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

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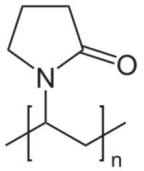
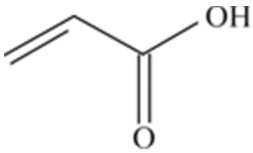
Supplementary Information

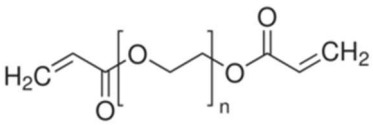
Molecular structures of monomers and crosslinkers.



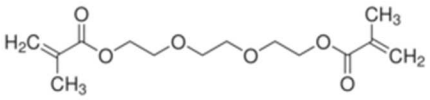
N-vinyl pyrrolidone



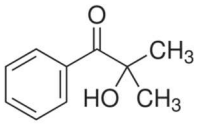
Acrylic acid



Poly(ethylene glycol) diacrylate



Triethylene glycol dimethacrylate



2-Hydroxy-2-methylpropiophenone

Definition of Terms

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)

C= concentration of backbone bonds (mol/m^3)

d = width of the damage zone (m)

ρ = dry rubber density (kg/m^3)

M = unit molecular weight (kg/mol) = Repeat unit mol wt. / no. of backbone bonds in repeat unit

n_r and l_r = number and length of rigid links per strand

$q = n/n_r = l_r/l$ is the number of strand units per rigid link

μ = shear modulus

R=gas constant (J/mol.K)

T= temperature (K)

Lake Thomas Equation

The original expression of Lake and Thomas to predict toughness is simply the product of the number of strands crossing a crack plane (Γ), the length of these strands (n) and the bond dissociation energy (U):

$$G_0 = \Gamma n U \tag{S1}$$

For a given fracture plane, the number of network strands passing through the plane of the crack (Γ) is related to the overall concentration of network strands and a Gaussian distribution of strand lengths so that

$$G_0 = \left(\frac{3}{8}\right)^{1/2} C^* d^* U \tag{S2}$$

The application of this form of the Lake Thomas equation requires knowledge of the concentration of backbone bonds in the swollen gel, which can be determined from the dry polymer density and swelling ratios. In addition, the defect zone distance is determined by the strand length which can be calculated from the concentration of backbone bonds and strand density. The latter is calculated from the measured shear modulus.

Calculation of Backbone Bond Concentration (C)

The concentration of backbone bonds (C; mol/m^3) can be determined from experimentally measured dry polymer density (ρ_P; kg/m^3) and the strand unit molecular weight (M; kg/mol = repeat unit mol wt. / no. of backbone bonds in repeat unit):

$$C = \frac{\rho_P}{M} \tag{S3}$$

This expression is simply derived from the fact that the dry polymer contains X network strands with n units per strand and each unit is associated with one backbone bond then there are a total of nX backbone bonds occupying a volume V_P. The concentration is then:

$$C = \frac{nX}{V_P} \tag{S4}$$

And the polymer density will be:

$$\rho_P = \frac{m_P}{V_P} = \frac{nXM}{V_P} = CM \tag{S5}$$

where m_p is the polymer mass. For solvent swollen rubbers, the concentration of network bonds (C^*) is reduced in direct proportion to the swelling ratio (Q^*):

$$C^* = \frac{nX}{V_P + V_S} \qquad \text{and} \qquad Q^* = \frac{V_P + V_S}{V_P} \tag{S6}$$

where V_p is the volume of solvent. Rearranging gives:

$$C^* = \frac{nX}{V_P + V_S} = \frac{nX}{V_P Q^*} = \frac{\rho_P}{MQ^*} \tag{S7}$$

This dilution effect applies to all swelling states.

Calculation of Fracture Zone Width (d)

The essence of the Lake Thomas theory takes this fracture zone width as the end-to-end distance of the network strands. From the Gaussian chain approach, this distance is simply:

$$d_1^* = q^{1/2} n^{1/2} l \tag{S8}$$

For isotropically swollen gels, the end-to-end distance is expanded:

$$d_1^* = q^{1/2} n^{1/2} l \left(\frac{Q^*}{Q'} \right)^{1/3} \tag{S9}$$

where Q^* and Q' are the swelling ratios in the state where the fracture toughness was measured and the as-synthesised state, respectively.

Calculation of Strand Length (n)

The concentration of backbone bonds in a swollen rubber is:

$$C = \frac{nX}{V_P + V_S} \tag{S10}$$

And if the concentration of network strands in the swollen rubber is:

$$N^* = \frac{X}{V_P + V_S} \tag{S11}$$

Then $C = nN^*$. From this simple relation, it is seen that a means to determine N^* will lead to a value of n.

Calculation of Strand Density (N^*)

Experimentally, the concentration of network strands can be obtained from the shear modulus of the swollen rubber. For a swollen rubber behaving as a Gaussian network:

$$\mu^* = N^* RT\lambda_S^2 \tag{S12}$$

where N^* is the network strand density in the swollen rubber and λ_S is the linear swelling of the rubber from its undisturbed reference state:

$$\lambda_S = \left(\frac{Q^*}{Q'}\right)^{1/3} \qquad N^* = \frac{N}{Q^*} \qquad N' = \frac{N}{Q'} \tag{S13}$$

where Q^* and Q' are the swelling ratios in the state where the modulus was measured and the as-synthesised state, respectively.

For dry rubbers: $Q^* = Q' = 1$ and $N^* = N$

$$\mu = NRT \tag{S14}$$

For swollen rubbers (synthesised in dry state): $Q' = 1$ and $N^* = N / Q^*$

$$\mu^* = NRT\left(\frac{1}{Q^*}\right)^{1/3} \tag{S15}$$

For swollen gels synthesised in a partly swollen state: $Q' > 1$ and $N^* = N / Q^*$

$$\mu^* = NRT\left(\frac{1}{Q^*}\right)^{1/3}\left(\frac{1}{Q'}\right)^{2/3} \tag{S16}$$

And if the modulus is measured in the as-synthesised state so that $Q = Q'$ then:

$$\mu' = NRT\left(\frac{1}{Q'}\right) = N'RT \quad \text{and} \quad \mu^* = \mu'\left(\frac{Q'}{Q^*}\right)^{1/3} \tag{S17}$$

where N' is the strand concentration in the as-synthesised gel and the strand concentration at any other swelling is:

$$N^* = N'\left(\frac{Q'}{Q}\right) \tag{S18}$$

Determination of q (number of backbone bonds per rigid link)

Taking each stand as n_r cubic units of cube volume l_r^3 where $n_r = n/q$ and $l_r = ql$ gives a strand volume of $v_P = q^2 n l^3$ and the total polymer volume is $V_P = X v_P$. The dry polymer density is then predicted to be:

$$\rho_P = \frac{m_P}{V_P} = \frac{nXM}{N_A V_P} = \frac{nM}{N_A v_P} = \frac{M}{N_A q^2 l^3} \tag{S19}$$

where N_A is Avagadro's number. This expression can be used to calculate q.