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Abstract

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A Sequential Debonding Fracture Model for Hydrogen Bonded Hydrogels

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ABSTRACT

Hydrogen bonds are known to play an important role in prescribing the mechanical performance of certain hydrogels such as polyether-based polyurethanes. The quantitative contribution of hydrogen bonds to the toughness of polymer networks, however, has not been elucidated to date. Here, a new physical model is developed to predict the threshold fracture energies of hydrogels physically crosslinked via hydrogen bonds. The model is based on consecutive and sequential dissociation of hydrogen bonded crosslinks during crack propagation. It is proposed that the scission of hydrogen bonds during crack propagation allows polymer strands in the deformation zone to partially relax and release stored elastic energy. The summation of these partial chain relaxations leads to amplified threshold fracture energies which are 10-45 times larger than those predicted by the classical Lake-Thomas theory. Experiments were performed on a hydrophilic polyurethane hydrogel where urea additions were used to control the density of hydrogen bonds. The measured fracture energies were in good agreement with the calculated values.

KEYWORDS: fracture energy model, polyether-based polyurethane, tough hydrogels, hydrogen bonds, Lake-Thomas Theory

INTRODUCTION

Tough hydrogels have attracted extensive attention in recent times, as their mechanical robustness makes them attractive for many applications in biomechanics and biomedicine such as soft actuators, artificial muscles, biosensors, and tissues engineering.¹⁻⁵ Unlike conventional hydrogels with fracture energies around 1-10 J/m², the new hydrogels are extremely tough with fracture energies of the order of 10²-10⁴ J/m².⁶ Toughness reflects the extent of energy dissipation during crack growth, and conventional hydrogels are limited

to just chain scission or chain pull-out as available dissipative processes. In contrast, tough hydrogels exploit additional energy dissipation mechanisms or extend the process zone of energy dissipation around the advancing crack tip so that more energy is dissipated per unit area of crack formed.

The low toughness of simple swollen gel networks can be explained by the classical Lake-Thomas theory that has successfully correlated network topology with fracture energies.⁷ This approach determines the fracture energy as the sum of the energy needed for scission of each

network strand that crosses the crack plane per unit crack area. The energy dissipated per strand is taken as the backbone bond dissociation energy multiplied by the number of backbone bonds per strand since the entire network strand is unloaded when one backbone bond is broken. Fracture energies calculated using this approach for single network hydrogels are of the order of 10 J/m^2 , or similar to the measured toughness of conventional hydrogels.

Additional energy dissipation processes are needed to increase the toughness above the baseline toughness based on network chain scission. For example, double network hydrogels introduce a second, sacrificial polymer network such that the scission and relaxation of short network strands becomes a major contributor to their high toughness.⁸ Similarly, detachment of network strands from physical crosslinks, such as ion pairs or hydrogen bonding, can dissipate energy by relaxing the stretched polymer chains.⁹ Viscous drag during chain pull-out is another possible contribution to the fracture energy, although it is strongly dependent on the rate of crack growth and the viscosity of the swelling solvent.¹⁰

Hydrogen bonds widely occur between polymer chains and have been reported to play a role in crosslinking some hydrogel networks and enhancing their mechanical properties.¹¹⁻¹³ However, more detailed quantitative investigations are still needed to better understand the toughening mechanism of hydrogen bonds in hydrogels. One class of polymers where the hydrogen bonds are present and exert a significant role in determining the mechanical properties is the polyurethanes. Polyurethanes (PU) are among the most prevalent polymers with highly customisable physical and mechanical properties. The physical nature of the hydrogen bonds in PUs make them mechanically recoverable and externally-responsive,¹³ facilitating various potential applications.

Depending on their molecular structures, PUs can be hydrophilic or hydrophobic. Previously, we used a range of polyether-based hydrophilic PUs to fabricate tough and stimuli-responsive hydrogels.¹⁴⁻¹⁵ The favourable mechanical behaviour of this type of hydrogels, such as high toughness and recoverability, as well as the ease of processing (*e.g.* casting or 3D printing), make them suitable candidates for fabrication of soft actuators.

The present study aims to gain a better insight into the origin of the high toughness of hydrophilic polyurethane hydrogels (HPU). These are simple, single networks that can be highly swollen but also display high toughness. A series of polyether-based HPUs were fabricated where the PU chains were physically crosslinked by the hydrogen bonds. No other crosslinking was present in these systems. To observe the impact of hydrogen bonds on the mechanical toughness of the sample hydrogels, the gels were soaked in urea solutions of different concentrations. Urea is a highly-polarised molecule that can disrupt the existing hydrogen bonds within the HPU network and reduce the crosslinking density. By evaluating the mechanical properties of HPUs in the presence of urea, a new quantitative mechanical model was developed to explain the correlation between the fracture toughness and hydrogen bonding of HPU networks.

EXPERIMENTAL

Materials

Polyether based polyurethane was purchased from AdvanSource Biomaterials (USA). Urea and ethanol were purchased from Sigma Aldrich (Australia) and used as received. Milli-Q water was used wherever water was required.

Fabrication of HPU films

Films of HPU were prepared via a solution casting method according to the previously established method. Briefly, 4 g PU was dissolved in 6 g aqueous solution of 50 wt.% ethanol. The solution was then poured into a

square plastic container and covered by a lid with tiny pores to control the evaporation rate of ethanol/water. After drying the PU films, they were hydrated with Milli-Q water and allowed to swell until their equilibrium swelling ratio was achieved. In another set of experiments, the water swollen HPU films were then further immersed for two days in aqueous solutions of urea with concentration ranging from 10 to 50 wt.%. This set of experiments aimed to manipulate the hydrogen bonds of HPU. The mass and dimension of HPU films were recorded at each stage.

Swelling ratio

The volumetric swelling ratio (Q^*) of HPU films was measured as the volume ratio of the fully swollen hydrogel at equilibrium to the dry film. The measurements were repeated three times, and the averages are reported here.

Mechanical measurements

All the mechanical measurements were performed on hydrogel films using an EZ-L mechanical tester (Shimadzu, Japan). Uniaxial tensile tests were performed on dumbbell-shaped samples with the gauge length of 25 mm and width of 4 mm. Engineering stress (σ) and extension ratio (λ) were then fitted to rubber elasticity theory¹⁶ to calculate the shear modulus (μ):

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

Fracture energies of HPU films were measured according to Rivlin-Thomas tearing tests¹⁷

where the sample hydrogel was cut into a trouser-like shape with a 20 mm long initial notch. Two arms of the sample were respectively attached to the upper and lower crosshead, and the notch was initiated to propagate by the crosshead displacement. The tearing fracture energy (G) was calculated as follows:

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

Where w was sample thickness and F_{ave} was the average of tearing force which was determined as the force when the crack propagation reached a stable state. All samples were tested at a single crosshead displacement rate of 50 mm/min to provide comparative fracture energies for samples prepared with different urea concentrations.

RESULTS AND DISCUSSIONS

Manipulating the hydrogen bonds in HPU with urea

The effect of urea on swelling and mechanical properties of HPU films was studied by measuring the swelling ratios, tensile properties, and toughness (Figure 1). The addition of urea to HPU network reduced the connections between the chains which resulted in more swelling (Figure 1a). Similarly, urea had a profound impact on mechanical properties. The shear moduli of HPU films reduced proportionally to the weight concentration of urea in the swelling medium (Figure 1b). The maximum shear modulus was observed for the HPU film prior to the urea treatment and was around 1200 kPa. By increasing the urea concentration up to 50 wt.%, the shear modulus decreased to 300 kPa. This trend of shear modulus was aligned with a similar four fold reduction in fracture energies, decreasing from 2800 J/m² for the untreated HPU film to 750 J/m² at 50 wt.% urea (Figure 1c). The HPU hydrogels also showed a high recoverability after loading and unloading (see Supporting Information) as a result of the reformability of the hydrogen bonds.

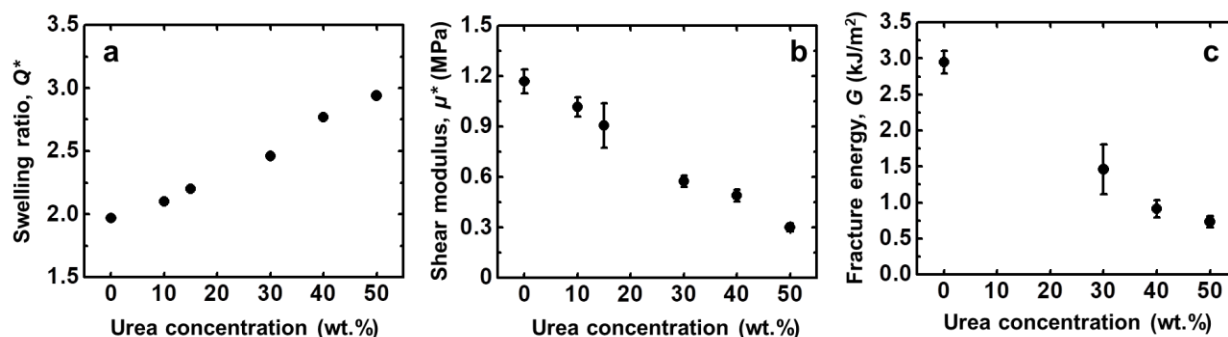


FIGURE 1 (a) Swelling ratio, (b) shear modulus and (c) fracture energy of HPU films at various urea concentrations. Strain rate: 50 mm/min.

The decline in elastic modulus with increasing urea concentration indicates that urea reduced the crosslinking density of HPU. These hydrogels are known to contain hydrogen bonds that formed via C=O (proton acceptors) and N-H (proton donors) in neighbouring polymer chains (Figure 2). The hydrogen bonds act as the physical crosslinks to form the gel network. Urea is known to be a highly-polarised molecule¹⁸ which could bind with polarised sites in the HPU network and disrupt the existing hydrogen bonds. Once the sample was treated with urea, the density of hydrogen bonds decreased, leaving fewer hydrogen bonds to crosslink the gel network. The reduction of the degree of crosslinking led to the observed decline in elastic modulus and increase in swelling ratio.

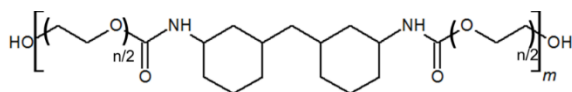


FIGURE 2 Chemical scheme of PEPU hydrogel in the present work

Effect of urea on network parameters of HPU

Modulus values and swelling ratios can be used to estimate the density and length of crosslinked network strands, as reported elsewhere.¹⁹ The shear modulus of hydrogels in the swollen state, measured in the tensile tests, was substituted into Equation (3) to give the

correlation between the gel's modulus and the density of network strands (N , mol/m³):

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

where μ^* is the shear modulus of the hydrogel at ideally-swollen state (kPa), N is the density of crosslinked polymer strands in the unswollen state (mol/m³), R is the gas constant (J/mol.K), and T is the absolute temperature (K). Q^* and Q' are the volumetric swelling ratios where the modulus is measured and the relaxed state, respectively. The relaxed state is where the polymer chains were un-stressed and unperturbed and in this study was taken as the dry-film state. Thus, the initial volumetric swelling ratio was $Q' = 1$, and Q^* was carefully measured and calculated as the ratio of the volume of the swollen hydrogel to that of the dry film (Figure 1a).

After calculating the strand density in the dry state (N) from Equation (3) the strand density in the swollen hydrogel (N^* , mol/m³) can be calculated by:

$$N^* = \frac{N}{Q^*} \quad (4)$$

Equation (5) estimates the average length of the network strand (n), which is here defined as the average number of backbone bonds per network strand:

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

In Equation (5), ρ is the density of dry polymer (1200 kg/m³ in this study), M is the repeating unit molecular weight divided by the number of backbone bonds in each repeating unit, and N' is network strand density. Since $Q' = 1$, then N' was equivalent to N as calculated in Equation (3). Finally, the calculated strand length (n) and the strand density of a swollen network (N^*) were used to estimate the concentration of single backbone bonds (C^* , mol/m³):

$$C^* = nN^* \quad (6)$$

All the calculated and measured parameters mentioned above are listed in Table 1. As can be seen, the hydrogel samples characterised by urea at different concentrations were varied in the swelling ratio (Q^*), elastic modulus (μ^*), strand density (N^*), strand length (n), and the concentration of backbone bonds (C^*). Increasing the urea concentration had the effect of decreasing the density of network strands, and the concentration of backbone bonds. The strand density was inversely-related to the strand length. The parameters listed in Table 1 confirm that a higher urea concentration could reduce the crosslinking density, *i.e.* hydrogen bond density.

TABLE 1 Physical and mechanical properties of PEPU after incubation at various urea concentrations

Urea wt.%	μ^* kPa	Q^*	N mol/m ³	N^* mol/m ³	n	C^* mol/m ³
0	1168	1.97	591	300	139	41721
30	548	2.46	298	121	275	33411
40	489	2.77	277	100	296	29672
50	300	2.94	173	59	473	27965

Applying Lake-Thomas Theory

Our first attempt to understand the effect of increasing urea concentration on the gel toughness used the classical Lake-Thomas theory.⁷ Using the network parameters of each hydrogel-urea composition presented in Table

1, the theoretical fracture energy (G_{LT}) based on the Lake-Thomas theory was calculated from:

$$G_{LT} = \left(\frac{3}{8}\right)^{1/2} C^* d^* U \quad (7)$$

where U is the dissociation energy of carbon-carbon bonds (J/mol), and d^* is the width of the crack zone (m) which is considered as the unstrained end-to-end distance based on Gaussian strands. In swollen state, d^* can be calculated as follows:

$$d^* = q^{1/2} n^{1/2} l \left(\frac{Q^*}{Q'}\right)^{1/2} \quad (8)$$

In Equation (8), l is the length of the carbon-carbon bond (~0.13 nm) and q represents the number of units per the rigid link. If l_r and n_r are the length and number of the rigid links per stand, $q = n/n_r = l_r/l$. The volume of each rigid link is taken as l_r^3 such that the strand volume is $q^2 n l^3$ and mass is nM/N_A where M is the repeating unit molecular weight divided by the number of backbone bonds and N_A is the Avogadro's constant. q is therefore determined by $\left(\frac{M}{N_A \rho l^3}\right)^{1/2}$. The detailed derivation of each equation and parameter mentioned above are available in our previous work.¹⁹

For the present study, the calculated Lake Thomas fracture energy G_{LT} was approximately 30-40 J/m² for all hydrogel samples with no significant difference for samples prepared with different urea concentrations. The calculated values were all considerably smaller than the experimental fracture energies measured in the tearing tests (Figure 1c). The fracture energy estimated by the Lake-Thomas approach is a minimum "threshold" toughness that only considers energy dissipation by chain scission and does not include contributions from other toughening processes. Fracture energies are also strongly dependent on crack propagation speed when energy dissipation mechanisms are time-dependent. In such cases the fracture energy increases with increasing crack growth rate and the threshold value corresponds to the quasi-static condition. The discrepancy between

the calculated Lake-Thomas toughness for the HPU-urea samples and the values measured using the tear test reflects the enhanced energy dissipation in these materials arising from additional toughening mechanisms and the possible rate-dependence of these processes.

The ratio of measured fracture energies to those calculated by the Lake-Thomas theory (G/G_{LT}) is shown in Figure 3. The toughness enhancement above the Lake-Thomas threshold toughness was inversely correlated to the amount of urea used for the hydrogel treatment, which suggests a connection between toughness enhancement and the density of hydrogen bonds in the network. Lake-Thomas' description of fracture in covalently-crosslinked networks considers that each network strand that spans the crack plane is stretched until one backbone bond fails and the entire strand is then fully unloaded. A hydrogen-bonded network is likely to behave differently. Indeed, hydrogen bonds are considerably weaker than covalent bonds and can reform after scission. As a result, the toughening mechanism of HPU may not satisfy the fracture processes described by Lake and Thomas. Other hydrogels crosslinked by physical associations have been widely reported to be mechanically tough and recoverable.²⁰⁻²² For instance, the so-called hybrid hydrogels exhibit very large fracture energies where crosslinking zones formed between alginate and Ca^{2+} dissipate energy during unzipping. Similar to hydrogen bonds, the ionic bonds have scission energy lower than covalent bonds but are capable of reforming after scission.²³⁻²⁵ The remaining question is to what extent do such transient physical bonds contribute to the toughening mechanism of hydrogel networks? In the remainder of this article, we attempt to address this question by quantifying this contribution to overall toughness.

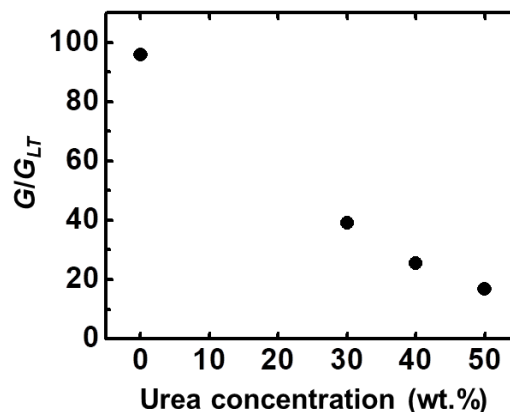


FIGURE 3 Ratio of the measured toughness to the threshold toughness (G/G_{LT}) for HPU hydrogels treated with various urea concentrations. G_{LT} is the fracture energy calculated from the Lake-Thomas theory.

Model development: a sequential debonding of hydrogen bonds

A new model is here proposed for fracture of the HPU, which explicitly includes the contribution of hydrogen bonds in toughening the hydrogel network. It is assumed in this model that the deformed network strands undergo repeated partial stress release by the dissociation of hydrogen bonds that link the strained strand to neighbouring strands in the gel network. Multiple sequential energy release through repeated loading and unloading of each network strand in the process zone around the crack tip supports the considerable toughening amplification observed in the HPU system (Figure 3).

Figure 4 gives an illustration of the toughening process considered by the model. Each of the black round dots represents a hydrogen bond acting as an effective crosslinking point and distributed along each network strand in the HPU. When the crack tip propagates (Figure 4a), the polymer strand across the plane with two hydrogen bonds on each side of the crack is deformed and stressed. Up to this point, the network deformation follows the assumptions used in the Lake-Thomas theory. However, the main difference between the new approach

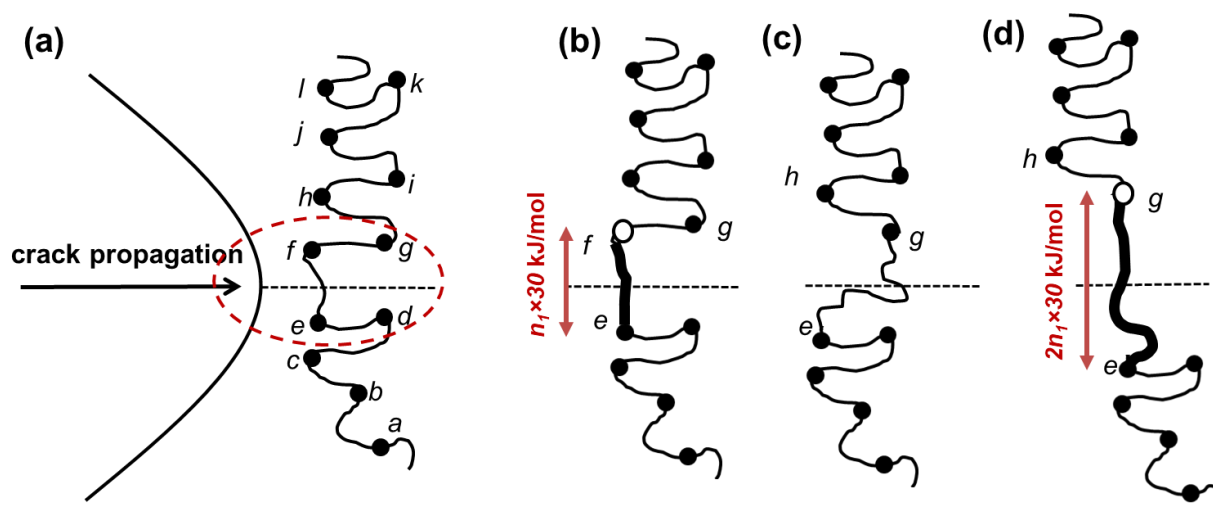


FIGURE 4 Toughening mechanism of hydrogen bonds in HPU and partial relaxation of network strands after the breakage of hydrogen bonds. (a) crack tip showing one network chain with multiple hydrogen bonded crosslinks; (b) deformation of the “*f-e*” strand; (c) partially relaxed strand after dissociation of hydrogen bonded crosslink “*f*”; and (d) deformation of “*g-e*” strand leading up to the dissociation of the second hydrogen bond “*g*”. Full “●” and open “○” circles indicate hydrogen bonds and dissociation of hydrogen bonds, respectively. The hydrogen bond scission energy is shown as 30 kJ/mol and n_1 is the initial number of backbone bonds in the first strand.

introduced here and the Lake-Thomas theory originates from the fact that hydrogen bonds are considerably weaker than covalent bonds. The average breaking energy of a hydrogen bond is ~ 30 - 40 kJ/mol which is almost 10 times lower than the carbon-carbon dissociation energy (~ 360 kJ/mol). In the Lake-Thomas theory, the chain strand is stretched until all bonds reach the breaking point (360 kJ/mol). Eventually, one carbon-carbon bond along the deformed strand chain dissociates releasing the whole energy stored by *all bonds* of the strand.

In the case of networks with hydrogen bond crosslinking, the strand deforms until one of the hydrogen bonded crosslinking points at one end of the strand fails (point “*f*” in Figure 4b). At this stage, all bonds along the strand “*f-e*” are equivalently stretched storing ~ 30 - 40 kJ/mol energy each. This assumption is similar to the core of the Lake-Thomas theory. Once one of the crosslinking hydrogen bonds is broken, the elastic energy stored on the entire network

strand will be partially released (Figure 4c). Yet, the network strand does not fail, as no backbone bond scission has taken place. Instead, the stress is transferred to the next-in-line hydrogen bond (“*g*” in Figure 4c), and a new longer strand (“*e-g*” in Figure 4c) bears the load. This strand begins deforming until all bonds store ~ 30 - 40 kJ/mol and the next hydrogen bond dissociates (“*g*” in Figure 4d). This process will continue until all hydrogen bonds on at least one side of the crack plane are consumed, and the strand is fully released allowing the crack to advance.

In this model, the breakage of each hydrogen bond acting as an effective crosslinker leads to the *partial* dissipation of the elastically-stored energy on the current strand. The energy dissipation can be understood by considering the first extension of strand “*f-e*”. When this strand is extended to the point that hydrogen bond “*f*” fails, then the extension of strand “*f-e*” is distributed evenly between crosslinks “*e*” and

“*g*” to partially unload strand “*f-e*” and to newly load strand “*g-f*”. If each strand deformation is linear elastic so that elastic energy scales with the square of strand extension, then the energy stored in strand “*g-e*” will be one half of that stored in strand “*f-e*” just prior to the dissociation of hydrogen bond “*f*” (see Supporting Information). The total fracture energy will then be the summation of the energy dissipated in the total number of the sequential “steps” needed to totally detach the strand from the network. The number of steps will be equivalent to the total number of the hydrogen bonds per single polymer chain. This assumption reflects the importance of the hydrogen bond crosslinking density on the fracture toughness of HPU as discovered in the present work. The mathematical expression of fracture energy by this model is:

$$G = \sum_i G_i = \sum_i \Gamma \Delta g_i \quad (9)$$

where G is the fracture toughness of HPU, Γ is the areal density of network strands (mol/m^2), n_i is the number of backbone bonds per strand at the i^{th} unloading step. i ranges from 1 to x , where x is the total number of steps *i.e.* the total number of hydrogen bonds per strand, and Δg_i is the energy dissipated during the relaxation of the strand when a hydrogen bond dissociates (Supporting Information). Of note, x is a variable and depends on the urea concentration as it affects the concentration of hydrogen bonds.

The number of repeating units per molecule of HPU was obtained from NMR and the length of polyether hydrophilic segment in each repeating unit. The molecular weight of HPU was 90 kg/mol, and the density of polymer chains was estimated as $\zeta=13 \text{ mol}/\text{m}^3$ based on the density of dry polymer ($\sim 1200 \text{ kg}/\text{m}^3$). Using the N^* (density of network strand in the swollen hydrogel) obtained from Equation (3) and Equation (4), the number of network strands per polymer chain (ϵ) was estimated. The number of hydrogen bonds behaving as the effective crosslinkers on each strand (x) would then be calculated as follows:

$$\epsilon = \frac{N^*}{\zeta} \quad (10)$$

$$x = \epsilon - 2 \quad (11)$$

Since N^* varies with urea concentration (see Table 1), ϵ and x are also both dependent on urea concentration. As per n_i , this is the number of backbone bonds that falls between two adjacent hydrogen bonds in the i^{th} step which increases linearly as a function of the number of steps (i), thus:

$$n_i = i \times n_1 \quad (12)$$

where n_1 represents the number of backbone bonds on the network strand before the first hydrogen bond is broken. Thus, it is the strand length when the hydrogel is in its initial and intact state before the crack propagation. This parameter can be calculated by:

$$n_1 = \frac{N_0}{\epsilon} \quad (13)$$

where N_0 is the total number of backbone bonds per polymer chain estimated from NMR results to be approximately 5,192. N_0 is considered as a constant here which is not dependent on urea concentration.

Finally, to estimate Γ which is the areal density of network strand crossing the crack plane, we assume the width of the crack plane to be the Gaussian length of a strand between the first two hydrogen bonds (d^*). Assuming a restricted random-walk model, we can use Equation (14), with b being the average length of a single atomic bond ($\sim 0.15 \text{ nm}$).

$$d^* = C n_1^{1/2} b Q^{*1/3} \quad (14)$$

Here C is a constant taking into account the rigidity of the chain, which for polyethers, C is around 4.1 ± 0.4 .^{26,27} Thus, Γ can be estimated by:

$$\Gamma = \left(\frac{3}{8}\right)^{1/2} N^* d^* \quad (15)$$

Substituting all the parameters into Equation (9), we have:

$$G = \left[\left(\frac{3}{8} \right)^{1/2} N^* C n_1^{1/2} b Q^{*1/3} \right] \times N_o U_h \left[1 + \frac{1}{x} \sum_i \frac{i}{i+1} \right] \quad (16)$$

with i ranges from 1 to x . The last phrase in the bracket in Equation (16) is the result of summation in Equation (9). For more details, see Supporting Information and in particular Equations (S12) and (S13).

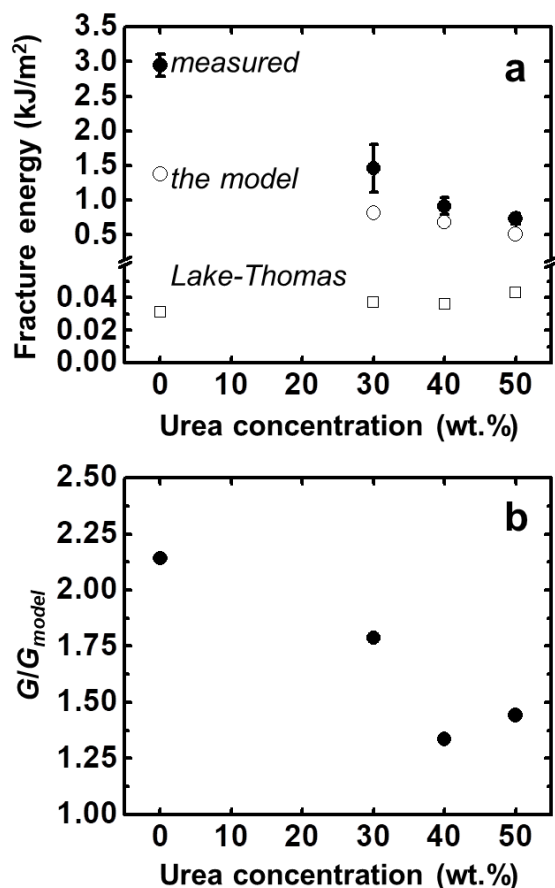


FIGURE 5 Comparison between calculated and measured fracture energies of HPU treated in different urea concentration. G is the measured fracture energies, and G_{model} is the fracture energies calculated by the new model.

Figure 5a demonstrates the comparison between the measured fracture energy and

theoretical fracture energy calculated by the new model as well as predictions from the Lake-Thomas model. The new model values are now within a factor of 2 compared with the experimentally measured fracture energies from the tear tests. The new model also correctly predicts the downward trend in fracture energy with increasing urea concentration although a gap still remains between the measured and calculated fracture toughness especially at low urea concentrations (Figure 5b). It should be noted here that the new model did not consider the reformation of the hydrogen bonds or any time-dependence of the energy dissipation during network strand loading and unloading. Both of these effects could further amplify the toughness through an effective increase in the number of hydrogen bonded crosslinks per chain but without reducing the strand length between crosslinks. Interestingly, the gap between calculated and the measured toughness reduce at higher concentrations of urea where hydrogen bonds have been suppressed to a greater degree. The reduced concentration of hydrogen bonding sites also reduces the opportunity to reform dissociated hydrogen bonds. If hydrogen bond reformation does not occur within the time frame of crack propagation, then the fracture values more closely match that calculated in the new model. In that case, the reasonable agreement between the calculated and measured values give support to the model and its underlying mechanism of repeated and sequential strand loading and unloading.

CONCLUSION

Polyether based polyurethane hydrogels (HPU) were prepared by swelling the dry polymer film in water. Once the swelling equilibrium was reached, the hydrogels were soaked in urea solutions with various weight concentrations. As urea is a highly-polarised molecule, this process altered the density of hydrogen bonds acting as physical crosslinks for HPU network.

Swelling ratio, toughness, and tensile properties of HPU treated with urea were systematically

measured to highlight the contribution of hydrogen bonds to the toughness of the hydrogels. It was found that with increasing the urea concentration, both the fracture energy and elastic modulus decreased significantly. Classic rubber elasticity was used to analyse the crosslinking density and network topology of the samples. The results showed that higher urea concentrations led to the decrease of crosslinking density and increase in network strand length.

The Lake-Thomas theory was utilised to estimate the baseline fracture energy of HPU films. However, the estimated values were 20-70 times lower than the measured toughnesses. It was found that the difference between measured toughness and those calculated from the Lake-Thomas decreased with increasing the urea concentration. A new mechanical model was proposed, assuming the elastically-stored energy of network strands were sequentially dissipated in a step-by-step scission of the hydrogen bonds along those polymer chains that span the crack plane. This sequential debonding model gave significantly higher fracture energies than obtained from the Lake-Thomas theory and the difference between measured and calculated toughness reduced to less than a factor of ~ 2 . The difference between the measured and calculated values was small at higher concentrations of urea. The differences that exist between the new model calculations and the measured fracture energy were attributed to the ability of the dissociated hydrogen bonds to reform since this contribution was not included in the model. In addition, additional factors such as chain pull-out, viscous drag, and carbon-carbon chain scission and crack speed effects could also contribute to toughness. The HPU films were found to display some viscoelasticity and the time-dependency of their fracture energy will be considered in future work.

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GRAPHICAL ABSTRACT

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A Sequential Debonding Fracture Model for Hydrogen Bonded Hydrogels

Hydrogen bonded hydrogels are easily fabricated, highly swollen polymer networks that are mechanically robust. The origin of their high toughness is explored by using urea to control the density of hydrogen bonds. The gel toughness is shown to be much greater than predicted by the classical Lake-Thomas theory. A new model giving good agreement with experiments is introduced based on the sequential debonding of successive hydrogen bonds along polymer chains that span the crack plane.

GRAPHICAL ABSTRACT FIGURE

