Fracture of Rubber

This lecture focuses on fracture of highly deformable materials, such as natural rubber, synthetic elastomers, and elastomeric gels. Before rupture, these materials are capable of large and elastic deformation.

Stretchability and Toughness

Many elastomers and gels are stretchable, but brittle. A sample without cut can be stretched several times its initial length. Once we introduce a small cut on the edge of the sample, its stretch to rupture reduces markedly. We call a material brittle when its stretch to rupture is sensitive to small cuts, and call a material tough when its stretch to rupture is insensitive to small cuts.

Demonstration. Demonstrate in class the effect of a crack. Use a wide rubber band, so that it is easy to see and easy to introduce a crack. Show that the rubber band can be stretched about six times its original length.

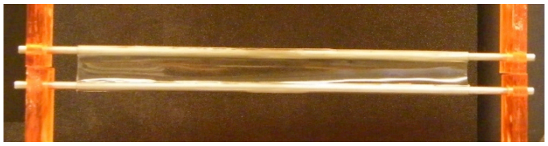
The large deformation of the rubber may hide its brittleness. To expose its brittleness, we show that the stretch to rupture of the rubber band is sensitive to cut. Use scissors to introduce a cut into an edge of the rubber band, pull the band, and show that the band ruptures at a stretch less than three. Before the rubber band ruptures, the tip of the cut blunts. Pass the scissors and some rubber bands around. Invite every student to try.

Do the same experiment using a long party balloon. Stretch the balloon without cut. Introduce a cut and stretch again. Show that the stretch to rupture is insensitive to the cut.

Rupture of a highly stretchable dielectric elastomer. 3M sells a double-sided adhesive tape called VHB (very high bond). In recent years, VHB has found a new use as a dielectric to make highly deformable transducers. In such a transducer, the two faces of a VHB membrane are coated with conformal electrodes, such as carbon grease. When the two electrodes are subject to a voltage, electric charges of the opposite signs accumulate on the two faces of the VHB membrane, causing the membrane to reduce its thickness and expand its area. The setup functions as an actuator: the electrical voltage causes mechanical motion. In applications, the membrane is also pulled in tension by a mechanical force.

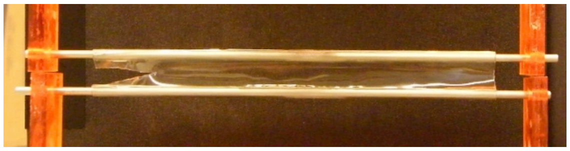
When the voltage is high enough, the dielectric membrane suffers electrical breakdown. The electrical breakdown makes a small hole in the membrane. Sometimes, after electrical breakdown, the mechanical force tears the entire membrane into two halves. We are now studying this phenomenon.

Here we look at the rupture of VHB under mechanical forces alone. A VHB tape, thickness 0.5 mm and width 152.4 mm, is wrapped around two steel cylinders of diameter 3.2 mm. The strong adhesion of VHB prevents the tape from slipping even at large stretches. A pristine tape can be stretched 9 its initial length without rupture.

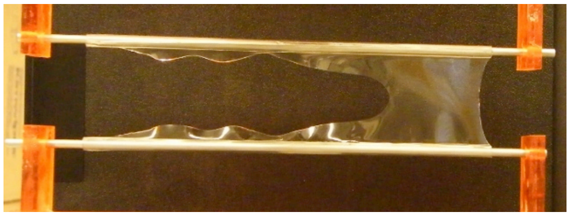


undeformed state

deformed state



undeformed state



deformed state

In a second experiment, we cut an edge of the tape by using surgical grade scissors. When we pull the tape, the tip of the cut blunts. When the tape is pulled to about 3.5 times its initial length, the cut extends steadily across the tape. VHB is viscoelastic; note the residual deformation in the wake of the crack.

- M. Pharr, J.Y. Sun and Z.G. Suo, Rupture of a highly stretchable acrylic dielectric elastomer. Journal of Applied Physics 111, 104114 (2012).

Why Are Elastomers and Gels Stretchable?

- L.R.G. Treloar, The Physics of Rubber Elasticity. Second Edition. Cambridge University Press, 2007.
- P.J. Flory, Principles of Polymer Chemistry. Cornell University, 1953.
- J.E. Mark and B. Erman, Rubberlike Elasticity. Third Edition. Oxford University Press, 1975.

Hybrid bonds, strong and weak. The molecular understanding came in 1930s. An elastomer consists of atoms of hybrid bonds, some strong and some weak. The elastomer is a three-dimensional network of polymer chains. The chains are cross-linked by strong, covalent, chemical bonds. Each chain consists of a large number of monomers, which also form covalent bonds. Between the chains, molecules interact through weak, physical bonds, such as hydrogen bonds and van der Waals interaction.

The two types of bonds—strong (chemical) bonds and weak (physical) bonds—together govern the behavior of the elastomer. The strong bonds make the elastomer solid-like, but the weak bonds make the elastomer liquid-like.

A gel is an elastomer swollen with a solvent. The network consists of covalent bonds, but the network and solvent interact through weak bonds.

Entropic spring. An elastomer is an entropic spring. Because the polymer chains interact through weak bonds, the configuration of an individual chain is essentially unaffected by the presence of other chains.

Along a chain, monomers link together by covalent bonds. The covalent bonds cannot be stretched much, just like the strong bonds in ceramics and metals. However, the covalent bonds in a polymer chain allow monomers to rotate relative to each other. This rotation allows the chain to take many configurations.

At a finite temperature, the monomers rotate relative to one another, and the polymer rapidly changes from one configuration to another. When a force pulls the two ends of the chain, the distance between the two ends changes. When the force is removed, the two ends of the chain recover the mean distance. The polymer chain is an entropic spring.

An analysis of this model of freely-joined chains is summarized in notes posted online (http://imechanica.org/node/288). Here we focus on the stretch of a chain.

Freely-joined chain and random walk. At a finite temperature, the chain jiggles, and the distance between the two ends of the chain is a random variable. In the absence of the applied force, what is the mean distance between the two ends of a chain? This result is readily found in the literature on random walks.

A chain consists of m monomers. Represent the chain by m steps of a random walk. Each step is a vector $\mathbf{r}_i$ of length a. The vector from one end of chain to the other end is $\mathbf{R} = \mathbf{r}_1 + \mathbf{r}_2 + ... + \mathbf{r}_m$. The square of the distance between the two ends of the chain is

$$\mathbf{R} \cdot \mathbf{R} = ma^2 + 2\mathbf{r}_1 \cdot \mathbf{r}_2 + 2\mathbf{r}_2 \cdot \mathbf{r}_3 ... + 2\mathbf{r}_{m-1} \cdot \mathbf{r}_m .$$

Let L be the mean distance between the two ends, defined by

$$L = \sqrt{\langle \mathbf{R} \cdot \mathbf{R} \rangle} .$$

For a random walk, $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle = \langle \mathbf{r}_2 \cdot \mathbf{r}_3 \rangle = ... = \langle \mathbf{r}_{m-1} \cdot \mathbf{r}_m \rangle = 0$. Thus,

$$L = a\sqrt{m} .$$

Limiting stretch of a chain. When a force pulls the two ends of the chain, the mean distance between the two ends increases. When the force is very large, the chain becomes straight. The length of the straight chain is

$$l = am .$$

The ratio l/L defines the maximum stretch of the chain, known as the limiting stretch. Designate the limiting stretch of the chain by

$$\lambda_{\lim} = \sqrt{m} .$$

Thus, a chain of 100 monomers has a limiting stretch of 10.

Fracture Mechanics without Field Theory

- R.S. Rivlin and A.G. Thomas, Rupture of rubber. Part I. Characteristic energy for tearing. Journal of Polymer Science 10, 291-318 (1953).

For a crack in an elastic body, the energy release rate is defined by using the elastic energy stored in the entire body (http://imechanica.org/node/7507). This definition invokes no field theory. Indeed, the energy release rate can be determined experimentally without measuring any field.

This definition is also economic in developing the theory of fracture: the same definition works for any elastic body, so long as we can obtain elastic energy of the body as a function of the area of the crack. Rivlin and Thomas (1953) extended the Griffith approach to bodies capable of large deformation prior to fracture. The paper reached two broad conclusions:

- The fracture energy of natural rubber determined by various types of test pieces is of a similar value. Thus, fracture energy is a material property.
- The fracture energy of natural rubber is much larger than the surface energy of the natural rubber.

A crack in a highly deformable elastic body. Consider a crack in an elastic body subject to a load. The system is characterized by two independent variables:

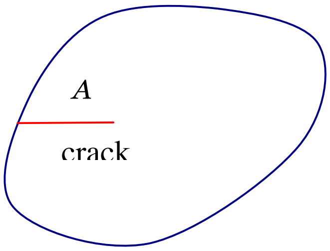
- Δ, the displacement of the load, and
- A, the area of the crack.

For a highly deformable material, the area of the crack can change substantially even when the crack does not extend. To specify the change due to the extension of the crack, we take A to be the area of the crack when the body is undeformed.

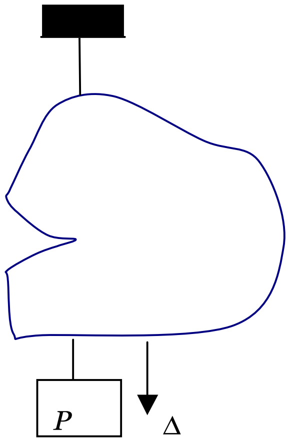
The elastic energy stored in the body is a function of the two independent variables, namely,

$$U = U\left(\Delta, A\right).$$

The two independent variables may be visualized by imagining many bodies, which are identical in the undeformed states except for the areas of the cracks. We then load these bodies in the same way. For each body, the crack does *not* extend when the load is applied.



Reference state



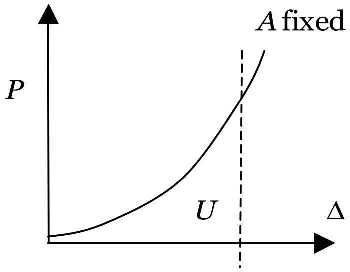
Deformed state

The function $U(\Delta, A)$ can be determined by experimental measurement. For a given cracked body, the load P can be measured experimentally as a function of the displacement Δ. The function can be plotted as the load-displacement curve.

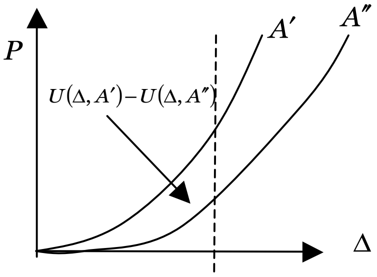
When the displacement changes by $d\Delta$, the load P does work $Pd\Delta$ to the body. When the crack does not extend, the work done by the load equals the change in the free energy, $Pd\Delta = dU$. We write this statement more precisely as

$$P = \frac{\partial U(\Delta, A)}{\partial \Delta}.$$

This expression has a usual graphic representation. When the area of crack is fixed, the area under the load-displacement curve is the elastic energy U stored in the body.



Energy release rate. Now consider two copies of the body: one copy has a crack of area A', and the other copy has a crack of a slightly larger area A''. The copy with the larger crack is more compliant—that is the load-displacement curve of the body with the larger crack is below the load-displacement curve of the body with the smaller crack. Consequently, at the same displacement, the body with a larger crack has lower elastic energy:



$$U(\Delta, A') > U(\Delta, A'').$$

Define energy release rate, *G*, as the reduction of the elastic energy associated with the crack increasing per unit area:

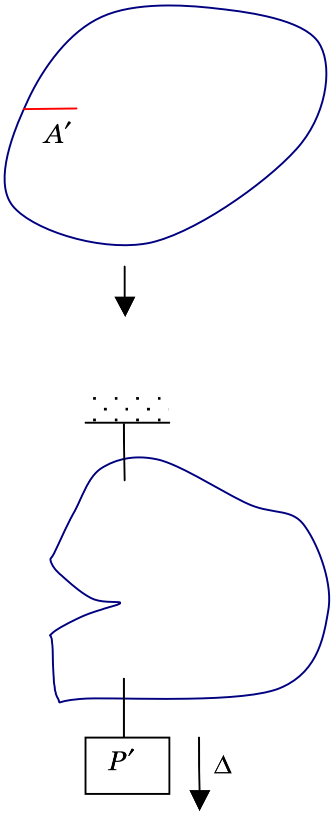
$$G = -\frac{U(\Delta, A'') - U(\Delta, A')}{A'' - A'}$$

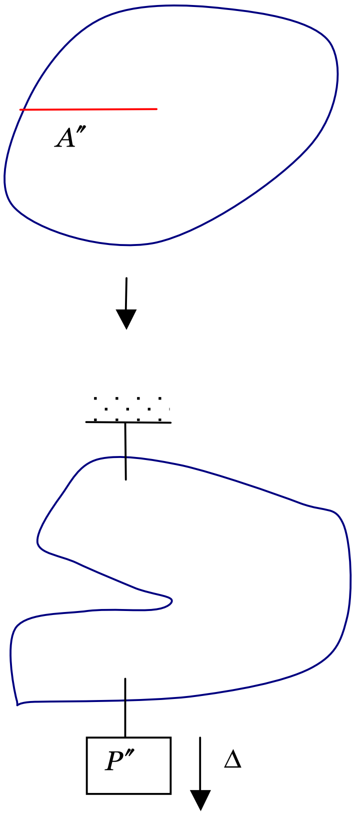
The displacement Δ is held fixed as the area of the crack changes. Write the above definition using the notation of calculus:

$$G = -\frac{\partial U(\Delta, A)}{\partial A}.$$

The energy release rate can be interpreted in the load-displacement diagram.

Once we know the function $U(\Delta, A)$, the above definition gives the energy release rate *G*. Thus, *G* is purely an elastic quantity, and we need to know nothing about the process of fracture to obtain *G*.





Increment of elastic energy. When the displacement of the load varies by $d\Delta$ and the area of the crack varies by dA, the elastic energy stored in the body varies by

$$dU = \frac{\partial U(\Delta, A)}{\partial \Delta} d\Delta + \frac{\partial U(\Delta, A)}{\partial A} dA .$$

We have interpreted the significance of the two partial derivatives:

$$P = \frac{\partial U(\Delta, A)}{\partial \Delta}$$

$$G = -\frac{\partial U(\Delta, A)}{\partial A}$$

Using these relations, we write the increment of the elastic energy as

$$dU = Pd\Delta - GdA .$$

Just as P is the thermodynamic force conjugate to the displacement Δ, the energy release rate G is the thermodynamic force conjugate to the area A.

Change of variable. It is sometimes convenient to use the load P as an independent variable, rather than the displacement Δ. To visualize P as an independent variable, we represent the load by a weight P, and regard the elastic body and the weight together as a system. The energy of this system, Π, is the sum of the elastic energy stored in the body and the potential energy stored in the weight, namely,

$$\Pi = U - P\Delta .$$

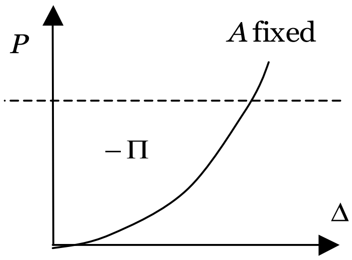
The quantity Π is known as the Gibbs free energy in thermodynamics, and the potential energy in solid mechanics. When the crack does not extend, the potential energy can be interpreted in the load-displacement diagram.

The above definition of Π, together with $dU = Pd\Delta - GdA$, leads to

$$d\Pi = -\Delta dP - GdA .$$

On the basis of this expression, we regard Π as a function of the load the area of the crack, namely,

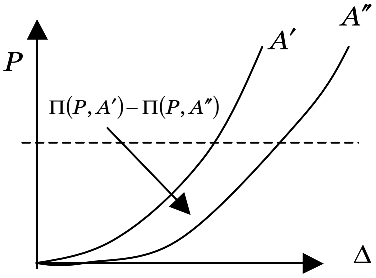
$$\Pi = \Pi(P, A).$$



The partial derivatives of this function are interpreted as

$$\Delta = -\frac{\partial \Pi(P, A)}{\partial P},$$

$$G = -\frac{\partial \Pi(P, A)}{\partial A}.$$



The graphical interpretation makes it evident that the two functions, $U = U(\Delta, A)$ and $\Pi(P, A)$, contain the same information. We should not fool ourselves into believing that we have learned anything really new by a change of variables.

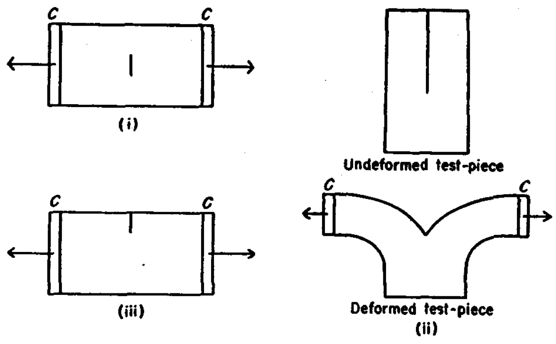


Fig. 1. Schematic diagrams of test-pieces.

Fracture energy. The fracture energy of material, Γ, is defined as the critical energy release needed to cause a pre-cut crack to extend. (Rivlin and Thomas called the fracture energy the characteristic energy of tearing, and designated the quantity by the letter *T*.) The fracture energy can be determined experimentally. Go through the procedure in class.

To ascertain if the fracture energy is independent of test pieces, Rivlin and Thomas tested a specific rubber by using test-pieces of three types. For each type of the test-pieces,

- Introduce cuts of various lengths.
- Record the load-displacement curve.
- Record the point at which tearing starts.

From these experimental data, Rivlin and Thomas estimated the fracture energy. This procedure showed that the point of tearing of all test pieces could be correlated by a single value of the fracture energy:

$$\Gamma = 3.7 \times 10^3 \mathrm{J/m^2}.$$

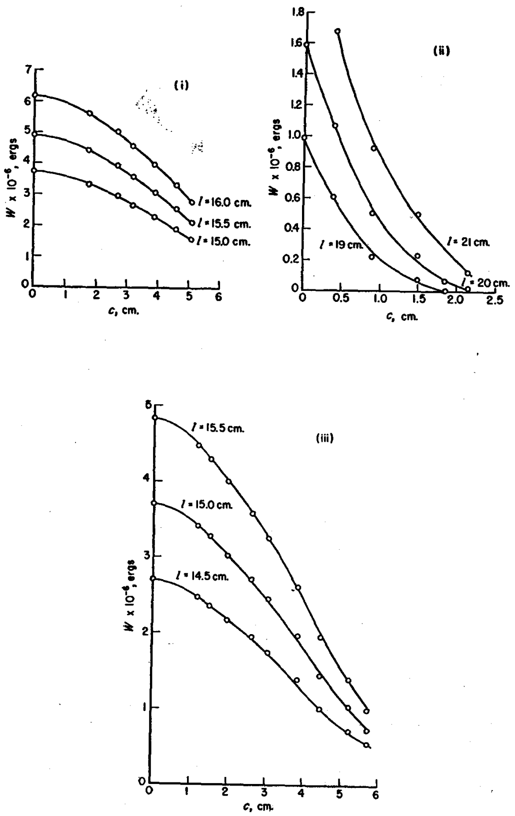


Fig. 5. Relations between W and c for given values of the overall deformation. Calculated from the curves of Figure 4.

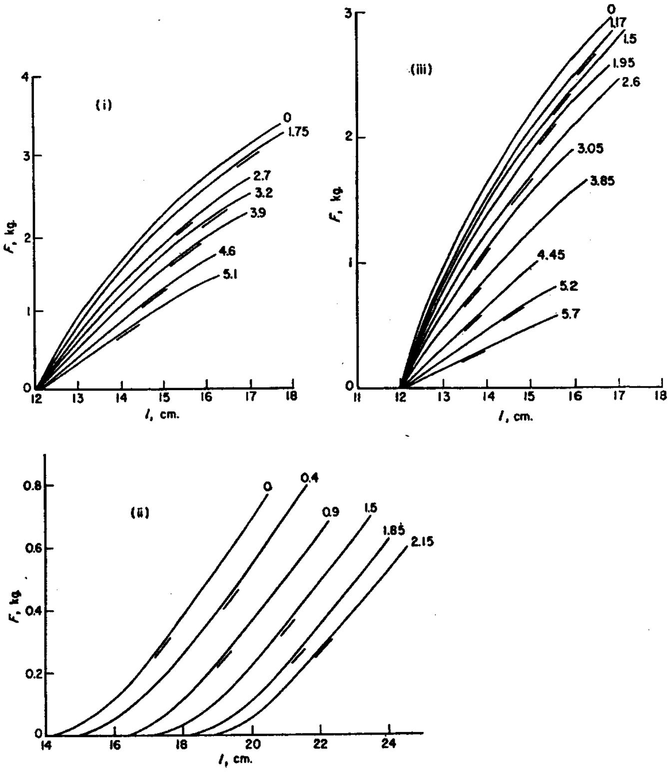


Fig. 4. Measured load-deformation relations for various cut-lengths c. Bars denote points at which incipient tearing occurred. Numbers against curves give values of c in cm.

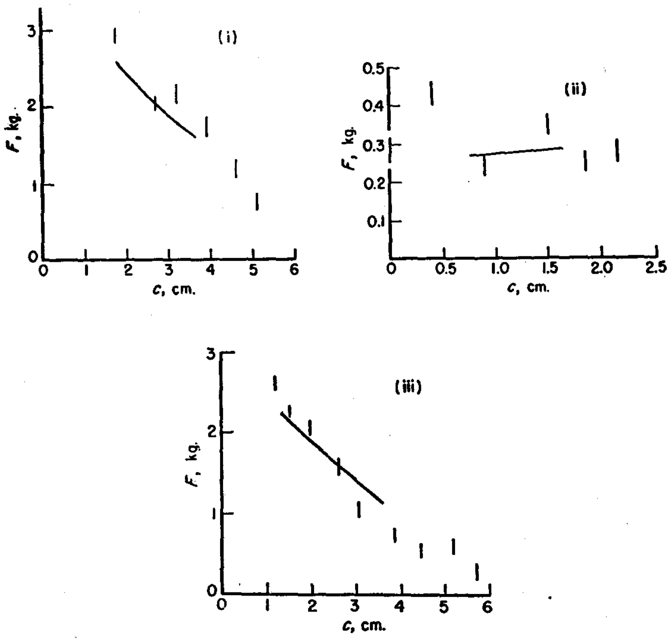


Fig. 6. Values of F at which tearing occurred for various values of c. The bars denote experimental values. The curves represent the calculated relations on the assumption that $T = 3.7 \times 10^6$ ergs/cm.^{2}.

Analytical expressions for the energy release rate for some test pieces. The above procedure to determine the fracture energy is tedious, using many test-pieces. In using the definition to determine the energy release rate from the experimental data, we need to measure load-displacement curves for test-pieces of the same type but with various lengths of the pre-cuts.

Rivlin and Thomas suggested an alternative approach. For some types of test-pieces, the energy release rate can be readily calculated analytically in terms of the stress-stretch curve of homogenous deformation.

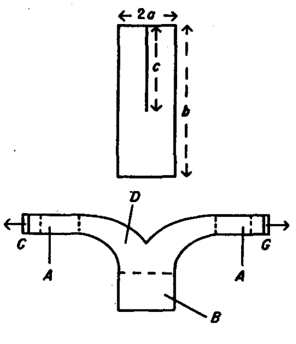


Fig. 7. Schematic diagram of "simple extension" tear test-piece.

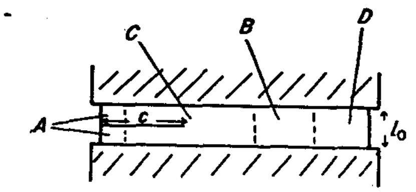


Fig. 8. Schematic diagram of "pure shear" tear test-piece.

The trousers test.

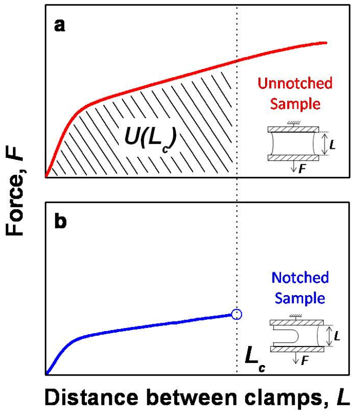
$$G = 2\lambda \frac{F}{t} - 2Wa$$

The pure-shear test. This test was described in Rivlin and Thomas (1953).

$$G = W_0 l_0.$$

We next describe a specific procedure (Sun et al., 2012). Separately pull two samples of the same material. One sample is unnotched, and the other sample is notched. The unnotched sample is pulled to measure the force-length curve. (To determine the fracture energy, it is unnecessary to pull the unnotched sample all the way to rupture.) When the two clamps were pulled to a distance L, the area beneath the force-length curve gave the work done by the applied force, $U(L)$. The notched sample was prepared by using a razor blade to cut into the gel a 40 mm-long notch. (The precise length of the notch was unimportant for this test.) The notched sample was pulled, and pictures were taken at a rate of ~30 frames/sec to record the critical distance between the clamps, L_c, when the notch turned into a running crack. The fracture energy was calculated from

$$\Gamma = \frac{U(L_c)}{a_0 b_0}.$$



A large sheet containing a small crack. Dimensional consideration dictates that the energy release rate takes the form

$$G = cf(\lambda),$$

where c is the length of the crack, and $f(\lambda)$ is a function of the applied stretch. This function depends on the stress-stretch behavior, and can be determined by finite element method.

- O.H. Yeoh, Relation between crack surface displacements and strain energy release rate in thin rubber sheet.

Why Is the Fracture Energy of Rubber so High?

- E.H. Andrews, Rupture propagation in hysteresial materials: stress at a notch. Journal of the mechanics and Physics of Solids 11, 231-242 (1963).
- G.J. Lake and A.G. Thomas, The strength of highly elastic materials. Proceedings of the Royal Society A 300, 108-119 (1967).

The experimentally measured fracture energy of rubber may be on the order of $10^4 \mathrm{J/m^2}$. This value is much higher than the fracture energy of silica, which is on the order of $1 \mathrm{J/m^2}$. This large difference is due to two effects:

- Inelastic deformation (Andrews, 1963)
- The process of bond breaking (Lake and Thomas, 1967)

For example, inelastic deformation can be due to viscoelasticity. The effect of viscoelasticity may be reduced by reducing the loading rate or increasing the temperature. Once the effect of inelasticity is eliminated, the measured fracture energy, is known as the intrinsic fracture energy. The intrinsic fracture energy is also reached at the beginning of the *R*-curve, or as the threshold of the growth of a crack under cyclic loads.

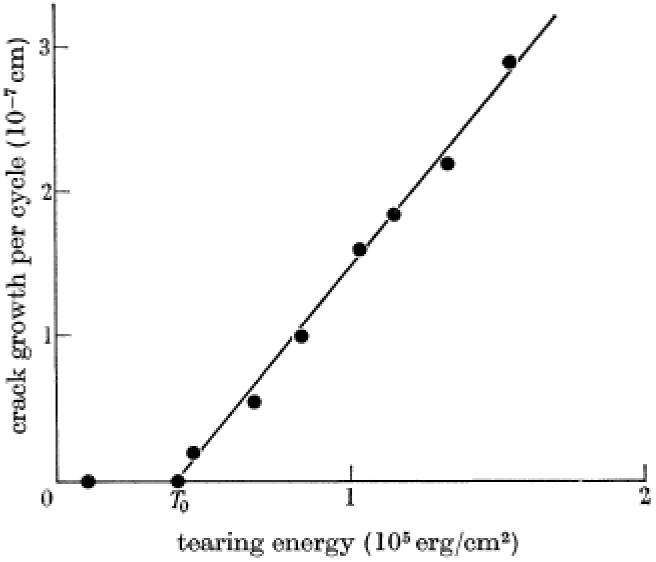


FIGURE 2. A typical crack growth characteristic for a rubber in the vicinity of the crack growth limit T_0.

The measured intrinsic fracture energy is about $50\mathrm{J/m^2}$. This value is still much larger than the energy needed to break a single layer of atomic bonds, which is about $1\mathrm{J/m^2}$. This difference is understood within the Lake-Thomas picture.

Lake-Thomas model. The rubber is a network of crosslinked long chains. Each chain consists of a large number of monomers. The chemical energy of the chain is stored in the C-C bonds.

At the front of a crack, the chains are stretched. Just before a chain breaks, all C-C bonds along the chain are pulled to the state near the breaking point. Consequently, the mechanical energy needed to pull the chain to the breaking point equals the chemical energy of the entire chain. Once the chain breaks, all the mechanical energy used to pull the chain is dissipated.

In this picture, both the strong bonds and the weak bonds play significant roles. The strong (chemical) bonds link monomers in a chain, crosslink chains in the network, and enable each chain to store high mechanical energy before rupture. The weak bonds between chains enable each chain to dissipate all its mechanical energy when the chain breaks. It is this mixture of the strong and the weak that gives the elastomer high fracture energy.

This model leads to an estimate of the intrinsic fracture energy. We next describe the key ingredients of the Lake-Thomas model.

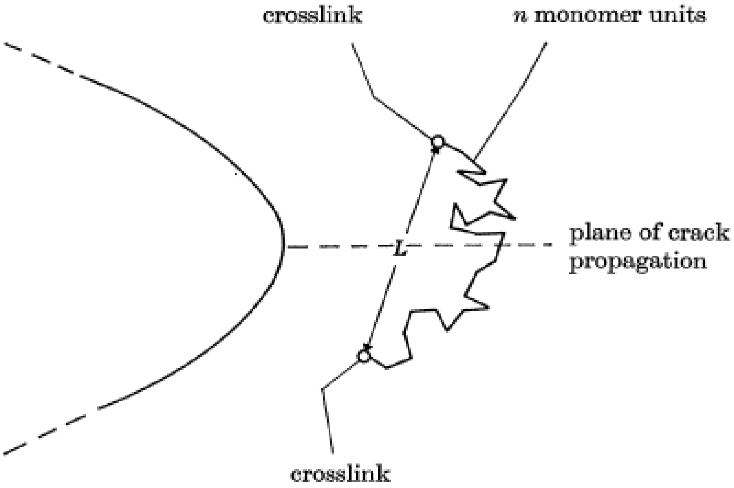


FIGURE 3. Schematic diagram showing a polymer chain lying across the plane of crack propagation.

The intrinsic fracture energy. Let us estimate the chemical energy in the undeformed state. Consider a single-chain layer. The Lake-Thomas model assumes that the intrinsic fracture energy is the chemical energy stored in the unit area of the single-chain layer:

$$\Gamma_o = eL,$$

where e is the chemical energy per unit volume, and L is the thickness of the single-chain layer in the undeformed state.

The energy per unit volume is

$$e = bJ,$$

where b is the number of single bonds per unit volume, J is the chemical energy of a C-C bond.

In the undeformed state, the thickness of the single-chain layer is estimated by the distance between the two ends of a chain:

$$L = a\sqrt{m},$$

where a is the length of the monomer, and m is the number of monomers in the chain.

Combining the three expressions, we obtain that

$$\Gamma_o = bJa\sqrt{m}.$$

For a typical natural rubber, the following approximate values hold: $b = 2.4 \times 10^{28}$ m^{-3}, $J = 3.3 \times 10^{-19}$ J, $a = 5 \times 10^{-10}$ m, and $m = 100$. The Lake-Thomas model gives $\Gamma_o = 40$ J/m^2.

By contrast, the chemical energy stored in the single-atomic layer per unit area is $bJa = 4\text{J/m}^2$. The difference between the intrinsic fracture energy of an atomic solid and that of a long-chain solid (an elastomer) is embodied in the factor $\sqrt{m}$.

Silica vs. elastomer. Both silica and an elastomer are elastic prior to rupture. Inelasticity is negligible in both cases. The elastic strain of silica is due to the stretch of atomic bonds, but the elastic strain of an elastomer is due to the change of the configuration of polymer chains. Silica is an atomic spring, whereas the elastomer is an entropic spring.

For silica, the surface energy is due to the missing bonds of one layer of atoms, and fracture dissipates one layer of atom bonds. Consequently, the surface energy is comparable to the fracture energy, both being on the order of J/m^2.

For the elastomer, the surface energy is due to the missing weak bonds of one layer of monomers, and fracture dissipates the energy of strong bonds in the single-chain layer. Consequently, the surface energy is much, much smaller than the fracture energy. The surface energy of an elastomer has a liquid-like value, on the order of 10^{-2} J/m^2. The intrinsic fracture energy is on the order of 10^2 J/m^2.

Fatigue and Stress Corrosion

Extension of crack under repeated stress. In practice, rubber articles rarely fail in single loadings. Rather, failure usually results from the extension of cracks under repeated loading. Thomas published the first paper in literature on the application of the Griffith approach to the growth of a crack under cyclic load. Thomas represented the cyclic applied load by a cyclic energy release rate. He found that the extension of the length of a crack per cycle is proportional to the amplitude of the energy release rate squared.

- A.G. Thomas, Rupture of rubber. V. Cut growth in Natural rubber vulcanizates. Journal of Polymer Science 31, 467-480 (1958).
- W.V. Mars and A. Fatemi, A literature survey on fatigue analysis approaches for rubber. International Journal of Fatigue 24, 949-961 (2002).

Extension of a crack under static load. Subject to a static load, a crack can grow at a finite rate. Possible time-dependent mechanisms include viscoelasticity and environmental attack.

- H.W. Greensmith and A.G. Thomas, Rupture of rubber III. Determination of tear properties. Journal of Polymer Science 18, 189-200 (1955).
- L. Mullins, Rupture of rubber. IX. Role of hysteresis in the tearing of rubber. Transactions of the Institution of the Rubber Industry 35, 213-222 (1959).
- G.J. Lake, and P.G. Mente. Ozone Cracking and Protection of Elastomers at High and Low Temperatures. Journal of Natural Rubber Research 7, 1-13 (1993).

Historical Notes

Passages from Autobiographic Postscript to the Collected Papers of R.S. Rivlin (1996). "With regard to the problem of tearing, my first idea was to examine the validity of a criterion of the Griffith type, according to which an existing tear in a test-piece held at constant extension will grow if the elastic energy thereby released exceeds the increase in the surface energy. Griffith was concerned with glass, for which the elastic deformations are small, so that classical elasticity theory can be used to calculate the energy release. In the case of vulcanized rubber the large deformations involved rendered similar calculations impossible at the time, although such calculations were carried out much later by Lindley using finite-element methods. We therefore devised experiments in which the necessity for elaborate calculations was avoided. My (not very firm) expectation was that the Griffith criterion would not apply. I was therefore somewhat surprised when we found it possible, by measuring force required to tear a test-piece with a preexisting cut, to calculate a characteristic tearing energy that could be used to predict the tearing force for test pieces for which the forces were orders of magnitude different. This characteristic energy was, however, many orders of magnitude greater than one would expect for a surface energy. We interpreted it as the energy expended in the irreversible processes that take place in a neighborhood of the crack prior to its formation.

"Although the work was not published until 1953, it was substantially completed by the summer of 1950, and I lectured on it in George Irwin's department at the Naval Research Laboratory in the fall of 1950."

A.G. Thomas, Goodyear Medal Address, The development of fracture mechanics for elastomers. Rubber Chemistry and Technology 67, G50-G60 (1994).