

hydrogels (Zhao 2014) have been very successful with several examples giving fracture energies exceeding 1000 Jm^{-2} and even approaching $10,000 \text{ Jm}^{-2}$. These improvements have also encouraged interest in the fundamental mechanisms involved in fracture of gels and these studies highlight the role of the network parameters (Xin et al. 2013).

The Lake-Thomas description of fracture in rubbers (Lake and Thomas 1967) provides a basis for linking network parameters to toughness. Fracture is assumed to involve a process where the network strands that span the crack plane are fully extended and subsequently broken as the crack propagates. The energy dissipated during crack growth is taken as equivalent to the energy needed to fully extend the network strands such that the strain energy per backbone bond in the network strands is equivalent to the bond dissociation energy, U . Longer strands contain more backbone bonds so they will dissipate more energy during fracture. It is important to note that while only one backbone bond actually breaks, the energy dissipated comes from entire elastic energy stored in the stretched network strand since all this energy is lost at the point of bond scission. The elastomer toughness, $G_{c,o}$, depends both on the length of the network strands between crosslinks and on the number of strands that cross the fracture plane:

$$G_{c,o} = \left(\frac{3}{8}\right)^{1/2} CdU \quad 37$$

where U is backbone bond dissociation energy (Jmol^{-1}), C is concentration of backbone bonds in the unstrained network (molm^{-3}), and d is the unstrained width of the damage zone (m). The concentration of backbone bonds is obtained from ρ/M_o , where ρ is the dry polymer density and M_o is strand average molecular weight divided by the number of backbone bonds. 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:

$$d = n_r^{1/2} r l_r = z^{1/2} n^{1/2} b \quad 38$$

where n_r and l_r are the number and length of rigid links per strand. The network strands have on average n backbone bonds of length b such that $z = n/n_r = l_r/b$ is the number of backbone bonds per rigid link, which is 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 $z^3 n b^3$ with mass nM_o/N_A where N_A is Avogadro's number. The number of strand units per rigid link is estimated from:

$$z = \left(\frac{M_o}{N_A \rho b^3}\right)^{1/2} \quad 39$$

The network toughness is then given by:

$$G_{c,o} = \left(\frac{3}{8}\right)^{1/2} \frac{\rho}{M_o} z^{1/2} b U n^{1/2} \quad 40$$

As illustrated by Equation 40, the fracture energy of unswollen rubbers is predicted to increase with increasing strand length (n), or decreasing crosslink density.

The effect of solvent swelling on the network toughness can also be accommodated in the Lake-Thomas approach. Swelling causes a decrease in the concentration of