Finite Strain Damage-Elastoplasticity in Double-Network Hydrogels

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ABSTRACT

Finite tensile behavior and fracture toughness of double-network (DN) and triple-network (TN) hydrogels synthesized from 3-sulfopropyl acrylate potassium salt (SAPS) and acrylamide (AAM) are discussed. The mechanical behavior of pseudo-semi-interpenetrating polymer network (pseudo-SIPN), pseudo-interpenetrating polymer network (pseudo-IPN) and TN hydrogels prepared from the two types of DN networks are considered. In general, the mechanical behavior of tough hydrogels is dependent upon the crosslink densities of the first and second networks in DN and TN hydrogels and the covalent connectivity of the second or third network to the previous network architecture. Pseudo-SIPN hydrogels, where no crosslinking agent is used to make the second network, exhibit necking for tensile deformations. When a very low concentration of crosslinking agent is used in the second polymerization step (pseudo-IPN), necking is suppressed and strain hardening occurs. Increasing the crosslink density of the second network produces more pronounced strain hardening, but also embrittlement of the hydrogel. For tough hydrogels where the first network is very brittle, i.e., very high crosslink density, it is difficult to prevent necking. The formation of a third, loosely crosslinked network within pseudo-SIPN and pseudo-IPN hydrogels that exhibit necking prevents necking and produces strain hardening. Loading – unloading tensile experiments conducted on DN hydrogels indicated that regardless of the stretch ratio used (high strains above or low strains below the yield point), the sample exhibited plastic flow and a residual strain. The value of the residual strain was insensitive to the magnitude of the strain at which the load was removed.

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INTRODUCTION

In 2003, Gong et al.¹ reported their discovery of a new hydrogel architecture that produced extraordinarily tough materials, which they termed a *double-network* (DN) hydrogel. The DN hydrogel was originally believed to be an interpenetrating polymer network (IPN) of a soft neutral polymer network within a more highly crosslinked polyelectrolyte network. Those hydrogels were prepared by a two-step sequential free-radical polymerization. The first step was the synthesis of a highly crosslinked polyelectrolyte network, and the second step involved swelling the polyelectrolyte network with a water soluble monomer that was then polymerized within the first network. The second polymerization step was conducted with or without adding a crosslinking agent – that is, the product was thought to be either an IPN or a semi-IPN (SIPN).

The IPN model for the microstructure of DN hydrogels was questioned by Nakajima et al.² who considered that residual vinyl (C=C) unsaturation in the first network may result in grafting of the second polymer to the skeleton of the first network. Shams Es-haghi et al.³ provided infrared spectra evidence for the residual vinyl unsaturation in the first, polyelectrolyte network in the synthesis of a DN hydrogel, which confirmed the concerns of Nakajima et al.² that during the polymerization of the second network of a DN hydrogel, grafting to the first network was a distinct possibility. More recently, additional infrared spectra evidence for grafting of the second polymer to the skeleton of the first network was reported by Shams Es-haghi et al.⁴, who also concluded that the grafting between the two networks is essential for achieving toughness of a DN hydrogel. Therefore, depending on whether crosslinking agent is used in second polymerization step or not, the actual microstructure of a tough DN hydrogel is either a *pseudo*-IPN or *pseudo*-SIPN, respectively, where the prefix *pseudo* denotes connectivity of the two networks.

DN hydrogels possess excellent strength and toughness, and a particularly notable characteristic of their mechanical behavior is that they often exhibit necking in uniaxial tension. The literature in the field is inconsistent with regard to the material characteristics required for necking. Necking in DN hydrogels was first reported by Na et al.⁵, who reported that if the crosslink density of the first, polyelectrolyte network was reduced, a very low, but finite, crosslink density of the second, neutral network, was required for necking to occur. That is, a *pseudo*-SIPN DN hydrogel would not exhibit necking. Tanaka et al.⁶, however, did observe necking in a pseudo-SIPN hydrogel. Note that the pseudo-SIPNs were referred to as SIPNs in refs. (5) and (6).

The requirements for necking become more uncertain with the report by Webber et al.⁷ of no necking in DN hydrogels similar to the ones used by Na et al.⁵ and by Kawauchi et al.⁸, who observed necking without reducing the crosslink density of the polyelectrolyte network. Myung et al.⁹ prepared DN hydrogels using a neutral polymer for the first, rigid network and a polyelectrolyte for the second, soft network, which was opposite of the design of the DN hydrogels developed by the Gong laboratory^{1,2,5-8}, and they did not observe necking in tensile tests. The confusion regarding the origin of necking in DN hydrogels is apparent when one considers that refs. (5-8) are from the same laboratory. One explanation for the different observations may be differences in the extent of connectedness of the two networks used in those studies, but at that time, the requirement of connectivity of the two networks for achieving a tough DN hydrogel was not known.

Another mechanical characteristic of DN hydrogels is that they exhibit hysteresis in loading – unloading experiments which has been attributed to damage to the internal structure of the material.⁷ Loading – unloading experiments conducted on those materials are reported to

form closed loops^{6,7,10,11} meaning that the unloading curves returned to zero strain. The one exception was a paper by Na et al.⁵ that reported a few percent of permanent strain after a tensile deformation, but the plastic flow represented by the permanent deformation was not considered significant.

Tanaka¹² and Brown¹³ developed simple phenomenological models to explain the extraordinary toughness and high fracture energy of DN hydrogels, and more recently Wang and Hong¹⁴ and Zhao¹⁵ proposed models and theory for finite tensile deformation of DN hydrogels. The models, however, do not consider plastic flow in DN hydrogels, nor do they address the difference between pseudo-IPNs (-SIPNs) and IPNs (SIPNs). In light of the effect on the mechanical properties of the connectivity of the two polymer networks in a conventional DN hydrogel,⁴ the failure to consider this in models for the mechanics is a serious deficiency.

One objective of the work described in this paper was to better understand the tensile mechanics of DN hydrogels and, specifically, to compare the mechanical properties of pseudo-SIPNs and pseudo-IPNs. A second objective was to characterize and understand the plastic flow in DN hydrogels by performing loading-unloading tensile tests. This study demonstrates the effect of the concentration of crosslinking monomer during the polymerization of the second polymer of a DN hydrogel on the tensile behavior of the hydrogel. It is shown that DN hydrogels exhibit plastic deformation upon tensile loading that is very different from what is commonly observed in other materials that undergo plastic deformation. A more comprehensive explanation for necking in pseudo-IPN and pseudo-SIPN DN hydrogels is proposed.

EXPERIMENTAL SECTION

Materials. 3-sulfopropyl acrylate potassium salt (SAPS) and acrylamide (AAm) were purchased from Sigma-Aldrich Chemical Co. and used as received. The crosslinking agent, N,N'-methylenebis(acrylamide) (MBAA) was purchased from Sigma-Aldrich Chemical Co. and was recrystallized from ethanol. A photoinitiator, 2-oxoglutaric acid (OXGA), was obtained from Fluka Chemical Co. and used as received.

Synthesis of Pseudo-SIPNs. Pseudo-SIPN hydrogels were synthesized by a two-step sequential free-radical polymerization. The first network was prepared by adding OXGA and MBAA to a 1 M solution of SAPS in deionized (DI) water. Dry nitrogen gas was bubbled through the reaction mixture for 5-10 min to remove oxygen and the solution was injected into a glass mold made of two parallel glass slides, which was then exposed to a 365 nm ultraviolet (UV) light source. The resulting SAPS gel, Scheme 1, was then immersed into a 2 M solution of AAm in DI water containing the photoinitiator, which had previously been deoxygenated with N₂, until an equilibrium swelling was achieved. The AAm-swollen SAPS gel was then placed between two parallel glass slides and exposed to 365 nm UV light, to produce a linear PAAm chain, Scheme 2, which is partly grafted to the SAPS network as a result of the residual double bonds that result from the first polymerization step^{3,4}.

Scheme 1. Synthesis of SAPS network. The squiggly lines denote the chain backbone.

Scheme 2. Synthesis of linear poly(acrylamide) chains.

Synthesis of Pseudo-IPNs. Pseudo-IPN hydrogels were synthesized by a two-step sequential free-radical polymerization similar to that used for the pseudo-SIPNs, except for the addition of a crosslinking monomer in the second polymerization step. After synthesizing the SAPS gel, it was immersed into a 2 M solution of AAm in DI water containing the photoinitiator and crosslinking agent, which had previously been deoxygenated with N_2 , until an equilibrium swelling was achieved. The AAm-swollen SAPS gel was then placed between two parallel glass slides and exposed to 365 nm UV light to produce a crosslinked PAAm, Scheme 3, which was partly grafted to the skeleton of the SAPS network.

Scheme 3. Synthesis of poly(acrylamide) gel. The squiggly lines denote the chain backbone.

Synthesis of Triple-Network Hydrogels. Triple-network (TN) hydrogels were synthesized from pseudo-SIPNs and pseudo-IPNs. A DN hydrogel was immersed into a 2 M solution of AAm in DI water containing the photoinitiator and crosslinking agent that had previously been deoxygenated with N_2 , until an equilibrium swelling was achieved. The AAm-swollen DN hydrogel was then placed between two parallel glass slides and exposed to 365 nm UV light to produce a crosslinked PAAm network similar to that shown in Scheme 3.

The resulting DN and TN hydrogel samples were immersed in DI water, which was replaced a number of times with fresh water to remove any unreacted monomer. Two UV intensities, 15 mW/cm^2 and 3 mW/cm^2 , were used for the photo-polymerization reactions, and the radiation exposure times for the two intensities were 10 min (dose = 9 J/cm^2) and 9 h (dose = 97 J/cm^2), respectively. The sample notation contains the information about the recipes used for the synthesis of the different networks. Each individual network is described by the name of the monomer used, followed by four numbers in parenthesis that indicate 1) the molar concentration of monomer in DI water, 2) the mol% of photoinitiator with respect to monomer, 3) the mol% of crosslinking agent with respect to monomer and 4) UV dose used for the reaction (i.e., intensity

x exposure time). Thus, SAPS(1,2,2,9) corresponds to the polymerization of a 1M SAPS solution using 2 mol % OXGA, 2 mol % MBAA and a UV dose of 9 J/cm². All DN and TN hydrogels synthesized and used in this study are summarized in Tables 1 and 2.

Table 1. DN Hydrogels synthesized in this study.

DN Hydrogel Notation	Formulation of SAPS gels (pphm) ^a			Formulation of AAm gels (pphm) ^a		
	OXGA	MBAA	UV Dose (J/cm ²)	OXGA	MBAA	UV Dose (J/cm ²)
SAPS(1,2,2,9)/AAm(2,0.1,0,97)	2	2	9	0.1	0	97
SAPS(1,2,2,9)/AAm(2,0.1,0.01,97)	2	2	9	0.1	0.01	97
SAPS(1,2,2,9)/AAm(2,0.1,0.05,97)	2	2	9	0.1	0.05	97
SAPS(1,2,2,97)/AAm(2,0.1,0.01,97)	2	2	97	0.1	0.01	97
SAPS(1,2,2,97)/AAm(2,0.1,0.05,97)	2	2	97	0.1	0.05	97

^a parts per hundred parts monomer

Table 2. TN Hydrogels synthesized in this study.

TN Hydrogel Notation	1st Network (SAPS) Formulation (pphm) ^a			2nd Network (AAm) Formulation (pphm) ^a			3rd Network (AAm) Formulation (pphm) ^a		
	OXGA	MBAA	UV Dose (J/cm ²)	OXGA	MBAA	UV Dose (J/cm ²)	OXGA	MBAA	UV Dose (J/cm ²)
SAPS(1,2,2,9)/AAm(2,0.1,0,97)/AAm(2,0.1,0.05,97)	2	2	9	0.1	0	97	0.1	0.05	97
SAPS(1,2,2,97)/AAm(2,0.1,0.01,97)/AAm(2,0.1,0.05,97)	2	2	97	0.1	0.01	97	0.1	0.05	97
SAPS(1,2,2,97)/AAm(2,0.1,0.01,97)/AAm(2,0.1,0.07,97)	2	2	97	0.1	0.01	97	0.1	0.07	97

^a parts per hundred parts monomer

Dynamic Modulus Measurements. Oscillatory shear modulus of the first polymer networks made from SAPS were measured with a TA Instruments ARES-G2 rheometer equipped with 25 mm parallel serrated plates geometry. The linear response region for the

dynamic experiments was determined with a strain sweep. Dynamic experiments were performed within a frequency range of 0.1-100 rad/s.

Tensile Testing. Uniaxial tensile tests were performed with an Instron 5567 universal testing machine equipped with a 100 N load cell, using a constant crosshead speed of 50 or 500 mm/min at room temperature. Rectangular samples with length = 40 mm, width = 10 mm, thickness = 2-3 mm and a gauge length of 30 mm were used. Sandpaper was used to prevent slippage of the samples in the grips. The tensile data are reported as engineering stress versus stretch ratio, where the engineering stress, σ_e , was obtained by dividing the force by the original cross-sectional area of the specimen and the stretch ratio, $\lambda \equiv L(t)/L_o$, where $L(t)$ was the instantaneous sample length and L_o was the original sample length. Note that $\lambda = \epsilon_e + 1$, where ϵ_e is the engineering tensile strain.

Crack propagation in pseudo-SIPN and pseudo-IPN hydrogels was measured with single-edge notch fracture experiments. A 1 mm notch was cut into the center of one of the sample edges with a sharp razor, and a tensile extension speed of 50 mm/min was used to deform the sample.

Loading-unloading tensile test were performed using a constant crosshead speed of 50 mm/min at room temperature.

RESULTS AND DISCUSSION

Previous work demonstrated that the first network in a DN hydrogel, which is usually the more highly crosslinked polymer, has residual double bonds as a consequence of the incomplete reaction of the crosslinking monomer during the first polymerization step^{3,4}. Those residual double bonds disappear during the second polymerization step, which indicates that at least some of the second polymer or network reacts with those bonds to graft chains of the second polymer

to the skeleton of the first polymer network⁴. For the case where no crosslinking monomer is used in the second polymerization step, the second polymerization produces high molecular weight linear chains. Thus, the actual microstructure of such DN hydrogels is a single highly crosslinked network with some linear PAAm chains grafted to it and some non-grafted, interpenetrating linear polymer chains, i.e., a pseudo-SIPN, Figure 1a. When a low concentration of crosslinking monomer is used in the second polymerization step, the microstructure consists of an interpenetrating network of the two polymers, **plus** some of the second network grafted to the first network, which produces a bimodal crosslink density of the first network, i.e., a pseudo-IPN, Figure 1b.

Figure 1. Schematic representation of microstructure of (a): pseudo-SIPN and (b): pseudo-IPN. The blue network is the first, highly crosslinked polymer network and the red lines are PAAm chains. In a pseudo-SIPN some PAAm chains are covalently attached to the first network and some are free linear chains interpenetrating the first network. For a pseudo-IPN, the PAAm chains are covalently crosslinked and interpenetrate the first network, but some PAAm is covalently attached to the first network. Thus, some PAAm forms an interpenetrating network with the first polymer and some becomes part of the first network – producing a bimodal crosslink density of the first network.

Figure 2 shows the mechanical behavior of three DN hydrogels made with SAPS(1,2,2,9) as the first network and three different second networks made of AAm. When no

crosslinking agent was used in the synthesis of the second polymer network, the sample SAPS(1,2,2,9)/AAm(2,0.1,0,97), exhibited necking and strain hardening in a tensile experiment (black circles in Figure 2). When a low concentration of crosslinking agent (0.01 mol % with respect to the monomer) was used in second polymerization step, necking was suppressed and the sample, SAPS(1,2,2,9)/AAm(2,0.1,0.01,97), exhibited more pronounced strain hardening (red circles in Figure 2). For a higher concentration of crosslinking agent in the second polymerization step, no necking was observed, the strain hardening became even more pronounced and the sample, SAPS(1,2,2,9)/ AAm(2,0.1,0.05,97), failed at a lower stretch ratio (blue circles in Figure 2).

Figure 2. Engineering tensile stress versus stretch ratio for three DN hydrogels that differed only in the amount of crosslinking agent used in the synthesis of the second (AAm) network (i.e., the third number in the parentheses following AAm in recipes used for second polymerization step). When no crosslinking agent was used (black circles) the DN hydrogel exhibited necking and strain hardening. For a low concentration of crosslinking agent, necking was suppressed and the DN hydrogel showed more pronounced strain hardening (red circles). For higher crosslinking agent concentration strain hardening was even more pronounced and the sample failed at lower strain (blue circles).

Previous work³ showed that the finite tensile deformation of DN hydrogels may be characterized by two regimes of deformation, and necking, which is the onset of plastic deformation, marks the transition between the two regimes. In the first regime of deformation the first, rigid network is the load-bearing component and in the second regime of deformation the second network assumes the load bearing role. For pseudo-SIPNs where some of the linear PAAm chains are grafted to the skeleton of the first network and some are physically trapped inside the first network, the mechanical contribution of the second network is due to the transient network of highly entangled, very high molecular weight PAAm chains.

The transient, entanglement network was studied using tensile tests at different extension rates. Figure 3 compares the mechanical behavior of a pseudo-SIPN, SAPS(1,2,2,9)/AAm(2,0.1,0,97), at two different extension rates. The black dashed line separates the two regimes of deformation. In the first regime the data for both experiments coincide, but in the second regime of deformation, where the PAAm chains assume the load bearing role, the data for the two extension rates deviate and the material achieves a higher stress for the higher extension rate. For the higher extension rate, the rate of chain disentanglement process is reduced and the chain segments between entanglements become more extended and support a higher stress than that for the lower extension rate. A consequence of the higher stress, however, is that the hydrogel fails at a lower extension ratio.

Figure 3. Engineering tensile stress versus stretch ratio for SAPS(1,2,2,9)/AAm(2,0.1,0,97) pseudo-SIPN hydrogel at two different extension rates. The dashed black line shows the demarcation from the first regime of deformation (before yielding) to the second regime of deformation (after yielding). The deviation of the stress for the two deformation rates in the second regime of deformation results from differences in the disentanglement time scales as a result of viscoelastic effects.

In contrast to the effect of strain rate on the stress-strain behavior of a pseudo-SIPN hydrogel, for a pseudo-IPN, where the PAAm chains in the second network are covalently crosslinked, the tensile deformation of the gels was independent of extension rate, Figure 4. In a pseudo-IPN, the chemical crosslinks between the PAAm chains restrict the mobility of the polymer chains, and as a consequence the chains cannot disentangle in the second regime of deformation and rate effects are completely suppressed. The strain hardening that occurs for pseudo-IPNs is due to the extension of polymer chains in the second regime of deformation.

Figure 4. Engineering tensile stress versus stretch ratio for two pseudo-IPN DN hydrogels: (a): SAPS(1,2,2,9)/ AAm(2,0.1,0.01,97) and (b): SAPS(1,2,2,9)/AAm(2,0.1,0.05,97) for two different extension rates.

Figures 3 and 4 demonstrate an important difference between pseudo-SIPNs and pseudo-IPNs that is due to the difference in their molecular structure. Yu et al.¹⁶ performed tensile tests at different strain rates on a pseudo-SIPN made of AMPS and AAm (note that in their paper, they did not recognize that their DN was actually a pseudo-SIPN). They did not report a rate-dependence of the mechanical behavior in the second regime of deformation, because their samples failed prematurely for the high stretch ratios achieved. Careful inspection, however, of their data reveals that the data for the higher extension rates did differ after the yield point (i.e., in the second regime of deformation). In the present study, the different behavior for low and high extension rates is clear, because of the larger difference in the rates used.

Another difference between pseudo-SIPNs and pseudo-IPNs is the mechanism of crack propagation. Figure 5 compares the tensile fracture behavior of notched samples of a pseudo-SIPN and a pseudo-IPN. This particular experiment measures the energy dissipation in propagating the crack. For the pseudo-SIPN, Figure 5(a), a neck first appears at the tip of the notch and it grows with increasing strain, which allows the material to achieve a high stretch

ratio. However, for the pseudo-IPN, Figure 5(b), the mobility of the PAAm network strands is restricted by the covalent crosslinks, which prevent translation or disentanglement of the PAAm chains. That eliminates an important mechanism for energy dissipation that occurs in a pseudo-SIPN, and as a consequence, the crack grows rapidly and the sample fails at a much lower stress and stretch ratio than the pseudo-SIPN.

Figure 5. Tensile load versus stretch ratio for (a): pseudo-SIPN [SAPS(1,2,2,9)/AAm(2,0.1,0,97)] and (b): pseudo-IPN [SAPS(1,2,2,9)/AAm(2,0.1,0.01,97)]. Inset pictures show the crack propagation in the samples.

Figure 6 compares the crack regions in a pseudo-SIPN and a pseudo-IPN prior to failure. Plastic deformation occurs in both samples, but for the pseudo-SIPN, disentanglement of PAAm chains at the tip of the notch provides an extra mechanism for energy dissipation. The two different mechanisms for crack propagation in a pseudo-SIPN and a pseudo-IPN are consistent with the mechanical behavior of the different DN hydrogels prepared from the same crosslinked SAPS first polymer network shown in Figure 2. Figure 2 shows that necking was suppressed and strain hardening became more prevalent when the second polymerization included a crosslinking agent.

Figure 6. Crack regions in (a) pseudo-SIPN [SAPS(1,2,2,9)/AAm(2,0.1,0,97)] and (b) pseudo-IPN [SAPS(1,2,2,9)/AAm(2,0.1,0.01,97)] prior to failure.

Figure 7(a) compares the tensile deformation of two pseudo-IPNs, SAPS(1,2,2,9)/AAm(2,0.1,0.01,97) and SAPS(1,2,2,97)/AAm(2,0.1,0.01,97), made from different first networks. Because the first networks were extremely brittle, it was not possible to run a static tensile experiment on them. Instead, the dynamic modulus of the SAPS networks was measured by oscillatory shear experiments, Figure 7(b), which show that the network prepared with the higher UV radiation dose, 97 J/cm^2 , had a dynamic modulus, G' , about 2.5 times that of SAPS(1,2,2,9). For a soft elastic solid (verified by the insensitivity of G' to frequency), the modulus is proportional to the crosslink density,¹⁷ so the SAPS(1,2,2,97) had a crosslink density 2.5 times higher than SAPS(1,2,2,9), which explains why it was more brittle. The higher slope for the tensile data at low stretch ratios for the pseudo-IPN hydrogel made from SAPS(1,2,2,97) in Figure 7(a) is also consistent with dynamic shear data that indicated a higher modulus for the

SAPS(1,2,2,97) network. Figure 7(a) also shows that pseudo-IPN made with the higher crosslink density SAPS network exhibited a much more distinct necking phenomenon. Both pseudo-IPNs exhibited strain hardening.

Figure 7. (a): Engineering tensile stress versus stretch ratio for pseudo-IPNs made from first SAPS networks with different crosslinking density. (b): Storage modulus versus angular frequency for the SAPS networks used to synthesize the pseudo-IPNs in part (a).

The results shown in Figure 7 indicate that using a crosslinking monomer in the second polymerization step does not necessarily prevent necking in a tensile deformation. The occurrence of necking is dependent on the crosslink density, or brittleness, of the first network. That conclusion is consistent with previous work that attributed the origin of necking in DN hydrogels to the brittle nature of the first network.³ The mechanical behavior of SAPS(1,2,2,97)/AAm(2,0.1,0.01,97) indicates that necking may occur in a pseudo-IPN provided that the first network is very brittle (i.e., has sufficiently high crosslink density).

The tensile behavior of a pseudo-IPN hydrogel is also influenced by the crosslink density of the second network. Figure 8 compares the mechanical behavior of two pseudo-IPNs made from a brittle SAPS(1,2,2,97) first network and second AAm networks with different crosslink density, AAm(2,0.1,0.01,97) and AAm(2,0.1,0.05,97).

Figure 8. Engineering tensile stress versus stretch ratio for two pseudo-IPNs made from the same first network, SAPS(1,2,2,97), and two different second AAm networks synthesized using different concentrations of crosslinking monomer. The pseudo-IPN, SAPS(1,2,2,97)/AAm(2,0.1,0.01,97) exhibited necking, but for SAPS(1,2,2,97)/AAm(2,0.1,0.05,97), where the crosslink density of the second network was increased, necking did not occur and the pseudo-IPN showed strain hardening, though it failed at a lower stretch ratio.

The AAm(2,0.1,0.05,97) network, which was synthesized with a higher concentration of MBAA had the higher crosslink density. It is clear from Figure 8 that increasing the crosslink density of the second network in a pseudo-IPN DN hydrogel can prevent necking and promote strain hardening. In fact, necking can be prevented by increasing **the crosslink density of the second network**. The mechanical behavior of the DN hydrogels shown in Figures 2 and 7

indicates that as the brittleness of the first network increases, a more highly crosslinked second network is required to fully suppress necking. There does, however, appear to be an upper limit for the crosslink density of the second network used, because too high a crosslink density embrittles the hydrogel so that it fails mechanically at a low stretch ratio, such as the SAPS(1,2,2,97)/ AAm(2,0.1,0.05,97) DN hydrogel in Figure 8.

The role of crosslinking density of the second network in determining the tensile behavior of a pseudo-IPN may be understood by considering the origin of the necking phenomenon in DN hydrogels and the structure of a pseudo-IPN. The failure of the first network during deformation produces strain localization in the sample that produces necking. However, chemical crosslinks in the PAAm chains of the second network tend to distribute and homogenize the stress during deformation in the DN hydrogel. Therefore, the crosslinked network can prevent strain localization due to the failure of the first network at the onset of plastic deformation. That explains the behavior of the pseudo-IPNs made from SAPS(1,2,2,9), see Figures 2 and 7. For pseudo-IPNs made with a more brittle first network, SAPS(1,2,2,97), the strain localization is so intense that a second network with a higher crosslink density is required to homogenize stress in the sample to prevent necking.

Figure 9 shows the crack growth of notched pseudo-IPN hydrogels made from the more brittle first network, SAPS(1,2,2,97). For SAPS(1,2,2,97)/AAm(2,0.1,0.01,97), a sharp neck appears at the tip of the notch but it does not propagate, and the sample fails at a relatively low stretch ratio ($\lambda \sim 3$). The energy dissipation at the notch tip was not high, because the mobility of the polymer chains in the second network was restricted by the chemical crosslinks. For SAPS(1,2,2,97)/AAm(2,0.1,0.05,97), crack growth was rapid, and the sample failed at a very low stretch ratio ($\lambda \sim 1.5$).

Figure 9. Crack propagation in prenotched pseudo-IPNs: (a) SAPS(1,2,2,97)/AAm(2,0.1,0.01,97) and (b) SAPS(1,2,2,97)/AAm(2,0.1,0.05,97).

Figure 10. Engineering tensile stress versus stretch ratio for a pseudo-SIPN DN hydrogel, SAPS(1,2,2,9)/AAm(2,0.1,0,97), and a TN hydrogel, SAPS(1,2,2,9)/AAm(2,0.1,0,97)/AAm(2,0.1,0.05,97). The pseudo-SIPN exhibit necking during a tensile deformation, while the TN did not exhibit necking, but did strain harden.

Figure 10 compares the tensile behavior of a pseudo-SIPN DN hydrogel, SAPS(1,2,2,9)/AAm(2,0.1,0,97), and a triple-network (TN) hydrogel, SAPS(1,2,2,9)/AAm(2,0.1,0,97)/AAm(2,0.1,0.05,97), made by polymerizing a loosely crosslinked network inside the pseudo-SIPN DN hydrogel. The pseudo-SIPN DN hydrogel exhibited necking during extension, while the TN hydrogel strain hardened, but did not exhibit necking. Moreover, the synthesis of a loosely crosslinked third network within a pseudo-IPN that exhibits necking upon tensile loading can suppress necking. Figure 11 shows the tensile behavior of a pseudo-IPN DN hydrogel, SAPS(1,2,2,97)/AAm(2,0.1,0.01,97) that exhibits a sharp neck upon tensile loading and two TN hydrogels made by synthesizing loosely crosslinked networks inside the pseudo-IPN, SAPS(1,2,2,97)/AAm(2,0.1,0.01,97)/AAm(2,0.1,0.05,97) and SAPS(1,2,2,97)/AAm(2,0.1,0.01,97)/AAm(2,0.1,0.07,97).

Figure 11. Engineering tensile stress versus stretch ratio for a pseudo-IPN, SAPS(1,2,2,97)/AAm(2,0.1,0.01,97), and two TN hydrogel made of that pseudo-IPN by synthesizing a loosely crosslinked AAm networks within it. The pseudo-IPN exhibits a sharp neck upon extension, but the TN hydrogels only show strain hardening. The black arrow identifies the strain softening that occurs due to strain localization at the onset of necking. The strain softening disappeared in the TN hydrogels.

The third polymer in the latter TN hydrogel had the higher crosslink density. The sharp neck in the pseudo-IPN disappeared in both TN hydrogels. In effect, the intensity of strain localization in the sample at the onset of necking, which manifests itself as strain-softening (see arrow in Figure 11) was reduced in the TN hydrogels. That is a consequence of a more homogeneous stress distribution inside the sample due to the loosely crosslinked third polymer of the TN hydrogel.

PLASTIC FLOW IN DN HYDROGEL

Figure 12 shows a clear manifestation of plastic deformation in the DN hydrogels. After loading a DN hydrogel to an arbitrary stretch ratio and then unloading to the original gauge length, the plastic strain can be easily observed.

Figure 12. Manifestation of plastic flow in DN hydrogels after deformation. A permanent strain of the sample results from tensile loading and then unloading to the original gauge length.

Figure 13 shows the mechanical behavior of SAPS(1,2,2,9)/AAm(2,0.1,0,97) for three loading – unloading tensile experiments using three different stretch ratios. The deformed hydrogel was unloaded at the three different strains: 1) the onset of necking, 2) the onset of

strain-hardening and 3) during strain hardening. Each experiment resulted in plastic strain of the sample (see inset in Figure 13). Although the stretch ratio varied by a factor of ~ 6 for the unloading part of the experiment, the plastic strains that resulted were similar, though it does appear in Figure 13 that the higher the loading strain used, the higher was the permanent deformation.

Figure 13. Engineering tensile stress versus stretch ratio for tensile loading – unloading experiments for SAPS(1,2,2,9)/AAm(2,0.1,0,97) DN hydrogel using different stretch ratios during loading. Black triangles: loading-unloading at the onset of necking; red triangles: loading-unloading at the onset of strain hardening; blue triangles: loading-unloading during strain hardening. The green dashed lines show the unloading paths that usually occurs in other materials

The green dashed lines in Figure 13 show the unloading paths that would be expected for other materials undergoing plastic deformation, such as metals and semi-crystalline polymers. Those materials show a permanent set and do not relax to nearly the original length, as did the

DN hydrogel, where the unloading curve was more analogous to the stress – strain behavior of a rubber-like material and the sample returned to near its original length. Another characteristic of DN hydrogels that makes their plastic deformation different from other materials is that when unloading was done at very low elongation, prior to yielding, the materials still exhibited plastic strain, Figure 14.

Figure 14. Engineering tensile stress versus stretch ratio for loading – unloading of SAPS(1,2,2,9)/AAm(2,0.1,0,97) DN hydrogel at low stretch ratio ($\lambda=2$).

The data discussed above raise two questions regarding plastic deformation of DN hydrogels: 1) what is the origin of plastic deformation? and 2) what distinguishes plastic deformation in these gels from that in materials such as metals and semi-crystalline polymers?

That is, what is the mechanism by which a DN hydrogel deviates from the green dashed lines shown in Figure 13 and allows the sample to recover to near its initial length?

In polycrystalline materials like metals and in semi-crystalline polymers plastic deformation involves dislocations in the crystalline lattice of the metal or unfolding of polymer chains within the crystalline portion of the polymer. The origin of plasticity is damage of the crystalline structure. When the load is removed during plastic deformation, the unloading path is parallel to the loading path in the elastic region, as represented by the green dashed lines in Figure 13. After unloading, a residual strain remains in the sample. In DN hydrogels, however, there is no such crystalline microstructure, but the skeleton of the first network is very brittle and prone to damage even for small deformations.³ In effect, plastic deformation in DN hydrogels occurs by damage to the internal structure of the material which begins at very low stretch ratios. As will be explained below the rubber elasticity tries to restore the deformation but there is still some permanent set in the sample due to the fracture of the network structure. The hysteresis observed in loading – unloading experiments is a representation of that damage process and its area under the stress – strain curve represents the amount of energy required to damage a unit volume of the material. Figure 14 clearly shows that hysteresis, i.e., network damage, occurs even for very low stretch ratios.

The deformation of DN hydrogels may be described by two regimes with different damage intensities.³ The first regime of deformation occurs before yielding, where the first network (SAPS network) is the load bearing component, and in the second regime the second network assumes the load bearing role (in this case, linear PAAm). During the first regime of deformation, the first network is not completely damaged, but the damage is sufficient that it no

longer is able to support the load. The remainder of the first network is damaged during the second regime of deformation.³

DN hydrogels are similar to metals and semi-crystalline polymers in that all three types of materials exhibit plasticity that is due to damage of their internal structure. In metals, however, there is no mechanism that can reduce the plastic strain when the load is removed and after unloading the sample, the plastic strain remains. The higher is the stretch ratio at which unloading is done, the higher is the plastic strain. In semi-crystalline polymers, when the sample undergoes plastic deformation, the polymer chains are locked in their extended conformations. In contrast to metals, rubber elasticity is a potential mechanism that tends to return the polymer chains to their highly favorable entropic conformations. However, in order to exploit the rubber elasticity effect, the sample must be heated to above its glass transition temperature but below the melting point. This allows the material to recover to near its original length.¹⁸. In DN hydrogels, however, the damaged material acts similar to an elastomer after unloading. As discussed above, during the second regime of deformation the PAAm chains in the second network become the load bearing component, and in that regime the remnants of the first network are further damaged by the sliding of the PAAm chains past each other when they pull out of the network. Therefore, the PAAm chains reach their extended conformations and an entropic force tends to return these extended conformations to a higher entropy level upon unloading. That elastic force is responsible for reducing the plastic strain and deviation from green dashed line in Figure 13.

The reason why unloading at very high stretch ratios results in small plastic strain, may be understood by scrutinizing the loading – unloading experiments. The work of deformation in the loading – unloading experiments can be divided into two contributions. One part is the area

enclosed by the hysteresis and the second one is the area under unloading curve which measures the elastic energy stored per unit volume (the elastic energy density) of the material during deformation. The cross-hatched area in Figure 15(a) represents the elastic energy density stored by the material during deformation up to stretch ratio λ^* . Figure 15(b) shows the variation of stored elastic energy density as a function of λ^* for the SAPS(1,2,2,9)/AAM(2,0.1,0,97) DN hydrogel. The stored elastic energy density increased with increasing λ^* , which allowed the length to recover upon unloading the sample. That result explains the relative invariance of the permanent strain of the DN hydrogel at low and high stretch ratios.

Figure 15. (a): The cross-hatched area is the elastic energy density stored by the material during deformation. (b): Elastic energy density as a function of the stretching ratio at which unloading occurs.

CONCLUSIONS

Double-network (DN) hydrogels synthesized by linear and nonlinear polymerization of a water soluble monomer inside a highly crosslinked polyelectrolyte network are called pseudo-SIPNs and pseudo-IPNs, respectively. The non-linear tensile properties of pseudo-SIPNs are rate-dependent, but for pseudo-IPNs they are not, which is a consequence of the viscoelastic behavior of a pseudo-SIPN versus elastic behavior of the pseudo-IPN. For a pseudo-SIPN the tensile response prior to yielding, however, is independent of the extension rate. The onset of extension rate dependency corresponds to the influence of disentanglement of the PAAm chains at a sufficiently high strain.

The non-linear tensile deformation of DN hydrogels is strongly dependent on the crosslink densities of the first and second networks. A pseudo-SIPN (i.e., zero crosslink density for the second network) shows necking in a tensile experiment, but when a very low concentration of crosslinking agent is used in the second polymerization step (i.e., to make a pseudo-IPN), necking is suppressed and the sample exhibits strain hardening. Strain hardening of pseudo-IPN hydrogels becomes more pronounced with increasing crosslink density of the second network and the sample breaks at lower strain.

The use of a crosslinking monomer in the second polymerization step does not necessarily prevent necking upon tension. The necking behavior depends on the crosslink density, or brittleness, of the first network. A pseudo-IPN made from a brittle first network may exhibit necking when the second network has a relatively low crosslink density. Increasing the crosslink density of the second network suppresses necking and promotes strain hardening. To

design a pseudo-IPN that shows strain hardening, the crosslink density of the second network must be tuned according to the crosslink density (brittleness) of the first network.

Crack propagation follows different mechanisms for pseudo-SIPN and pseudo-IPN DN hydrogels. A pseudo-SIPN hydrogel dissipates energy at the tip of the crack and the sample fails at high strains. For pseudo-IPNs, crack propagation depends on the crosslink densities of the first and second networks. When the first network is very brittle, such that by itself it exhibits necking in tension, a sharp neck appears at the tip of the crack in a DN, but the neck does not propagate to allow energy dissipation. In that case, the sample fails at low strain. When the crosslink density of the second network is also high, such that the pseudo-IPN exhibits strain hardening, the crack grows very rapidly and the sample fails at very low strain. The latter behavior is also observed if the pseudo-IPN is made from a first network with relatively low crosslink density, i.e., it is less brittle.

The formation of a third, loosely crosslinked network within a tough pseudo-SIPN DN hydrogel that exhibit necking upon tensile loading, prevents necking and produces strain hardening. The suppression of necking is also observed in a TN hydrogel made by polymerization of a third loosely crosslinked network within a pseudo-IPN hydrogel. The presence of a loosely crosslinked third network changes the mechanical behavior of pseudo-SIPNs and pseudo-IPNs by homogenizing the stress within the sample for finite deformations.

In contrast to several experimental works (Refs. 6,7,10,11) in the literature, we found that DN hydrogels exhibit a small permanent set in loading-unloading tensile tests. This permanent set is attributed to the damage to the structure of the gels during deformation that occurs even at very small deformations. Once a DN hydrogel is unloaded from an arbitrarily stretch ratio, it

behaves like an elastomer and an elastic force returns the sample to near its original shape, however, due to its damaged structure some permanent set remains in the sample.

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Graphical abstract

Finite Strain Damage-Elastoplasticity in Double-Network Hydrogels

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