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A Deformation Mechanism for Double-Network Hydrogels with Enhanced Toughness

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Summary: The long-standing pursuit of a synthetic equivalent to tissue cartilage has sprouted significant new activities in strategies for new material synthesis, among them a noticeable one being the double-network hydrogels (DN-gels) scheme. DN-gels were prepared from the combination of an anionic polyelectrolyte network and a lightly crosslinked neutral polymer. These hydrogels exhibit an intriguing combination of properties intrinsic to natural cartilage: a low surface friction coefficient and a fracture toughness much higher than either of the constituent materials. The reinforcement of a hard, brittle polymer gel with a soft, viscoelastic neutral polymer is counter-intuitive. Based on our recent results from neutron scattering measurements, we proposed a deformation mechanism where the molecular association between these two polymers plays a pivotal role. In this work, we further evaluate the proposed mechanism by performing mechanical measurements on DN-gel samples with different polyelectrolyte network structure. The experimental results provide qualitative support for the proposed deformation mechanism.

Keywords: crosslink; double network; hydrogels; polyelectrolyte; toughness

Introduction

Hydrogels are crosslinked polymer networks that can absorb water many times their volume, and have found use in numerous applications such as stimuli-responsive materials, drug delivery, tissue engineering, and as potential replacements for articular cartilage. However, the fracture strength of a chemically crosslinked synthetic hydrogel is usually low, typically about a few hundred kPa. Many approaches, such as double network,[1] nanocomposite hydrogels[2–5] and slide-ring gels[6–8] have been taken to significantly improve the mechanical properties of hydrogels needed for mechanical applications. A relatively new approach, incorporating a high molecular weight neutral polymer (lightly crosslinked chains) within a swollen polyelectrolyte network, double-network hydrogels (DN-gels), was recently discovered and developed.[9–17] Surprisingly, DN-gels have the highest fracture strength in compression (≈20 MPa) among crosslinked hydrogels and have proven to be the closest synthetic analogues to articular cartilage. The fracture toughness of DN-gels prepared from many different polymer pairs was shown to be much higher than that of the individual components.[1] The use of soft, lightly crosslinked polymer chains to reinforce the mechanical properties of a crosslinked network is intriguing but not well-understood. To identify the molecular mechanism of enhanced toughness in DN-gels, we have conducted small-angle neutron scattering (SANS) measurements with deuterium-labeled materials to characterize the structure of each polymer component both under static conditions and under a uniaxial

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deformation[13–15]. From the static structure results of the solution blends, not the DN-gel samples, the thermodynamic interaction parameters among the polyelectrolyte, the neutral polymer and water were determined; a favorable intermolecular association between the two polymers constituting the DN-gel with superior properties was identified.

A mechanism to account for the superior toughness of DN-gels was first proposed by Gong et al.[17] They proposed that a multiple fracture process that turns the polyelectrolyte network into pieces of a few hundred nanometers in the linear dimension provides a pathway for irreversible energy dissipation. This mechanism was further supported by four recent studies based on detailed mechanical measurements.[18–21] In a previous publication,[15] we developed a molecular model to stipulate one of the necessary conditions for multiple fractures to occur in the polyelectrolyte network of DN-gels. In the present work, this molecular model is further delineated with mechanical test data from DN-gel samples in which one of the important molecular attributes used in the deformation model is selected as an experimental variable. In particular, we prepared DN-gel samples by synthesizing polyelectrolyte networks under different conditions such that their fracture stress, σ_{1c}, became different. Throughout this work, the polyelectrolyte network is denoted as component 1, the neutral, lightly crosslinked polymer as component 2, and water as the third component. The subscript in σ_{1c}, therefore, denotes the critical stress for the fracture of component 1, the polyelectrolyte network.

Experimental Part

DN-Gel Preparation

Two types of DN-gel samples were prepared with their main difference being in the extent of possible covalent bonding between components 1 and 2. In the so-called ''common'' DN-gels, there exists the possibility of some chemical crosslinking between the polyelectrolyte and the neutral polymer chain. Work is on-going in the synthesis of the so-called *truly-independent* DN-gels (*t*-DN-gels) in which the inter-species crosslink possibility was suppressed. Only the results of ''common'' DN-gels will be discussed in this work. Some preliminary results of ''true'' DN-gels just became available and will be discussed in future publications. Suffice to mention that no noticeable difference exists between these two types of DN-gels in their mechanical behaviors within the context of current discussions. Polyacrylamide (PAAm) was used as the neutral polymer and poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) was chosen as the polyelectrolyte. DN-gels made from many polymer pairs have been synthesized and tested,[1] among them the PAMPS-PAAm pair stands out due to its superior mechanical strength and is also the most studied pair. Details of the synthesis are given as follows.

Common DN-Gels

These double network hydrogels were synthesized by a two-step free radical polymerization. The PAMPS gel was synthesized by UV (365 nm) irradiation of solutions containing 1 M of AMPS monomer, 4 mol% of *N,N′*-methylenebis(acrylamide) (MBAA) as crosslinking agent and 0.01 to 10 mol% of 2-oxoglutaric acid as UV activated free radical initiator. All the molar percentages are referred to the monomer concentration and all the reactions were conducted under an argon atmosphere. The resulting PAMPS gels were then immersed in an aqueous solution containing 2 M of AAm monomer, 0.01 mol% of MBAA and 0.01 mol% 2-oxogultaric acid until swelling equilibrium was reached in 6 to 8 hours. In practice, we allowed a 24 hours immersion time to ensure that swelling equilibrium was reached. The swollen PAMPS gels were then sandwiched between two glass plates and the AAm monomers were polymerized with UV irradiation under an argon atmosphere. Freshly prepared DN-gels were immersed in a large amount of water for at least 5 days to remove residual monomers and other unreacted species. In this DN-gels preparation scheme, the UV initiator loading during the synthesis of the PAMPS gels is the only experimental variable. A high initiator loading is expected to result in networks with many imperfections including dangling ends, hence, a low value of σ_{1c}, the fracture strength of the first network.

Mechanical Measurements

Tensile test measurements were performed on dumbbell-shaped gel samples prepared in accordance with the dimensions specified in JIS-K6251-7 (length: 40 mm; width: 10 mm; thickness; 2-3 mm; gauge length: 12 mm; inner width: 2 mm), commonly used for tensile test of vulcanized rubbers. JIS stands for Japan Industrial Standard. The crosshead speed in the tensile test was set at 100 mm min^{-1} for all the measurements. Nominal stress and nominal strain were calculated based on the initial sample cross sectional area and the initial gauge length, respectively.

Results and Discussion

Figure 1 shows the tensile test results of the "common" DN-gels prepared with eight different initiator contents during the synthesis of PAMPS gels. All the samples exhibit a prominent necking behavior after a well-defined yield stress, σ_{1c}, defined schematically in this figure together with the definition of the plateau strain ε. As expected, high initiator loadings did lead to more imperfections within the PAMPS network, and, hence, a low value for σ_{1c}, concurrently, a large plateau strain. The interplay between ε and σ_{1c} will be the focus in the remainder of this manuscript. The incipient of the stress plateau region during the tensile test always coincided with the formation of a necking zone and the end of the stress plateau region marks the completion of the necking zone propagation across the entire sample gauge length. The deformation within the stress plateau region is thus highly heterogeneous along the gauge length. After the stress plateau region, further elongation resulted in a stress upraise and the deformation became homogeneous hereafter. It is noteworthy that the three samples with low initiator concentrations, i.e. at 0.01, 0.1 and 0.3 mol%, exhibited fracture prior to the stress upturn point. The tensile test results of these samples will not be included in the following data analysis since their values of ε are not well defined. From a simple stress

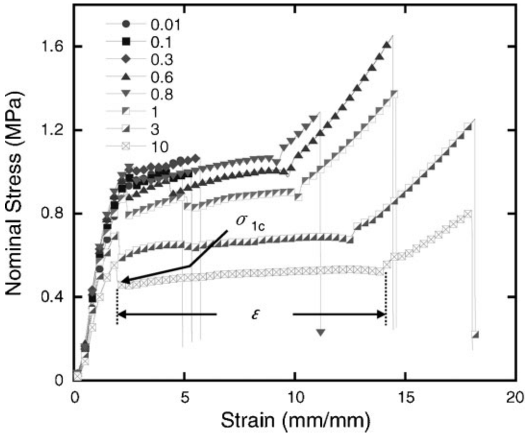

Figure 1.
The stress-strain curves of "*common*" DN-gels in which the PAAm chain was synthesized with 0.01 mol% of MBAA, the crosslinking agent. The labels denote the initiator concentration used in the synthesis of the PAMPS network while the crosslinking agent concentration remained unchanged at 4 mol%.

transfer viewpoint, we reached the following relation between the yield stress σ_{1c} and the distance t_c between two adjacent cracks in one of our previous publications,[15]

$$t_c = \left(\frac{cd_2\sigma_{1c}}{3\pi\phi_2\tau_c\ell}\right)^{0.5} b \tag{1}$$

τ_c denotes the critical shear stress required to detach a PAAm-PAMPS bond, b denotes the repeat length of the PAAm chain and its value is taken to be 4.5 Å by accepting a characteristic ratio of 8.5 between the unperturbed dimension h_o^2 of PAAm in water and $n\ell^2$; n is the number of repeating units and ℓ is the repeat distance at 1.54 Å. ϕ_2 denotes the volume fraction of the PAAm component and factor c is introduced to account for the fact that only a fraction of the chains bridging a crack can be considered as load bearing or tie chains. Based on our knowledge of oriented semi-crystalline polymers, the magnitude of c is estimated to be on the order of 10^1 to 10^2, i.e. only a few percent of the chains between crystallites can be considered as load bearing tie chains. d_2 in the above Equation denotes the diameter of the PAAm chain and it is approximated by $V_2^{1/3}$, where V_2 is the monomer volume of AAm of 82.54 Å^3 mol^{-1}. This leads to $d_2 = 4.35$ Å.

It is noteworthy that throughout the eight "common" DN-gel samples in Figure 1, all the above-mentioned parameters stay unchanged since the only experimental variable is the initiator concentration. By varying the initiator concentration in the synthesis of the polyelectrolyte network, one does not expect to change neither the composition of the DN-gels nor the association strength between PAMPS and PAAm; this association strength is parameterized as τ_c in the above Equation and it depends only on the monomer types. The fracture strength σ_{1c} of the first network is thus the only parameter affected by the initiator concentration loading. Based on the above discussions, Eq. 1 can be simplified to $t_c \propto \sigma_{1c}^{0.5}$, i.e. the distance needed for the stress exerted on the PAMPS network to reach σ_{1c} increases as $\sigma_{1c}^{0.5}$. Inside a crack, the stress is completely exerted on the flexible PAAm chains and gets transferred gradually to the rigid PAMPS network. The distance t_c is defined with the edge of the initial crack as the starting point. The exponent 0.5 arises from a Gaussian coil approximation for the PAAm chains conformation within the PAMPS network under tensile stress. This is a rather crude approximation and we will return to it later.

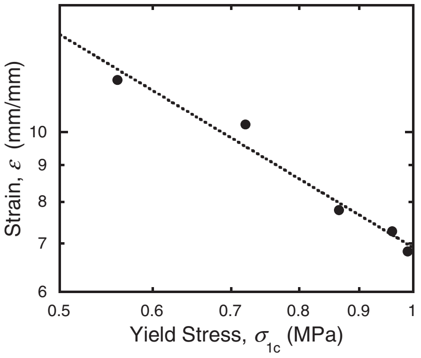

Figure 2.
Experimental results of the plateau strain (ε) and the yield stress (σ_{1c}) from "*common*" DN gels (solid symbol).

The number of cracks, N, within the tensile gauge length at the end of the stress plateau region or at the completion of the necking propagation must be proportional to $1/t_c$. Assuming that the crack opening distance depends only weakly on the applied stress in the stress plateau region, we have the following relation between the plateau strain and the total number of cracks as $\varepsilon \propto N$ which leads to $\varepsilon \propto \sigma_{1c}^{-0.5}$. Experimental results of ε and σ_{1c} from Figure 1 are plotted in Figure 2 as the solid symbols and they follow a simple scaling relation of $\varepsilon \propto \sigma_{1c}^{-0.98}$, with the absolute value of the exponent being considerably greater than 0.5. This high value suggests that the Gaussian coil approximation for the PAAm chains inside the PAMPS network under tensile stress is an overly simplified one; the PAAm chains become long-drawn-out and taut under tensile stress and this can lead to a high exponent. It is possible that under a tensile stress near

σ_{1c}, the PAAm chain within the PAMPS network adopts a conformation which closely resembles what modeled by de Gennes as a single chain confined inside a tube.[22] In this model, the length t_c scales linearly with the contour length of the PAAm chain; the corresponding exponent between ε and σ_{1c} is simply unity.

Conclusion

In summary, the observed scaling relation between the yield stress and the plateau strain is qualitatively consistent with the notion that stress transfer between PAAm and the PAMPS network plays an important role in the toughening mechanism of the DN-gels. The exponent determined from experimental results between ε and σ_{1c} suggests that the PAAm chains within the PAMPS network are rather drawn-out instead of being Gaussian coils.

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