate on gel fracture. Compared to Agar/PAM DN gels, ϕ_m of PAMPS/PAM DN gels reached 90% at the yielding point and 100% at the end of necking.[37] As described above, Agar/PAM DN gels exhibited simultaneous necking, with no stable platform in stress–strain curves (Figure 3). The multiregions in Figure 4 may be resulted from this unique simultaneous necking; i.e., the end of the second region (ε_{max} ~ 6) indicates the end of the necking.

To better understand energy dissipation upon the facture process of Agar/PAM gels, Figure 5a shows the dependence of

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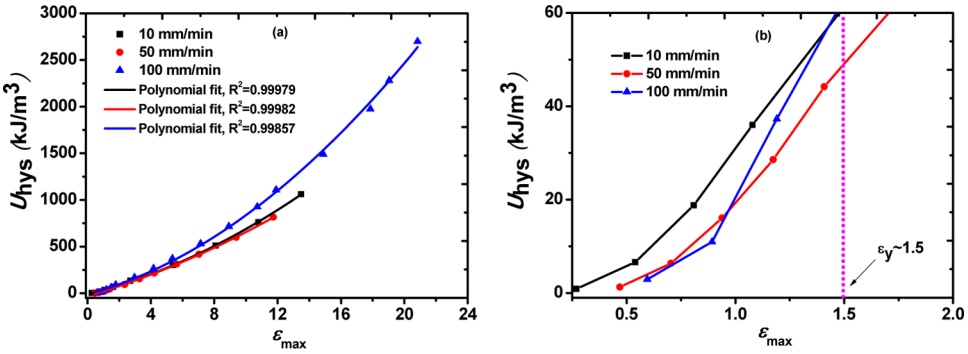

Figure 5. Energy dissipation upon the facture process of Agar/PAM gels: (a) dependence of dissipation energy (U_{hys}) on ε_{max} at different stretching rate; (b) a close-up of (a) at small values of ε_{max}.

the amount of dissipated energy U_{hys} on ε_{max}, while Figure 5b shows a close-up of Figure 5a before the yielding point of ε_y = 1.5. In Figure 5b, all gels tested at different stretching rates exhibited evident hysteresis at far below $\varepsilon_y \sim 1.5$. The U_{hys} became more pronounced at the smaller ε_{max} and at 10 mm/min. These results suggest that the fracture of agar first network occurs far below the yielding point, and fracture timing could be even earlier at low stretching rate. Beyond the yielding point, all U_{hys} increased gradually and nonlinearly with ε_{max}, and all curves were fitted very well by polynomials ($R^2 \sim 0.999$). Different from U_{hys} in Agar/PAM gels, after the yielding point,[37] both necked and unnecked regions coexist, and U_{hys} in PAMPS/PAM gels increased linearly with ε_{max} due to increase of the necked region, which dissipates energy.

To qualitatively estimate the efficiency of energy dissipation, Figure 6 shows the relationship between U_{hys}/W and ε_{max} at

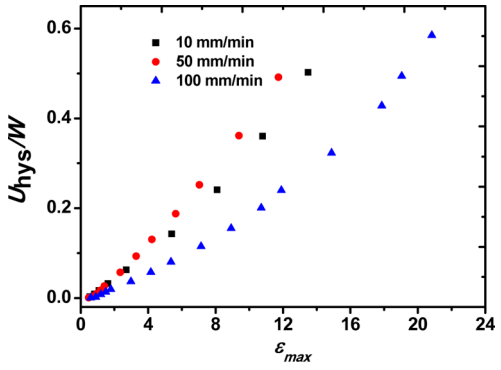

Figure 6. Dependence of U_{hys}/W on ε_{max} at different stretching rates.

different stretching rates, where W is the work done by extension and the ratio of U_{hys}/W represents the fraction of the irreversible work caused by the internal structure change of the agar network within a total of work of extension. A strong dependence of stretching rates on energy dissipation efficiency was clearly observed. For a given ε_{max}, the resulting values of U_{hys}/W at 10 and 50 mm/min were similar to each other, but they were much larger than the corresponding values at 100 mm/min. Lining with the rate-dependent tearing energy in Agar/PAM DN gels, this observation indicates that the lower stretching rates enable to dissipate energy more efficiently than the higher ones. Moreover, final values of U_{hys}/W reached to 0.5–0.6 at a breaking point, suggesting that 50–60% of work is used to fracture the first agar network during the deformation process. Thus, overall energy dissipation efficiency of Agar/PAM DN gels was 50–60%, comparable to that of vulcanized rubbers (59–67%), but smaller than that of PAMPS/PAM DN gels (~85%).[37] It is, more importantly, to note that after the yielding point U_{hys}/W exhibited completely different behaviors between our Agar/PAM gels and PAMPS/PAM DN gels; i.e., after the yielding point, U_{hys}/W in Agar/PAM gels continuously increased to 50–60%, while U_{hys}/W in PAMPS/PAM gels remained almost unchanged at ~85% regardless of the increase of the strain.[37]

3.4. Possible Facture Mechanisms. The failure of a material generally involves two sequential processes of the initial fracture formation (nucleation) and the following fracture propagation (growth).[19] A general strategy to toughen the gel is to reduce the probability of initial fracture formation, which often occurs in the first network. Experimental results from ours and others clearly demonstrate that the fracture of the first network has a strong influence on the DN properties,[37,38,41] independent of network topology. But, the details of fracture process and associated energy dissipation mechanisms are likely different between hybrid physically/chemically linked Agar/PAM gels and chemically linked PAMPS/PAM gels.

In Agar/PAM DN gels, a gradual increase of U_{hys}/W during the whole deformation process was consistently observed at three stretching rates tested, suggesting there is no phase transition from *continuous* to *discontinuous network* in the gels (Figure 6). As illustrated in Figure 7, we proposed a chain pull-out mechanism to interpret the continuous fracture of the first agar network. Upon applying small strains on the gels, the aggregated agar helical bundles start to separate from each other, while the agar chains start to unzip and pull out progressively from agar bundles as well. Meanwhile, the first

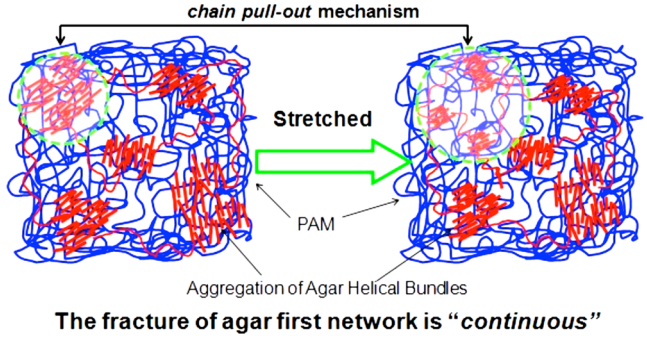

Figure 7. Schematic illustration of the "chain-pulling-out" fracture mechanism of the first agar network in Agar/PAM DN gels.

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network still retains unbroken, resulting in pronounced hysteresis for energy dissipation. The disaggregation of helical bundles causes the loss of the bulk modulus of the agar gel. As a result, Agar/PAM DN gels become softening as ε_{max} increases. The chain-pull-out behavior can occur throughout the whole deformation process (i.e., at three stages of before/after yielding or hardening). At lower stretching rates, such behavior becomes more obvious as indicated by to earlier hysteresis (Figure 5b). Kown et al.[44] also suggested that agarose SN gel obeyed the chain pull-out mechanism without chain scission at low stretching rates. Based on rate-dependent facture behavior as described above, the pull-out agar chains do not fragment into small clusters due to its physically cross-linked nature.

For chemically linked PAMPS/PAM DN gels, Gong et al.[37] proposed a two-step internal fracture of PAMPS network in PAMPS/PAM DN gels: (1) At the prenecking region with small strains applied, the stress is concentrated on the connecting PAMPS chains and consequently causes the chains to break preferentially. After breaking the connecting chains, the first PAMPS network becomes *discontinuous* and cannot bear more and stronger stress even at small strains. (2) At the subsequent necking and hardening regions, the stress is transferred from the PAM network to the PAMPS small gel clusters (microgels) due to the entanglement between the two networks. Generally speaking, at all three stages, the first network is permanently rupture into small clusters to different extents, and these broken clusters are likely to have irregular distribution of cross-linking points and lengths and act as sacrificial bonds to increase the resistance against the crack propagation by forming a large damage zone. Such permanent damage is almost irreversible and unrecoverable. As a result, U_{hys}/W remains constant after the yielding point because the breakage of the connecting chains in the first PAMPS network leads to a phase transition of PAMPS network from the continuous to discontinuous phase.

Taken together, both Agar/PAM and PAMPS/PAM DN gels exhibit some similar macroscopic mechanical behaviors including yielding, necking, hysteresis, softening, and high toughness. The fracture of first network in both DN gels also occurs at far below yielding point. On the other hand, both DN gels also exhibit some intrinsic differences in fracture details and mechanisms. In PAMPS/PAM DN gels, the threshold strain was usually observed after yielding point, which represents a phase transition of the first PAMPS network from the continuous to discontinuous phase. However, in our Agar/PAM DN gels, no threshold strain was presented at yielding point and even at the end of the necking. Such difference could come from different network structures between PAMPS and agar networks. Unlike PAMPS gels, agar gels are physically cross-linked, and thus no chain scission would occur upon deformation. Moreover, in PAMPS/PAM DN gels, the first PAMPS network fractures into small clusters at yielding point because the connecting chains of PAMPS are broken. The PAMPS clusters are further redivided at necking and hardening regions. At yielding point, 85% of work is used for the internal fracture of the PAMPS network. However, in Agar/PAM DN gels, the agar first network does not fracture into small clusters; instead, agar helical bundles simply disassociate with each other without breaking chains. Further stress beyond the yielding only leads to the homogeneous distribution of agar helical bundles in the network, as evidenced by gradual increase of U_{hys}/W with ε_{max}. During the deformation process, the agar first network is able to retain its continuous phase, with agar chains being pulled out of the first network. This is fundamentally different from PAMPS/PAM DN gels or other chemically linked DN gels, in which the fracture of the first network is caused by irreversible and permanent covalent bond breakings that often be described by the Lake−Thomas theory.[49] Owing to the continuous phase of the first agar network, the structure of Agar/PAM DN gels appears to be bicontinuous during deformation. The bicontinuous structure is similar to the poly(styrene-*b*-butadiene) $(PS-PB)_n$ mutliblock copolymers, whose easily fragmented glassy portions (PS) can disperse in a rubbery continuous domain (PB).[50]

Moreover, the yielding behavior of Agar/PAM DN gels is also different from that of chemically linked DN gels because chain scission does not occur in the agar network. Gong et al. designed novel St-TPEG/PAM DN gels with a nearly homogeneous first network of tetra-PEG.[51] Apart from excellent mechanical properties of St-TPEG/PAM DN gels, the gels experienced substantially different fracture processes before yielding point as compared to highly heterogeneous structure PAMPS/PAM DN gels. They suggest that the yielding (necking), caused by the catastrophic internal fracture of the first network in conventional DN gels, occurs only after the first network reaches a certain homogeneous level. With such stress concentration at this moment, the chains in the first network break sequentially in an order of chain lengths, and consequently the unbroken chains yield a narrow chain-length distribution. Both effects cause the first network to become relatively homogeneous with an increase of strain.[51] In Agar/PAM gels, the agar first network achieves homogeneous structure differently. A number of studies on agar/agarose SN gels have revealed that the network of agar/agarose SN gels alone is structurally heterogeneous, as confirmed by the polydispersity arrangement of helices by SAXS[52] and SANS.[53] Distinct mechanical hysteresis at far below yielding point (prenecking region) also suggests the inhomogeneity of agar/agarose SN gels occurring at low yielding stress/strain. Because of the polydispersity arrangements of agar helices, hydrogen bonding between agars has a wide range of interaction patterns and strengths on different locations. Upon applying strains on the gels, these weak associations and positions between agar helices become vulnerable targets for chains to be pulled out from the network (Figure 7). As the strain strength increases, the pull-out chains are gradually evenly distributed in the network with similar length. Eventually, the agar network becomes a certain homogeneous as the yielding occurs. We should note that the first network of DN gels is still far from fully homogeneity compared to the nearly homogeneous tetra-PEG hydrogels with high strength of 27 MPa, which contain negligible dangling chains and entanglements in the network.[54,55] In other words, both agar and PAM networks are not homogeneously formed in Agar/PAM DN gels at both initial and deformation states. Based on the chain-pulling mechanism, the disassociated agar chains at large deformation state are likely to be more homogeneously distributed in the PAM network than those agar chains at the initial state, although agar chains are still away from fully homogeneous distribution. Different from chemically linked DN gels, the yielding point in Agar/PAM DN gels does not necessarily mean that the agar network is catastrophically fractured.

4. CONCLUSIONS

In this work, we synthesize and characterize Agar/PAM DN gels with a unique network combination of a physically linked,

first agar network with a chemical-linked, second PAM network, with particular attention to the effect of internal fracture process of the agar network on mechanical properties of DN gels. Agar/PAM DN gels demonstrate their superior mechanical properties, with fracture energies of 10^2−10^3 J/m^2, as compared to ∼10^1 J/m^2 for agarose gels, ∼10^0 J/m^2 for PAM gels, 10^2−10^3 J/m^2 for PAMPS/PAM DN gels, 10^2−10^3 J/m^2 for cartilages, and rubbers for ∼10^3 J/m^2. Unlike most of chemically linked DN gels, Agar/PAM DN hydrogels exhibit notable rate-dependent fracture behaviors due to the physically cross-linked first network. The slower stretching rates enable to achieve the higher fracture stress/strain and toughness. Energy dissipation efficiency (U_{hys}/W) of Agar/PAM DN hydrogels is 50−60%, and the nonlinear increase of U_{hys}/W as ε_{max} after yielding is completely different from the almost unchanged U_{hys}/W in PAMPS/PAM DN gels, indicating the fracture of the first agar network during deformation is continuous and the fracture behavior is mainly governed by the chain pulling-out mechanism. This work expands our current knowledge of DN gels from synthesis method to toughening mechanisms that mainly come from chemically cross-linked DN gels. We hope that the method and the DN gel systems developed in this work could provide a more complete picture for a better understanding of the intrinsic structure−property relationship of DN gels that help to design the next generation of DN gels with desirable properties.

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Notes

The authors declare no competing financial interest.

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