# Tear Strength Theory of Semicrystalline Polymers

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## Synopsis

A theoretical model describing how the tear strength of semicrystalline polymers depends upon the interaction of the crystalline and amorphous phases is presented. It is based upon the "free-volume" theory and a "Hooke's law–lattice energy" treatment. The tear strength $T_M$ is hypothesized to be partitioned between the crystalline $Q_c$ and amorphous $Q_a$ phases. Therefore $T_M \propto Q_c \cdot Q_a$, $T_M = T_0 \cdot Q_c \cdot Q_a$, where $Q_c = NKTE/bY^2$ and $Q_a = e^{-V/V_f} = G/G_0\tau$. Proof of this theory is obtained by measuring the oxygen transmission rates of 11 polyethylene film samples varying in tear strength. Good agreement exists between $T_M$ (experimental) and $T_M$ (theoretical) for 9 of the polyethylene samples. The other 2 samples differ from the theory by a factor of 2. One explanation of this departure is that $\tau$ varies from unity.

## INTRODUCTION

One of the least discussed mechanical properties of semicrystalline polymers in the literature is tear strength. One reason for this is that it is without theoretical foundation. During the past 50 years theories have evolved from the Griffith[1] "crack theory" to describe the impact, tensile, and tear strengths of glassy material. Rivlin and Thomas[2] developed the theory of tear strength of amorphous rubbers. So far, no theory has been advanced to describe the tear strength of semicrystalline polymers.

Presented in this paper is a theoretical model describing how the tear strength of semicrystalline polymers depends upon the interaction of the crystalline and amorphous phases. It is based upon the "free-volume" theory and a "Hooke's law–lattice energy" treatment.

Since it is know that soft, ductile materials have high tear strength, one must concentrate on the translational movement of the molecules. This brings into focus the molecular theories of diffusion and liquid viscosity. However, the problem is complicated by the semicrystalline nature of the polymer; therefore, we also must consider a mechanism describing how chains are pulled from the crystal lattice without the polymer fracturing. An illustration of this deformation is given in Figure 1. Figure 1(a) shows that folded chain lamallae in the crystalline phase are connected by randomly coiled amorphous chains. In order for the crystalline chains to be pulled out of their lattice, two conditions must be met. First, there must be enough amorphous chains connected to the crystalline chains.

Second, the amorphous chains must be mobile enough so that the covalent C—C bonds rearrange and support the force rather than weak London dispersion forces. Figure 1(b) shows this alignment. If the amorphous chains cannot rearrange in time to accommodate the applied stress, then fewer C—C bonds will support the stress. This condition is shown in Figure 1(c).
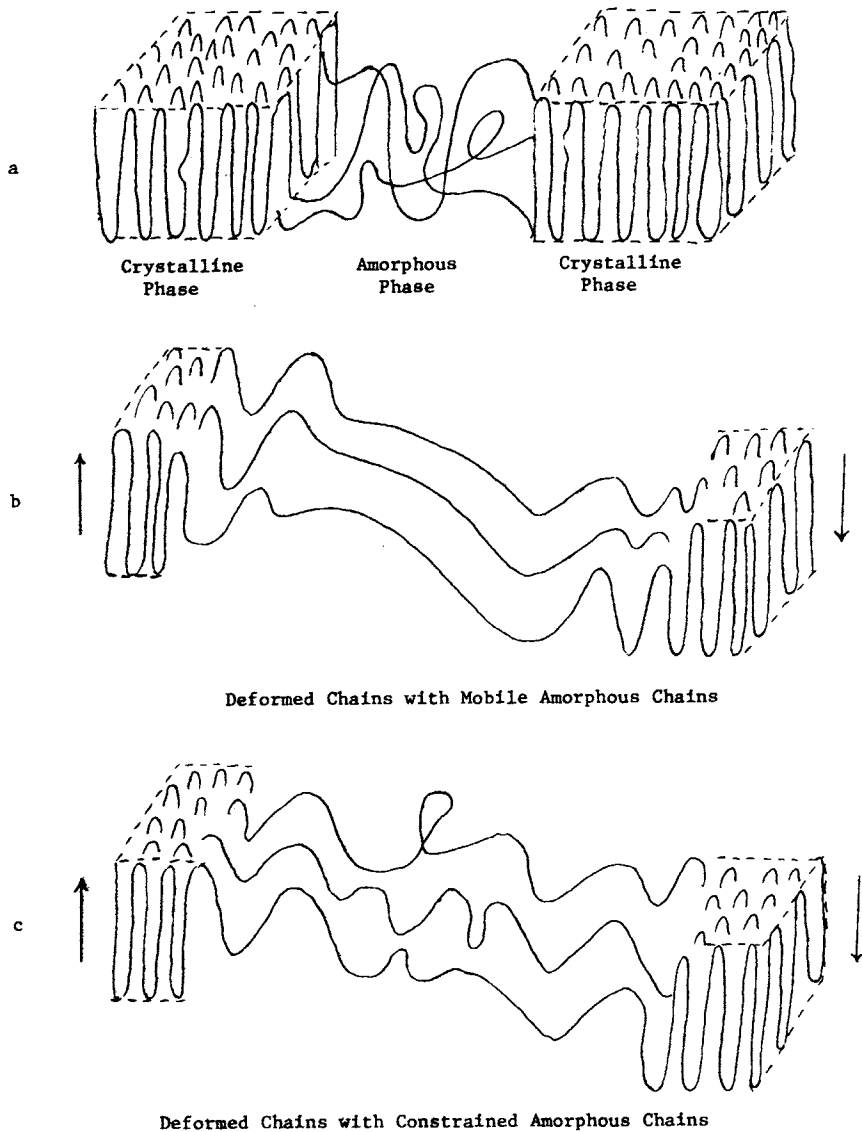
a

Crystalline          Amorphous          Crystalline
Phase               Phase              Phase

b

Deformed Chains with Mobile Amorphous Chains

c

Deformed Chains with Constrained Amorphous Chains

Fig. 1. Deformation model of semicrystalline polymer chains in a shear field.

The tear strength $T_M$ is assumed to be partitioned between the crystalline $Q_c$ and amorphous $Q_a$ phases:

$$T_M = T_0 Q_c \cdot Q_a \qquad (1)$$

A "Hooke's law–lattice energy" treatment originated by Orowan[3] has been applied to the crystalline phase and the "free-volume" theory to the amorphous phase.

## HOOKE'S LAW–LATTICE ENERGY THEORY

Consider the stress–separation curve between chains in a crystal lattice (Fig. 2), where $\sigma$ = stress, $Y$ = yield stress of the bulk polymer, $b_0$ = equilibrium dis-
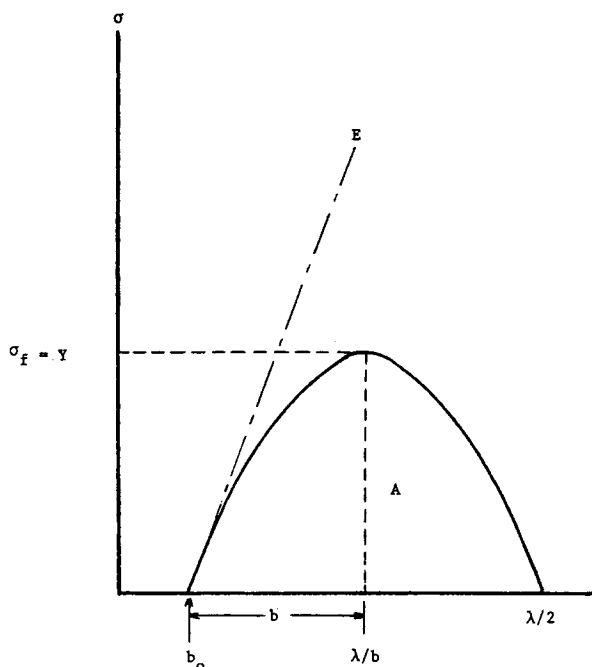
Fig. 2. Stress–separation curve between chains in a crystal lattice.

tance between chains, $A$ = area under the curve, $\lambda$ = frequency of a sine wave, $E$ = Young's modulus, $b$ = distance between chains at the yield stress. The sine wave equation

$$\sigma = \sigma_f \sin(2\pi u/\lambda) \tag{2}$$

approximates the above curve and the area $A$ equals the surface free energy $2\gamma$; therefore

$$2\gamma = \int_0^{\gamma/2} \sigma_f \sin \frac{2\pi u}{\lambda} du \tag{3}$$

Integrating leads to

$$\gamma = \sigma_f \lambda/2\pi \tag{4}$$

Applying Hooke's law,

$$\sigma \propto \epsilon \tag{5}$$

where the strain

$$\epsilon = \lambda/2\pi b \tag{6}$$

and

$$\sigma_f = Y = E\lambda/2\pi b \tag{7}$$

Combining eqs. (4) and (7) to eliminate $\lambda/2\pi$ gives

$$Y = \sqrt{E\gamma/b} \tag{8}$$

$Y$ is assumed to be the level of stress where the chains are pulled from their crystal

lattice, and depends upon modulus, surface-free energy, and separation distance.

## FREE VOLUME THEORY

The free volume model is the foundation of many well-known theories that describe the local motion, transport, and diffusion of molecules in the liquid and gaseous states.[4]  To name a few, it is the basis of the Eyring, "viscosity of liquids" and "transition-state" theories, WLF equation of $T_g$, and explains Fick's law of diffusion for polymers.

Free volume is a measure of the looseness of the structure of matter, and it is plausible to associate looseness with molecular mobility.  For a molecular segment in the amorphous phase to undergo translational motion, an adjacent hole larger than the size of the segment must be present.  This hole is called "free volume."  The ease at which the segment can move into the hole is related to its diffusion constant $D$

$$D = \theta S^2/6 \tag{9}$$

where the jump frequency $\theta$ is the number of times a segment of a polymer chain can move from one position to another and $S$ is the jump distance.  The diffusion constant can be obtained in a second way:

$$D = KT/f_0 \tag{10}$$

where $f_0$ is a molecular friction constant.  This is defined as the force needed to pull a segment through its surroundings at a unit speed.  $K$ is Boltzmann's constant and $T$ is temperature (°K).

The probability that a segment will jump into the hole is given by

$$D = KTe^{-V/V_f}/f_0 \tag{11}$$

The assumption is made that at the stress level $Y$, where the chain in the crystal lattice began to separate:

$$\gamma = Nf_0 \tag{12}$$

where $N$ is the number of chains/cm$^2$; therefore,

$$f_0 = Y^2b/NE \tag{13}$$

Substituting eq. (13) in eq. (11) gives

$$D = (NKTE/bY^2)\, e^{-V/V_f} \tag{14}$$

The final assumption is that

$$T_M \propto D \tag{15}$$

Therefore,

$$T_M = (T_0NKTE/bY^2)\, e^{-V/V_f} \tag{16}$$

In eq. (1)

$$Q_c = NKTE/bY^2$$

TABLE I
Table of Data: 1.5-mil LDPE Film

| Sample | $G[cm^3(STP) \cdot cm/ cm^2 \cdot s \cdot cm\ Hg]$ | $T_0 \times Q_c$ (ergs/cm$^2$) |
|--------|-----------------------|--------------------------|
| 1 | $7.30 \times 10^{-11}$ | $7.39 \times 10^8$ |
| 2 | $1.04 \times 10^{-10}$ | $1.24 \times 10^8$ |
| 3 | $1.00 \times 10^{-10}$ | $1.23 \times 10^8$ |
| 4 | $1.35 \times 10^{-10}$ | $1.39 \times 10^8$ |
| 5 | $9.09 \times 10^{-11}$ | $1.04 \times 10^8$ |
| 6 | $9.29 \times 10^{-11}$ | $1.37 \times 10^8$ |
| 7 | $8.89 \times 10^{-11}$ | $9.22 \times 10^8$ |
| 8 | $8.16 \times 10^{-11}$ | $9.17 \times 10^8$ |
| 9 | $8.38 \times 10^{-11}$ | $1.31 \times 10^8$ |
| 10 | $9.05 \times 10^{-11}$ | $1.39 \times 10^8$ |
| 11 | $8.38 \times 10^{-11}$ | $1.24 \times 10^8$ |

and

$$Q_a = e^{-V/V_f} \tag{17}$$

## PROOF OF THEORY

In the past researchers have used gas permeability measurements to estimate $V_f$.[5] This method was used here for 11 polyethylene films varying widely in their tear strengths. Their oxygen transmission rates $G$ were measured, and these values were used to calculate $T_M$ from eq. (20). The dependence of $V_f$ upon $G$ is as follows:

$$(1/\tau)G \propto D = D_0\, e^{-V/V_f} \tag{18}$$

$$G_0 = D_0 \tag{19}$$

where $\tau$, commonly called the "tortuosity factor," accounts for the impedance of flow afforded by the irregular intercrystalline passages. The proportionality constant in eq. (18) is the solubility constant.

TABLE II
Comparison of Calculated Tear Strength with Experimental Tear Strength of LDPE Films

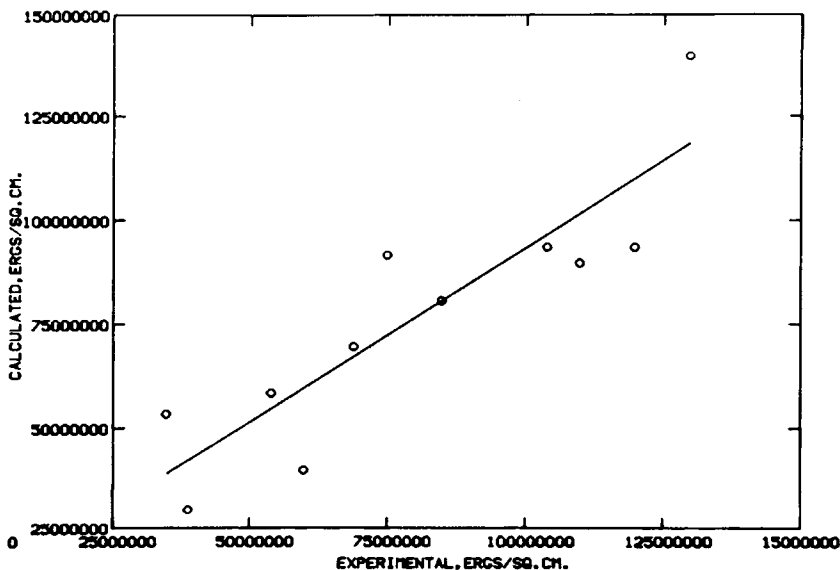| Sample | Experimental $T_M$ (ergs/cm$^2$) | Calculated $T_M$ (ergs/cm$^2$) |
|--------|--------------------------------|-------------------------------|
| 1 | $6.2 \times 10^7$ | $3.9 \times 10^7$ |
| 2 | $1.2 \times 10^8$ | $9.4 \times 10^7$ |
| 3 | $1.1 \times 10^8$ | $9.0 \times 10^7$ |
| 4 | $1.3 \times 10^8$ | $1.4 \times 10^8$ |
| 5 | $6.9 \times 10^7$ | $7.0 \times 10^7$ |
| 6 | $1.04 \times 10^8$ | $9.4 \times 10^7$ |
| 7 | $5.4 \times 10^7$ | $5.9 \times 10^7$ |
| 8 | $3.5 \times 10^7$ | $5.4 \times 10^7$ |
| 9 | $8.5 \times 10^7$ | $8.1 \times 10^7$ |
| 10 | $7.5 \times 10^7$ | $9.2 \times 10^7$ |
| 11 | $4.0 \times 10^7$ | $3.0 \times 10^7$ |

Fig. 3. Calculated vs. experimental tear strength.

Substituting eqs. (17), (18), and (19) in eq. (1) gives

$$T_M = T_0 Q_c G / G_0 \tau \qquad (20)$$

The following terms are constant for this series of samples: $T_0 = 1.20 \times 10^5$ ergs/cm$^2$, $N = 6 \times 10^{14}$ chains/cm$^2$, $K = 1.38 \times 10^{-16}$ ergs/°K, $T = 298$°K, $E = 3.5 \times 10^{10}$ dyn/cm$^2$, $b = 5 \times 10^{-8}$ cm, $G_0 = 1.35 \times 10^{-10}$ [cm$^3$ (STP)/cm$^2$·s·cm Hg], $\tau =$ unity. $Q_c$ for each sample along with $G$ is given in Table I.

A comparison of the calculated and experimental $T_M$'s is shown in Table II and Figure 3. Good agreement exists among samples 2–10, giving proof that the theory holds. Samples 1 and 11 differ by about a factor of 2. One explanation for this departure is that $\tau$ varies from unity for these two samples. A least squares line fit to the data was made which has a 0.78 correlation coefficient. Statistical analysis, using the Student's $t$ test, shows that the calculated tear strengths agree with the experimental tear strengths to within 99%.

## APPENDIX: NOMENCLATURE

| | |
|---|---|
| $b$ | distance between chain in crystal lattice[6] (cm) |
| $E$ | Young's modulus of crystal lattice[6] (dyn/cm$^2$) |
| $G$ | gas transmission rate [cm$^3$ (STP)/cm$^2$·s·cm Hg] |
| $\overline{G}_0$ | gas transmission rate constant [cm$^3$ (STP)/cm$^2$·s·cm Hg] |
| $K$ | Boltzmann's constant (ergs/°K) |
| $N$ | number of chains/cm$^2$ |
| $T$ | absolute temperature (°K) |
| $T_0$ | proportionality constant (ergs/cm$^2$) |
| $V_f$ | free volume |
| $Y$ | yield stress of bulk polymer |
| $\tau$ | (tortuosity factor) = unity |

## References

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