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Molecular weight distribution of network strands in double network hydrogels estimated by mechanical testing

Abstract

The remarkably high toughness of double network (DN) hydrogels is related to the energy dissipation that occurs due to the scission of network strands in the most tightly crosslinked of its two interpenetrating networks. The loading curve during tensile testing of DN hydrogels usually takes a complex shape and sometimes shows yielding. Wang and Hong recently proposed a model [1] based on the successive scission of the shortest remaining elastically active strands during tensile loading that predicts the shape of the loading curve of one DN hydrogel reasonably well. In the present study, the model was modified slightly and applied to five different DN gels prepared with different crosslink densities in the first (tight) network. The model fit parameters provide a description of the network strand length distribution in the tight network and show that the network strand concentration increases and the network strand length decreases when a higher crosslinker concentration was used to prepare the tight network. Such network strand distributions estimated from analysis of the tensile loading and unloading curves may be one of the first successful attempts to estimate the molecular weight distribution of a crosslinked polymer. 2014 Elsevier Ltd. All rights reserved.

Keywords

strands, network, distribution, double, hydrogels, mechanical, estimated, molecular, weight, testing

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Effect of First Network Topology on the Toughness of Double Network Hydrogels

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ABSTRACT

The fracture toughness of a double network (DN) hydrogel is shown here to be directly proportional to the toughness of the first-formed network. A series of DN gels was prepared in which the crosslink density of the first (tighter) network was controlled by varying the monomer and crosslinker concentrations. The toughness, tensile strength and elastic modulus of the DN gels increased significantly with an increase in the crosslink density of the first network and with identically-prepared second networks. Moreover, the toughness of the double network was found

to be linearly related to the toughness of the first network with an amplification factor of ~150 times. Existing models of DN fracture based on network strand scission are utilised to quantify the relationship between the first network toughness and the DN toughness.

INTRODUCTION

Hydrogels are highly water swollen polymer networks of interest for fluid management and smart materials applications such as sensors and actuators. Until quite recently, synthetically produced hydrogels were notoriously brittle and applications somewhat limited¹. In the past decade or so, several new tough hydrogels have been introduced that have opened up the possibility of new applications, particularly in biomedicine. These new materials also highlight interesting new aspects of polymer physics, since the enhanced toughness is derived from particular network topologies that facilitate energy absorption processes at a growing crack tip. Several recent review articles summarise the current state of understanding of these new tough gels²⁻⁵.

The focus in the present study is the origin of enhanced toughness in double network (DN) hydrogels. These materials were first introduced by Gong and co-workers in 2003⁶ and have fracture toughnesses of the order of 500-1000 J/m² in comparison to <10 J/m² typical of conventional (single network) hydrogels. DN gels are interpenetrating networks prepared sequentially with the first hydrogel infiltrated by the second network monomer that is subsequently polymerised. Extensive studies by Gong's group⁷⁻⁹ and others^{10, 11} have shown that high toughness occurs when the first network is more tightly crosslinked than the second network and the molar ratio of the second network monomers to the first network monomers at the point of synthesis of the second network is greater than ~5. Topology based toughening

models introduced by Brown¹² and Tanaka¹³ show that the enhanced toughness is derived from energy dissipation as a result of scission of network strands. That is, relatively large damage zones develop where fractured first network is stabilised by second network strands. The presence of the second network allows for more damage to accumulate before macroscopic crack propagation occurs. Scission of first network strands releases strain energy, as described by Lake and Thomas for elastomers¹⁴. The proposed models by both Brown and Tanaka correctly predict the order of magnitude increase in toughness of the DN gel in comparison to the equivalent single network hydrogels.

Since the toughness of DN gels is thought to be derived mostly from the scission and unloading of first network strands, here we report an experimental study where the first network topology is systematically changed. A series of DN gels were prepared with different crosslink densities in the first network but essentially equivalent second networks. The measured toughnesses of these gels are used to further evaluate current theories relating to DN gel toughening.

EXPERIMENTAL

Gel preparation. DN gels were synthesized using N-vinyl pyrrolidinone (NVP) as the first network monomer and acrylic acid (AAc) as the second network monomer. The chemical crosslinkers used for the first and second network were poly(ethylene glycol) diacrylate (PEGDA, molecular weight 258 g/mol) and triethylene glycol dimethacrylate (TEGDA, molecular weight 286 g/mol), respectively. 2-hydroxy-2-methylpropiophenone (HMP) was used as initiator for both networks. All chemicals were supplied by Sigma-Aldrich and used as received.

Two series of DN gels were prepared. In series 1, the crosslinker concentration of the first network was varied as 2, 3, and 4 mol% with respect to the monomer concentration. The monomer concentration was fixed at 2M. In series 2 the monomer concentration of the first network was altered between 1.5M and 2.5M with fixed crosslinker concentration at 4 mol%. For both series, the initiator concentration for the first and second network was fixed at 0.1 mol% of the monomer (NVP or AAc) and the crosslinker concentration of the second network was kept at 0.01 mol% of the second network monomer (AAc). In the following sections, each gel is abbreviated by its characteristic crosslinker or monomer concentration for simplicity.

DN gels were synthesized via a two step sequential technique. For example, to prepare the 4% DN gel, the first network aqueous solution containing 2M NVP, 0.1 mol% HMP and 4 mol% PEGDA was prepared. The solution was bubbled with nitrogen for 15 mins and then by using syringe poured into a glass mould composed of two glass plates separated by silicon rubber spacer of 2 mm thickness. The glass mould was then further purged with nitrogen for 15 mins using two syringes introducing nitrogen in and out respectively. The reaction mould was then placed in a ultra-violet (UV) chamber in a nitrogen atmosphere for 24 hours for the gelation of the first network. The obtained single network gel was immersed into nitrogen-purged 7M AAc aqueous solution containing 0.01 mol% TEGDA and 0.1 mol% HMP until swelling equilibrium was reached. The swollen gel was exposed to UV again for 6 hours so that the second network poly(acrylic acid) (PAAc) formed in the presence of the first network poly(N-vinyl pyrrolidinone) (PNVP). All the obtained DN gels were immersed in deionised water for 7 days until the equilibrium was reached.

Mechanical Measurements. All the mechanical tests were carried out on a commercial mechanical tester: an Instron 5566. Strain was determined from the grip displacement with a crosshead displacement rate of 10 mm/min used in all tests. Dumbbell shaped samples were

used in the tensile test with gauge length of 20 mm and width 4 mm (ISO 37: Type 2). Shear moduli (μ) for samples were calculated by fitting engineering stress (σ) and extension ratio (λ) data to the rubber elasticity theory¹⁵:

$$\sigma = \mu \left(\lambda - \frac{1}{\lambda^2} \right) \quad (1)$$

Fracture energies were obtained using the trouser tear test on a rectangular sample (50mm x 7.5 mm) with a 20mm long initial notch. The thickness was measured by a digital calliper. The fracture energy of a DN gel was calculated as:

$$G = 2F_{ave}/w \quad (2)$$

where the F_{ave} is the average tearing force and w is the thickness of tested samples.

RESULTS

The gels were characterised in terms of swelling ratios and moduli which provide insight into the network topology (Table 1). Swelling ratios for the first network were obtained by making identical single networks, swelling to equilibrium and measuring swollen mass, and then drying fully to determine the polymer mass. A soluble fraction of polymer which is assumed to not contribute to the mechanical properties is removed in the swelling step. The first network swelling ratios were slightly different for networks prepared at a common monomer concentration, since the degree of crosslinking was not identical in all cases. Both an increase in crosslinker concentration and monomer concentration for the first network result in DN gels with a higher modulus and reduced equilibrium swelling ratio. The modulus of an ideal swollen gel (μ^*) is given by¹⁵:

$$\mu^* = NRT \left(\frac{1}{Q^*} \right)^{1/3} \left(\frac{1}{Q'} \right)^{2/3} \quad (3)$$

where N (mol/m³) is the concentration of network strands in the unswollen state; R is the gas constant (J/mol.K); T is the absolute temperature (K) and Q^* and Q' are the volumetric swelling ratios in the state where the modulus was measured and the as-synthesised state, respectively. In the present study the moduli of the first networks were measured in the as-synthesised state ($Q^* = Q'$) so that:

$$\mu' = NRT \left(\frac{1}{Q'} \right) = N' RT \quad (4)$$

where N' is the concentration of network strands in the as-synthesised state.

Table 1 Moduli (μ) and swelling ratios (Q) of the first network in DN gels prepared with different first network crosslinking and consistent second network (7 M monomer concentration and 0.01% crosslinker). Strand density (N'), strand lengths (n) and backbone bond concentration (C^*) calculated for the first network are also given.

% crosslinker (1 st Network)	Monomer Concentration (1 st Network) (M)	Q' (when 1 st network synthesised)	μ' (kPa) (when 1 st network synthesised)	Q'' (when 2 nd network synthesised)	Q^* (at DN swelling equilibrium)	N' (M) (as synthesised)	n	C^* (M) (at DN swelling equilibrium)
2	2	6.20	0.77	22.81	477	0.31×10^{-3}	12231	0.049
3	2	5.84	3.03	22.03	141	1.22×10^{-3}	3302	0.166
4	2	6.60	3.58	18.23	64	1.44×10^{-3}	2474	0.363
4	1.5	10.44	0.96	34.09	318	0.39×10^{-3}	5828	0.074
4	2.5	4.94	5.86	15.05	42	2.35×10^{-3}	2018	0.547

Table 1 lists the network strand densities (N') and average strand lengths for each of the first network gels. The strand densities were calculated using equation (4) from the measured as-synthesised moduli. Increasing crosslinker concentration and monomer concentration result in a higher strand density and, therefore, lower average strand length. The average number of backbone bonds per strand (n) was calculated from the dry polymer density (ρ) and unit molecular weight (M) where the latter is the repeat unit molecular weight divided by the number of backbone bonds in each repeat unit.

$$n = \frac{\rho}{MN'Q'} \quad (5)$$

The density of dry polyNVP was taken as 1160 kg/m^{316} and unit molecular weight 0.056 kg/mol . Calculated strand lengths decrease with increasing crosslinker and monomer

concentrations used to prepare the first network. Zhang et al.¹⁷ also found a linear dependence of increasing shear modulus with increasing acrylamide (AAm) monomer concentration at constant monomer to crosslinker ratio above a low monomer concentration threshold. The indication of these observations is that the crosslinking reaction in these systems is more efficient at higher monomer concentrations and higher crosslinker concentrations. It should be noted that in all cases (and as previously reported by Zhang et al.¹⁷, the network strand lengths are far longer than expected for ideal networks where all crosslinking molecules form effective crosslinks. Cyclization reactions and the formation of multiple crosslinks commonly occur in free-radical polymerisation in dilute solution^{16, 18} partly due to the higher reactivity of the crosslinker compared to the monomer and the dilution effect. Several other reports¹⁹⁻²¹ of low shear moduli (< 10 kPa) at similar swelling ratios from single networks formed by free-radical polymerization of vinyl monomers/crosslinkers suggest that incomplete crosslinking is a common occurrence in such gels.

Typical stress-strain curves for the two series of DN gels at their equilibrium swelling are shown in Figure 1. All curves demonstrate a “yielding” type shape where the stress tends to plateau above an extension ratio of ~2. The extension ratio is taken relative to the unstrained DN gel in its equilibrium swelling state. In some cases the stress decreased slightly indicating the onset of necking. Indeed, close visual observation of some samples showed a distinct neck region of a slightly cloudy appearance in contrast to the transparent gel in the un-necked region. The increased light scattering causing the cloudy appearance would be consistent with the type of damaged network described by Gong *et al*²², consisting of islands of the undamaged DN in a matrix of damaged DN. When it occurred, the necked region extended throughout the cross-section of the sample and increased in length during continued stretching of necking samples. While the formation of neck regions could not be confirmed for all samples, the appearances of

the stress-strain curves indicate that all samples either necked or were on the verge of neck formation, which is expected as the strain softening following yield was relatively small.

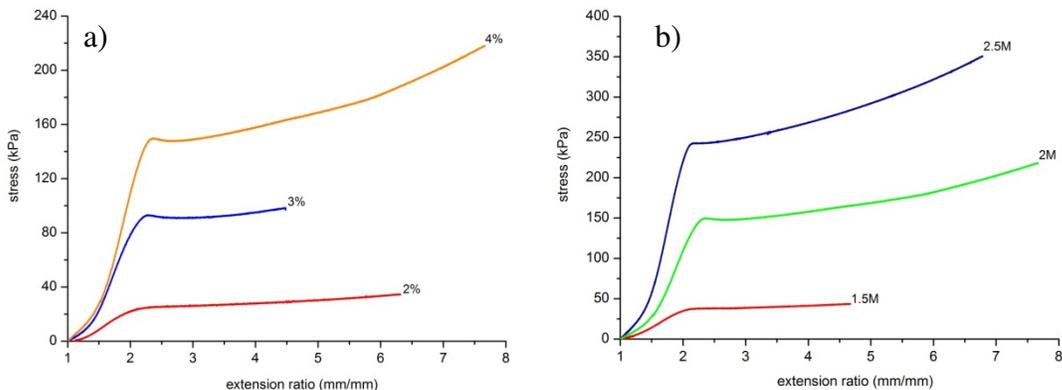


Figure 1. Typical stress-extension curves obtained for DN gels prepared with a) different crosslinker concentrations (2M monomer); and b) different monomer concentrations (4% crosslinker).

The tensile strength and toughness of the two series of hydrogels are shown in Figure 2. The strength and toughness values are typical of DN gels reported for different monomer types^{6, 10, 18}. Figure 2 illustrates the very large increase in toughness and strength with an increase in both the crosslinker concentration and monomer concentration used to prepare the first network. It is apparent that the first network topology has a strong influence on the strength and toughness of the DN gel with increases in strength and toughness associated with a more tightly crosslinked first network.

A strong correlation between the fracture energy (trouser tear test) and the tensile strength (tensile test) is also apparent for all gels. The tensile stress strain curves (Figure 1) also show that the tensile strength was similar in magnitude to the yield strength for all gels. The correlation between fracture energy and yield strength suggests that the yielding process involved fracture of

network strands leading to softening and eventual neck formation. A similar correlation has been previously reported by Baumberger *et al.* for biopolymer single network gels²³.

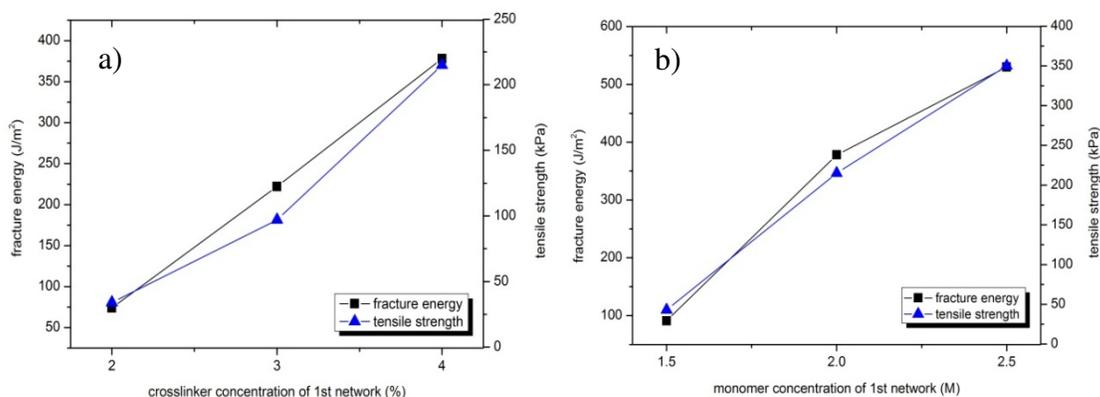


Figure 2. Tensile strength and toughness of DN gels in which the first network has been prepared with a) varying initiator concentration; and b) varying monomer concentration.

DISCUSSION

The experimental results clearly demonstrate that first network topology has a significant impact on the toughness and strength of DN gels. A higher level of crosslinking and a higher monomer concentration during the first network synthesis both significantly increase the tensile strength and toughness of the DN gel with the second network prepared identically in all cases. The reasons why the first network has such a strong influence on the DN properties will be evaluated here with reference to the widely-supported mechanism that the fracture toughness of gels is directly related to the energy dissipated through network strand breakage. In simple single networks the scission of a network strand precipitates a cascade of chain scission that leads to macroscopic crack growth and fracture at low strains¹⁷. The toughness is low in single networks because there are comparatively few strands that need to be broken per crack area. In contrast, the DN gels can tolerate the fracture of the shorter first network strands without macroscopic crack growth through the stabilising effect of the second network. Consequently, the damage

volume is much larger and significantly more network strands need to be broken during crack propagation in DN gels in comparison to conventional single networks. The following sections consider how the first network topology in a DN gel influences these bond scission processes and affects the DN fracture toughness.

Brown has developed a quantitative model that relates DN gel toughness to the properties of the individual networks¹². The model is based on a fracture mechanism involving two stages where scission of first network strands produces a damage zone of multiple cracks in the first network. The second stage of fracture involves the full extension of the longer second network strands and their eventual scission. The energy dissipated during crack growth is thought to be mainly due to the formation of a highly cracked first network in a damage zone surrounding the main crack. Brown was able to estimate the width of the damage zone and predict the double network toughness as:

$$G_{DN} = \frac{4G_1G_2}{(\lambda_m - 1)E_2\Delta b} \quad (6)$$

where G_1 and G_2 are the toughness of the first and second networks, respectively.

The parameters of the denominator are mainly related to the properties of the second network: λ_m is the maximum extension of the damaged network which is determined by the extension of the second network and the degree of cracking in the first network; E_2 is the elastic modulus of the second network; and Δb is the crack opening displacement of the first network and is related to the contour length of the second network¹². For DN gels prepared with a fixed second network, equation 6 can be simplified to:

$$G_{DN} = KG_1 \quad (7)$$

with the constant K determined mainly by the second network properties.

The gel toughness values for the double network and first network in equation 7 assume the same swelling ratio, since the swelling degree will likely affect toughness by reducing the number of chains per unit volume. Unfortunately, the single network cannot be swollen in water to the same extent as the DN. In addition, the first networks prepared as single networks were very brittle and it was difficult to measure the toughness directly. Because of these problems, the Lake-Thomas theory¹⁴ for determining the toughness in elastomers was used to estimate the values of G_c at the DN swelling equilibrium.

The minimum fracture toughness of elastomers has been successfully modelled by Lake and Thomas by estimating the energy dissipated in unloading the network strands that cross the crack plane²⁴. This threshold fracture energy occurs at low crack velocities when viscoelastic contributions to the dissipated energy are negligible. The energy dissipated in each strand is the backbone bond dissociation energy times the number of bonds in the strand since bond scission occurs when all bonds are stretched to near their limit. The fracture toughness is the energy dissipated per unit area of crack produced and is estimated by the energy needed to break all the bonds in the fracture zone, although only one such bond per strand actually breaks. The damage zone is a strip of material defined by the fracture area and extending to a width d . Assuming a Gaussian distribution of strand lengths, Lake and Thomas took this width to be related to the unstrained length (end-end distance) of the network strands (see Supplementary Information). Figure 3 illustrates the fracture process.

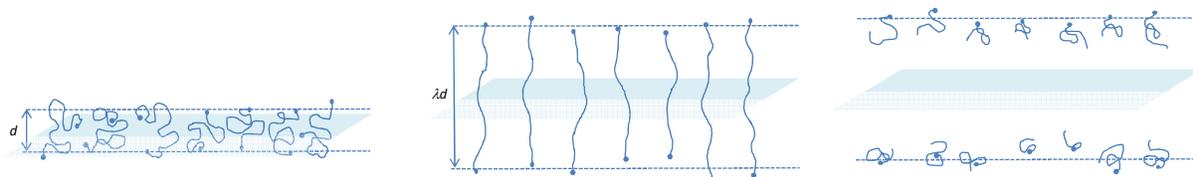


Figure 3. Network strands crossing the crack plane in the unstrained state, fully extended state and after fracture.

The Lake-Thomas approach can be applied to elastomers, solvent-swollen elastomers and gels with the fracture energy (G_0) determined by the number of backbone bonds within the damage zone per unit crack area.

$$G_0 = \Gamma nU = \left(\frac{3}{8}\right)^{1/2} N^* d^* nU = \left(\frac{3}{8}\right)^{1/2} C^* d^* U \quad (8)$$

Γ = areal density of strands crossing the crack plane per area of crack (mol/m^2)

n = number of units per strand- a ‘unit’ is defined as the atoms that are associated with one backbone bond

U = backbone bond dissociation energy (J/mol)

N^* = concentration of network strands in the unstrained network (mol/m^3)

C^* = concentration of backbone bonds in the unstrained network (mol/m^3)

d^* = unstrained width of the damage zone (m)

The $(3/8)^{1/2}$ numerical factor reflects the fact that only a fraction of the network strands are parallel to the applied stress and need to be fractured. The numerical value applies to networks with a Gaussian distribution of strand lengths²⁵. The concentration of backbone bonds (C^*) can be obtained from

$$C^* = \frac{\rho}{MQ^*} = nN^* \quad (9)$$

where n and N^* are determined from equations (3)-(5) with

$$N^* = \frac{N}{Q^*} \quad N' = \frac{N}{Q'} \quad N^* = N' \left(\frac{Q'}{Q^*} \right) \quad (10)$$

To obtain the number of backbone bonds in the damage zone, the unstrained width of this zone must be used, since the concentration of bonds is based on unstrained dimensions. The width of the fracture zone is taken as the unstrained end-end length of the strands. In a dry elastomer this length is estimated based on Gaussian strands:

$$d = n_r^{1/2} l_r = q^{1/2} n^{1/2} l \quad (11)$$

n_r and l_r = number and length of rigid links per strand such that $q = n/n_r = l/l_r$ is the number of strand units per rigid link referred to as the characteristic ratio. By assuming that each strand rigid length is a cube with volume l_r^3 the strand volume is $q^2 n l^3$ with mass nM / N_A where N_A is Avagadro's number. The number of strand units per rigid link is then estimated from:

$$q = \left(\frac{M}{N_A \rho l^3} \right)^{1/2} \quad (12)$$

The solvent swelling causes an increase in the width of the unstrained damage zone with isotropic swelling giving:

$$d^* = q^{1/2} n^{1/2} l \left(\frac{Q^*}{Q'} \right)^{1/3} \quad (13)$$

The correlation between the fracture toughness of dry (G_0) and solvent-swollen (G_0^*) elastomers are then obtained by combining the above equations:

$$G_0 = \left(\frac{3}{8} \right)^{1/2} \frac{\rho}{M} q^{1/2} l U n^{1/2} \quad (14)$$

$$G_0^* = \left(\frac{3}{8} \right)^{1/2} \frac{\rho_P}{M} \left(\frac{1}{Q^*} \right)^{2/3} \left(\frac{1}{Q'} \right)^{1/3} q^{1/2} l U n^{1/2} = G_0 \left(\frac{1}{Q^*} \right)^{2/3} \left(\frac{1}{Q'} \right)^{1/3} \quad (15)$$

The fracture energy of dry rubbers is predicted to increase with increasing strand length (n), or decreasing crosslink density. Close agreement has been observed^{14, 25, 26} between carefully measured threshold fracture energy in various elastomers prepared with different amounts of

crosslinking and the Lake-Thomas fracture energy (equation 14). The fracture energy for a given elastomer also decreases with increasing swelling as illustrated by poly(dimethyl siloxane) (PDMS) elastomers swollen to different extents in m-xylene²⁵. These data provide fracture toughness measurements and modulus values at well-defined swelling ratios. With the additional parameters required for the calculations given in Table 2, the calculated and experimental fracture energies are compared in Figure 4. The calculation procedure was as follows:

1. Strand density (N^* , equation 4 and 10) based on shear modulus, swelling ratio and temperature;
2. Concentration of backbone bonds (C^* , equation 9) based on dry density, unit molecular weight and swelling ratio;
3. Average units per strand (n , equation 9);
4. Units per rigid link (q , equation 12 unless otherwise available) based on dry density, unit molecular weight and backbone bond length;
5. Damage zone width (d^* , equation 13); and
6. Toughness (G_o^* , equation 8)

Table 2 Parameters used for calculating toughness of various elastomers and gels.

	<i>cis</i> -polyisoprene	PDMS	Polyacrylamide	Poly(N-vinyl pyrrolidone)
Backbone Bond Energy (kJ/mol)	346 ²⁵	367 ²⁵	360 ²⁷	360

Backbone Bond Length (nm)		0.115 ²⁵	0.143 ²⁵	0.154 ²⁸	0.15
Dry Polymer Density (kg/m ³)		920 ²⁵	970 ²⁵	1440 ²⁹	1160 ³⁰
Strand Molecular Weight (kg/mol)	Unit	0.017	0.037	0.035	0.056
Backbone Units per Rigid Link (q)		1.74 ³¹	6.25 ³¹	3.32	4.87
				[Calculated]	[Calculated]

As illustrated in Figure 4, the calculated fracture toughness for elastomers (dry and swollen) agrees closely with measured values. The figure contains data for various elastomers prepared with different crosslink densities. In most cases the measured values agree very closely with their predicted toughness. The measured toughness of *cis*-polyisoprene was almost 2-3 times larger than the predicted values. Since the calculated values were based on several assumptions, this level of agreement is considered excellent by previous researchers^{14, 23}. The figure also contains two data sets from single network hydrogels. The gel toughness for polyacrylamide gels reported by Tanaka³² and those by Zhang¹⁷ also agree within a similar accuracy with the predicted values. Within these limits of accuracy, the data shown in Figure 4 illustrate that the Lake Thomas theory can adequately account for the decrease in toughness resulting from solvent swelling of network polymers including hydrogels. While this theory predicts an increase in toughness for elastomers of decreasing crosslink density, the toughness of gels prepared with different amounts of crosslinking is less clear, since an increase in crosslinking (decreasing n) will also decrease the swelling (Q^*) at equilibrium.

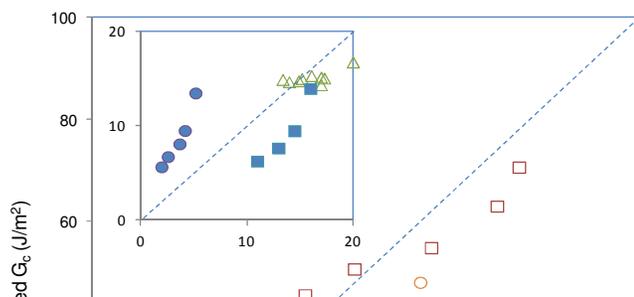


Figure 4. Measured fracture toughness and calculated toughness values (Lake Thomas theory) for dry and swollen networks taken from literature sources: cis polyisoprene [unfilled diamonds²⁵]; poly(dimethyl siloxane) [unfilled squares²⁵]; solvent swollen poly(dimethyl siloxane) [unfilled triangles²⁵]; polyacrylamide hydrogels [filled circles¹⁷ and filled squares³²]; styrene-butadiene rubber [unfilled circles²⁶]; neoprene rubber [filled triangles²⁶]. The dashed line indicates exact agreement between calculated and measured values.

The Lake-Thomas approach was used to calculate toughnesses of the first networks prepared here for the DN gels. Figure 5 shows the calculated toughness along with network strand length for each of the first networks. The measured swelling ratio at the DN equilibrium is also given and the first network toughnesses were calculated at this degree of swelling. The strand length and associated equilibrium swelling increased significantly when lower concentrations of crosslinker and monomer were used to prepare the first networks. The network toughness decreases with increasing strand length in contrast to the behaviour observed for dry elastomers because of the dilution of chains by the solvent. The decrease in toughness of gels formulated with fewer crosslinks is related to the dilution effect since the looser networks are able to swell more and therefore have fewer network chains that cross the crack path.

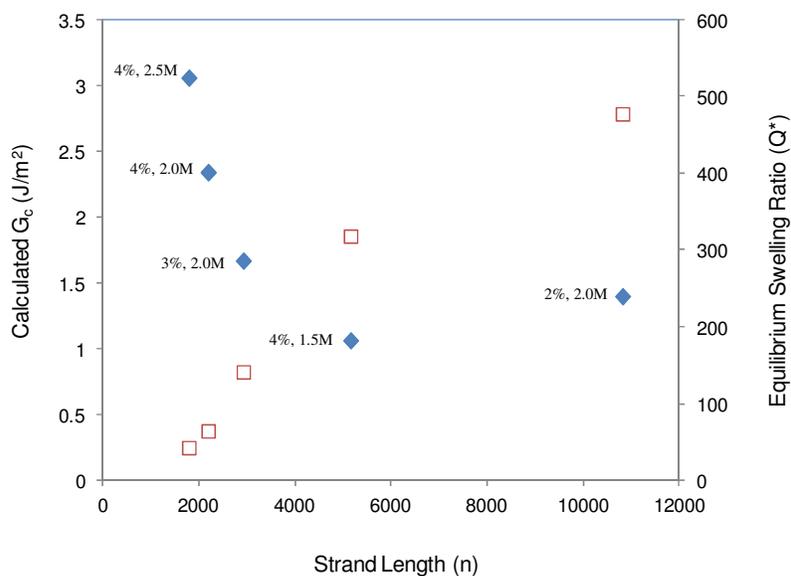


Figure 5. Calculated fracture toughness (diamonds) and swelling ratios (squares) for first networks when prepared as double networks and swollen to equilibrium. Network strand lengths were calculated from the first network shear modulus and swelling ratio measured in the as-synthesised condition. The fraction of crosslinker and molar concentration of monomer used to prepare the networks are as indicated.

Finally, the measured toughness of the DN gels can be compared with the calculated toughness for each of the first networks. As shown in Figure 6, a strong correlation exists between the DN toughness and the first network toughness. The data fall close to a linear relation as predicted by equation 7, suggesting that Brown's toughness model captures the important aspects of the contribution of each network to the DN gel toughness. The value of constant K in equation (7) is assumed to be determined mainly by the second network and the linear trend of the data shown in Figure 6 supports this assumption. The second networks were synthesised in the same manner each time, however, their swelling ratios (between their as-synthesised and equilibrium states)

varied from 3 to 21 which likely affects their properties. The approximately linear trend shown in Figure 6 suggests that the different swelling of the second network has a relatively small effect on the DN toughness for the systems investigated here. Indeed, the value of parameter K obtained from a least-squares linear fit to the data (forced through the origin to comply with equation 7) shows that the DN toughness is amplified by a factor of ~ 150 compared with the first network toughness. Previously, Brown¹² has estimated an amplification factor of ~ 800 based on typical values of first and second network properties. Given the assumptions involved this estimate is in good agreement with the value obtained in the present study. This giant amplification of toughness occurs since the second network stabilises cracks that develop in the first network, preventing their catastrophic growth and thereby increasing the number of first network strands that are broken.

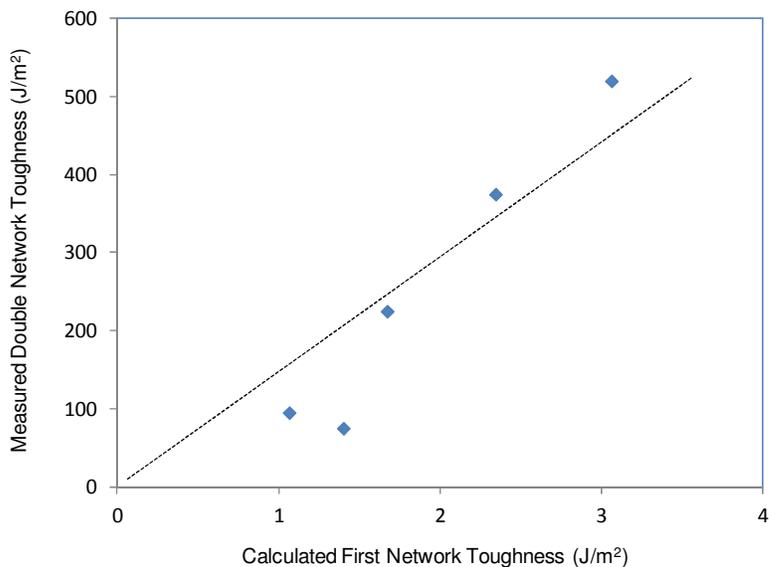


Figure 6. Measured fracture toughness of DN gels at their equilibrium swelling and the calculated fracture toughness of the first networks determined at the DN swelling equilibrium.

CONCLUSIONS

Here it is shown that the properties of the first network in a double network gel have a direct and significant effect on the equilibrium swelling, modulus, strength and toughness of the DN gel. The toughness of the DN gel is directly proportional to the first network toughness, reinforcing the concept that most of the energy dissipated during DN gel fracture is attributed to strand scission and crack formation in the first network. The greater is the toughness of the first network, the more energy can be dissipated during fracture of the DN gel. The toughness of the first network was modelled by the Lake Thomas theory and was found to decrease with increasing strand length because of the reduction in areal density of network strands in the equilibrium swollen state. While the toughness of the first network has been shown to be an important contributor to the overall DN gel toughness, the major effect is the toughness enhancement due to the presence of the second network. In the present study, the second network increases the toughness compared with the first network by a factor of 150 times.

ASSOCIATED CONTENT

Supporting Information Available: full derivation of fracture toughness equations. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Effect of First Network Topology on the Toughness of Double Network Hydrogels

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