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A Model of the Fracture of Double Network Gels

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ABSTRACT: I propose a very simple model accounting for the very high toughness of double network gels based on the assumption that the first, stiff network will break up forming multiple cracks when the stress is above a defined value. These cracks are held together by the second network. A multiply cracked damage zone will form around any macroscopic crack in the material, causing energy dissipation and shielding the second network. The toughness enhancement by this process is estimated to be about ×40. The effect of cross-linking of the second network is discussed and explained.

Introduction

Chemically cross-linked polymer networks that are highly swollen in a liquid are normally very brittle. In spite of their low modulus, they typically fail by crack propagation at strains of just a few percent. This very low resistance to crack propagation can be understood in terms of the classic Lake−Thomas[1] model of crack propagation in an elastomer. In this model the energy dissipated in crack propagation is the energy required to stretch all the main chain bonds to their dissociation energy in each chain strand (length of chain between cross-links) that must be broken for the crack to propagate. The strands that must be broken are those that cross the crack plane so that they have adjacent cross-links on either side. This energy, typically called G_c, is often just a few J/m^2, giving little resistance to crack propagation. In bulk elastomers other energy dissipation mechanisms, such as viscoelastic dissipation or crystallization/melting, normally increase the crack propagation resistance to well above the Lake−Thomas prediction, but the presence of a large amount of solvent in a gel tends to suppress these other dissipation processes.[2]

Gong, Osada, and co-workers have demonstrated in a series of papers that it is possible to make double network (DN) gels that are very tough, with a G_c value of up to 1 kJ/m^2. Typically the first network is made by normal radical polymerization of a monomer and cross-linking agent in a solution containing about 80 wt % water. This first network is often made from a strongly ionic monomer and is fairly highly cross-linked and stiff. After formation, the first network is swollen to equilibrium in a solution of a second, typically uncharged, monomer containing a very small amount of cross-linking agent. The second monomer is then polymerized to form a second, very loosely cross-linked, network within the gel whose total polymer concentration is typically about 10 wt %. The toughness values obtained in this final double network can be remarkably high, particularly considering how little polymer it actually contains. Interestingly, the gels formed in this way show not only high toughness, but also are fairly stiff, because the first network is highly cross-linked and stretched by the swelling process to form the second network.[3−7]

The aim of this paper is to present a model for the failure processes in these double network gels that can explain why they are so tough. The model is based on the Lake−Thomas concepts of the amount of energy dissipated on failure of a polymer strand mentioned above but suggests that the particular double network microstructure causes a large enhancement of the number of strands that have to be broken.

A number of other techniques for the toughening of gels have been demonstrated. However, the literature is a little confused because the resistance to small scale deformation (modulus or stiffness) is often not distinguished from the resistance to failure or crack propagation (strength or toughness). At least three techniques other than forming double networks have been demonstrated that increase the toughness of chemically cross-linked gels. One technique consists of forming gels using polymer chains that can themselves form intrachain and interchain hydrophobic associations.[8] This technique can increase the toughness by about a factor of 10 over the equivalent gel without hydrophobic association. It is believed that the extra energy is dissipated in pulling apart the hydrophobic associations in the highly strained regions close to the crack tip. In two other techniques described to form tough gels, it is not entirely clear whether the gels are best described as chemical gels. Topological gels have been described that are highly swollen but still can be stretched to at least twice their original length.[9] In this material the cross-links should be considered as slip-links, ensuring an even distribution of chain force. Tough nanocomposite gels have also been synthesized, but here the authors emphasize that cross-linking must only come from adsorption of initiator fragments to the exfoliated clay.[10]

Properties of Double Network Gels

1. Toughening effect occurs in a range of chemically different systems but is most prominent when the first network is charged and the second network is neutral.[3]
2. The polymer component on the DN gels is mainly second network.[3]
3. The toughness increases with decreasing cross-link density of the second network, and a high toughness can be obtained with a zero cross-link “second network” as long as (i) the degree of polymerization of the second network is very high[6] and (ii) the first network is continuous. (If two slabs of the first network are placed together, then the second network is formed to give a high toughness interface the second network must be cross-linked.[11])
4. Some double network gels show necking in tension.[7] They show large, time-independent mechanical hysteresis even when they do not neck.[12]
5. The G_c of DN gels changes slowly with increase in crack growth rate.[5]

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6. The toughness of DN gels increases with increasing inhomogeneity of the cross-linking of the first network.[11]

7. The individual toughness of the two networks at the final swelling ratio is 0.5 and 10 J/m^2 (the latter with a molar density of cross-linked of 10^{-4} per monomer), respectively, while that of the DN gels is in the range 300−100 J/m^2.

A Model of Crack Propagation in DN Gels

In the model presented here crack propagation is considered to occur in two stages. In the initial stage failure occurs just within the first network which has a high cross-link density and is swollen by the process of forming the second network and so is relatively brittle. In most cases this network is relatively stiff because it is made of charged monomers, but in the interest of simplicity that issue will be ignored here. It is assumed that the cracks within the first network are bridged by the second network so the sample remains continuous as the first network cracks. In the first part of the model the aim is to calculate the external stress σ_a required to propagate long cracks, and hence many cracks, in the first network. When the external stress increases above σ_a, then multiple cracks form in the first network, leaving a damaged zone of material around the primary crack with much reduced elastic modulus controlled by the (low) cross-link density of the second network.

The second stage of failure involves propagating a crack in the second network. It is assumed that the region around a crack in the second network is a zone (really a strip of material close to the crack) where the first network has broken up by the formation of numerous cracks. This zone is rather like a yield zone around a crack in a ductile polymer or metal, but unlike in a yield zone, this region of material is still elastic but with a modulus much reduced from the bulk value. Because of the big reduction in modulus, the energy available to break the strands and propagate the crack in the second network is entirely the elastic energy in this strip, so the damaged zone or strip grows in thickness until this energy available is equal to the toughness of the second network. The macroscopic toughness is mainly a measure of the energy dissipated in the formation of the multiple cracks involved in breaking up the first network in the damaged strip around the crack and so increases with the width of the highly damaged strip. In contrast, a single network gel fails just by forming a single crack in the network with no damaged strip.

Crack Propagation in the First Network. We need to find the strain energy release rate available for propagating a crack in the first network when the crack is bridged by the second network. Such a crack must be parallel sided, as shown in Figure 1, with the stress across it, which is held by the second network, being very close to the external stress σ.

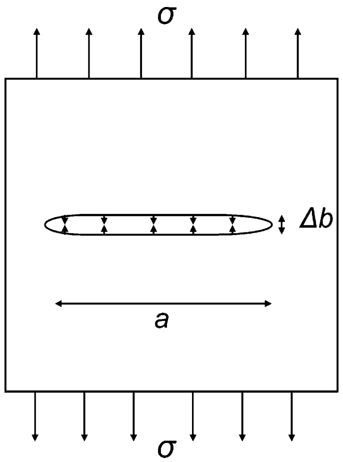

Figure 1. This figure shows a crack in the first network of length *a*. The stress across it is applied by the second network so that it is parallel sided with an opening Δb.

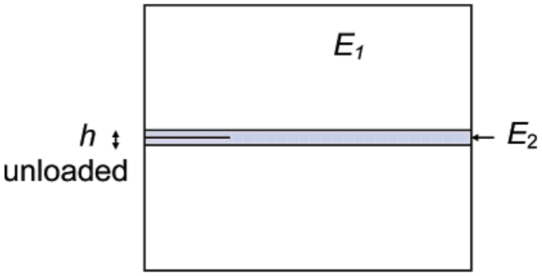

Figure 2. Geometry of the damaged zone around the crack.

The strain energy release rate G for this situation is the energy per unit length to close this crack. The closure is done by application to the crack faces of additional stresses that increase from zero when the crack opening is Δb to σ when Δb is zero. If the second network is assumed to be linearly elastic, then

$$G = \Delta b\sigma/2 \tag{1}$$

The maximum opening of such a crack is likely to be close to the contour length of the strands in the second network, which typically contain about 10^4 repeat units giving a contour length of 3 μm. Assuming a first network toughness G_c of 0.5 J/m^2, this gives a stress to cause long crack growth in the first network, σ_a, of 0.3 MPa. This value is close to the necking stress (0.2 MPa) that was measured for one particular DN gel that did fail by necking.[7] It is worth noting that the assumption that the opening of the crack is close to the contour length of the second network strands is consistent with the fact that the estimated value of σ_a (and the measured necking stress) are much greater than the modulus of the second network.

It would seem likely that when the stress on the DN gel exceeds σ_a, multiple cracks will grow long within the first network provided that there are sufficient inhomogeneities in the first network to initiate them. The number of such first network cracks, and hence toughness, will increase with first network inhomogeneity, consistent with property 6 mentioned above.

Crack Propagation and Failure of the DN Gel. We consider here the situation for a crack to propagate through the total DN gel. The stress situation is similar to that seen in plain stress failure in metals and crazing failure in glassy polymers. A planar zone of highly damaged material will form beside and in front of the crack tip. This is normally referred to as a Dugdale zone.[13] The stress on the edge of the zone is σ_a. Because of the considerable amount of damage to the first network of the material within the zone, its elastic properties are close to those of the second network. For simplicity, it will be assumed to be elastic with a modulus E_2. The modulus of the undamaged material is mainly controlled by the first network and is assumed to be E_1 where $E_1 \gg E_2$. The situation is shown in Figure 2.

For a crack to propagate within the second network there has to be sufficient elastic energy available within the low modulus damaged strip of material whose unloaded width is h. This problem is equivalent to crazing failure in polymer glasses[14] which itself, to the first approximation, can be considered as similar to the pure shear deformation fracture mechanics sample that is used for elastomers. The strain energy release rate G available to propagate the crack is given by

$$G_{\text{local}} = h(\lambda_m - 1)^2 E_2/2 \tag{2}$$

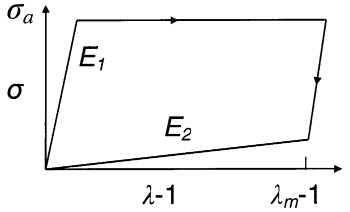

Figure 3. Assumed stress−strain relation for the DN gel showing the yieldlike situation caused by multiple cracking on the loading part of the cycle and the very low modulus of just the second network on unloading.

where the damaged material has an average extension ratio λ_m. For a crack to propagate through the whole gel, G_{local} must equal the toughness of the second network, G_2. From that we can extract the maximum thickness that the damaged zone can achieve without fracturing and which is given by

$$h_{max} = \frac{2G_2}{(\lambda_m - 1)^2 E_2} \tag{3}$$

Reasonable numerical values for G_2 (10 J/m^2), $\lambda_m - 1$ (10), and E_2 (1.5 kPa) can be estimated from the literature. The values of $\lambda_m - 1$ and E_2 come directly from the experimental observations reported in the figures of ref 7. Using these values, the thickness of the damaged zone found to be of the order of 130 μm. However, the actual measured macroscopic G_{global} is the work necessary to entirely break the first network over a thickness h_{max}.

If the idealized loading−unloading curve for the DN gel is shown in Figure 3, the macroscopically measured toughness G_{global} of the DN gel can be obtained from the energy required to grow the damaged zone to the width h_{max}, and so

$$G_{global} = h_{max}(\lambda_m - 1)\sigma_a \tag{4}$$

Now σ_a is directly related to the structure of the first network through eq 1 and can be also written as

$$\sigma_a = \frac{2G_1}{\Delta b} \tag{5}$$

where G_1 is the toughness of the first network alone. Substituting eq 3 and eq 5 into eq 4, we obtain

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

With the values estimated above, the toughness of the DN gel is predicted to be 400 J/m^2, a value that is entirely consistent with experimental results. As G_{local} is about 10 J/m^2 (see assumption 7), this toughness corresponds to an enhanced toughening given by

$$G_{global}/G_{local} = 2\sigma_a/E_2(\lambda_m - 1)$$

which is of the order 40.

Discussion

This very simple model of the failure of DN gels is very much based on the work of the group of Professor J. P. Gong, who have developed and published extensively on the materials. First it is worth considering if this model is consistent with all the properties of the gels.

The toughness of DN gels has been shown to increase as the cross-link density of the second network decreases. Qualitatively this observation seems consistent with the model because decreasing the second network cross-link density will increase its toughness and decrease its modulus, in both cases increasing G_{global}. However, it will also tend to increase the maximum extension in the damaged regions $\lambda_m - 1$ and decrease σ_a by increasing Δb, so within the model the effect of cross-link density on total gel toughness is not strong and would require a more sophisticated representation of the elastic properties of the networks to evaluate. The two separate parameters Δb and $\lambda_m - 1$ are used here to emphasize that the first refers to the opening of a crack in the first network held together by second network, while the latter is the extension of the composite containing both broken blocks of first network and second network. The value of Δb can be obtained from knowledge of the cross-link density of the second network, but $\lambda_m - 1$ is an experimentally obtained parameter related to the extension ratio of the second network and the distance between cracks (assuming the extension ration of the first network is comparatively small, ~2). From the assumption that the degree of polymerization of the second network strands is 10^4, the extension ratio of the second network must be ~10^2. To give a $\lambda_m - 1$ of ~10 the relaxed width of the cracks in the first network (the relaxed mesh size of the second network which is ~30 nm) must be ~10% of the distance between cracks. Hence, the width of the blocks between cracks in the first network must be ~300 nm.

The maximum toughness in double network gels has been shown to occur when the second “network” is not actually cross-linked.[5] However, the chains of the second “network” need to have a weight-average molecular weight M_w greater than ~2 × 10^6 g/mol to give a material with high toughness.[6] At first sight this observation would seem inconsistent with the model presented here. However, in very recent work, Gong and co-workers have measured adhesion mitigated by the second network. They showed that when two blocks of the first network are placed together and then the second network is formed, high interface toughness can only be obtained if the second network is cross-linked with a cross-link density of at least 10^{-4} mol (Gong, unpublished work). This observation shows that the first network has to undergo actual chain scission to give a high toughness gel if the second network is un-cross-linked or very lightly cross-linked.

These experimental results and the proposed model can be reconciled by consideration of the chemical processes that are likely to occur after a chain in the first network undergoes scission. On scission, two chain-end radicals are formed. These radicals exist in an aqueous environment where the organic component is mainly the material of the second network. Some of these radicals are very likely to abstract a hydrogen atom from another chain, most likely a chain of the second network as it is the majority component, and then that radical may easily terminate on a first network chain end radical or on another radical in the second network. In either case the end result is to cross-link the second network in the region close to the cracks in the first network. Hence, initial cross-linking of the second network is not required for toughness as long as the first network undergoes scission. Of course, in the adhesion situation where crack propagation does not require chain scission in the first network, this cross-linking of the second network does not happen, and failure will occur at low toughness by chain pullout of the second “network” when the latter is not cross-linked. If the second network is sufficiently cross-linked, then the stress across the interface can become high enough that multiple cracks will form in the first network, giving high interface toughness. To give the high toughness the molecular weight of the linear, second "network" chains must have an M_w of $\sim 10^7$ g/mol ($\sim 2 \times 10^5$ degree of polymerization),[6] significantly higher than the inverse of the second network cross-link density required to give high toughness (10^{-4}) in the adhesion situation. This shows that to give high toughness the linear chains of the second "network" need to undergo a number of cross-linking events in the damaged zone.

The suggestion, that radical reactions are essential to give high toughness when un-cross-linked second network chains are used, is eminently testable. If a radical scavenger is added after forming the gel with an un-cross-linked second network, then the toughness should drop as the grafting reactions are inhibited. For a sufficiently cross-linked second network the presence of the radical scavenger should have no effect. Such experiments are currently being undertaken. It also follows from this suggestion that the toughness of gels with un-cross-linked second network is likely to decease with time as the water in the gels slowly absorbs oxygen. The oxygen may react with the radicals formed by fracture of the first network and so suppress the cross-linking reactions.

As mentioned above (point 6), the toughness of a DN gel can be increased by increasing the inhomogeneity of the first network. The inhomogeneity was increased by decreasing the concentration of the first network initiator. This observation is entirely consistent with the model presented here. Increasing inhomogeneity in the first network will increase the density of cracks that form and are held together by the second network, thereby increasing the energy dissipation around the crack. It is valuable to emphasize that within this model the only energy dissipation assumed is that proposed by Lake and Thomas. However, failure of the DN gel requires very much more chain scission than their model predicts.

Conclusions

The toughness of double network gels can be understood in terms of a simple model of the failure processes in the material. The first network is shown to start to form multiple cracks at a stress of ~0.3 MPa. These cracks are held together by the second network so forming a damaged zone around the tip of any crack through the total material. The energy dissipated in the formation of this damaged zone is found to increase the toughness over just the second network by a factor of about 40 times. The observation that the second network does not have to be cross-linked if its molecular weight is high enough can be explained by cross-linking reactions caused by the radicals formed on cracking of the first network.

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