

Fundamental Mechanism of Slow Crack Growth in Semi-Crystalline Polymers under a Constant Load

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Abstract

The purpose is to quantitatively present in a single equation all the factors that affect the failure time by Slow Crack Growth (SCG) in a semi-crystalline polymer (SCP) under a constant load. The fundamental mechanism of fracture is displayed at the molecular level. The rate of fracturing is determined by the Eyring theory of thermal activation. The resulting equation includes the important molecular properties of therein, the length and density of the tie molecules. The underlying microfracture process is the unfolding of the chains in the crystal under the action of the tie molecules.

Keywords

Failure, Semi-Crystalline Polymer

1. Introduction

When a SCP structure is exposed to a sufficiently low constant tensile stress under plain strain conditions, it will ultimately fail by a brittle fracture process commonly called “slow crack growth” [SCG]. Polyethylene (PE), the most widely used SCP, was first used on a large scale in gas pipes in 1965 manufactured by the DuPont Company. The phenomenon of SCG has been subjected to extensive research throughout the world, because it is very important to know how long a gas pipeline will function before it fails. Much of the published research on PE was produced by Lu and Brown and coworkers at the University of Pennsylvania, as for example in reference [1], nevertheless, up to now, a completely quantitative expression taking into account all the factors that influence the failure time by SCG does not exist. It is important to know the aspects of molecular structure of the PE that influences SCG in order to help the resin producers im-

prove their product. By knowing all the factors that influence SCG, the engineer can better design structures made of PE.

1) Failure by SCG only occurs when the structure is subjected to a tensile stress less than about $1/2 Y$ under plain strain conditions where Y is the yield point. When the stress is greater than $1/2 Y$, ductile failure is produced by the macroscopic accumulation of plastic strain. Below $1/2 Y$, the amount of macroscopic plastic strain is negligible and brittle failure is produced by a crack. The failure in a pressurized pipe exhibits a dramatic difference between the modes of failure above and below $1/2 Y$. The failure above $1/2 Y$ consists of a bulge in the pipe whose dimensions are on the order of the pipe diameter. The failure below $1/2 Y$ consists of a leak in the form of a slit whose width is a very small fraction of the wall thickness of the pipe.

2) The dependence of the failure time on stress at various temperatures in notched specimens is exhibited in **Figure 1** (from Lu and Brown in Ref. [2]). The transition from ductile failure to SCG failure occurs in the jog where a crack is initiated at a point of stress concentration. At the stress above the jog the plastic strain blunts the stress concentrators. In the jog where the stress is reduced, the sharpness of the stress concentrator is increased to the point where the process of SCG takes over. Then the failure time, t , depends on the temperature. In agreement with the Arrhenius theory where $t = A \exp[Q/kT]$. The experimental value of Q ranges from about 85 to 110 kJ/mol. for all PE.

3) Fracture always initiates at points of stress concentration. It is widely opined that practical structures contain points of stress concentration. The stress concentrators can take many forms such as inclusions, sharp corners, scratches and molding defects. **Figure 2** shows the single edge notch stress concentrator that is frequently studied with the applied stress perpendicular to its length, a . This is called the K_I fracture mode.

The stress concentrator is conventionally described by the stress intensity, K , where $K = g a^{1/2} s$, g is a geometric factor determined by the ratio of a with respect to the macroscopic dimension of the specimen and s is the global stress. The subsequent analysis shows that c must be included in the description of the stress concentrator order to completely account for all the factors that determine the time to produce failure under a constant load.

4) It is necessary to know the common morphology of all SCP at the molecular level. SCP are linear. Lamella crystals are formed that consists of folded molecules whose thickness may vary from about 40 to 100 nm. The folded chains are parallel to the thickness direction. There is an amorphous boundary about 15 nm thick between the crystals. The microstructure is depicted in **Figure 3(a)**. There are some molecules that connect one crystal to an adjoining crystal. These molecules are called "tie molecules" [TM]. If TM did not exist, PE would be a completely brittle material. Sometimes a molecule from one crystal can be entangled with a molecule from the adjacent crystal in the amorphous boundary. This entanglement can function as a TM.

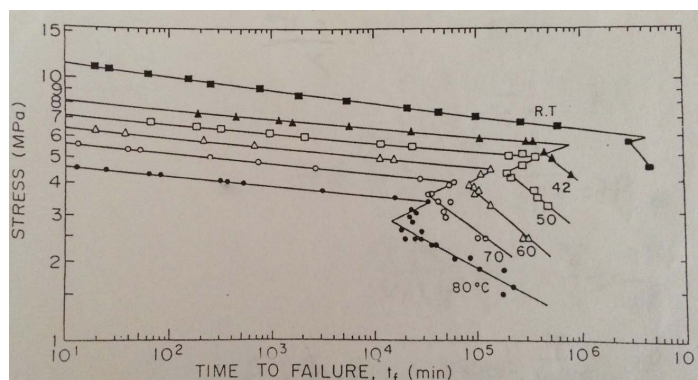


Figure 1. Stress vs. failure time various temperatures.

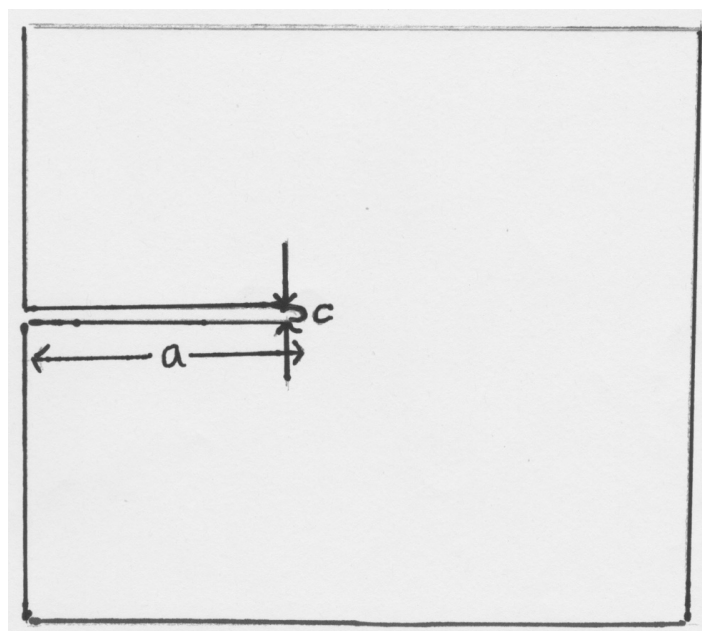


Figure 2. A representative stress concentrator; c is the sharpness factor.

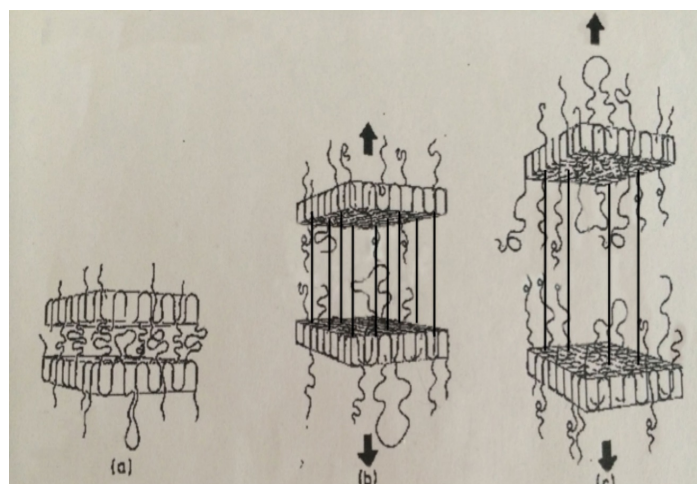


Figure 3. Morphology of a fibril. a: before loading; b: after loading; c: during incubation.

5) When a tensile stress less than $1/2 Y$ is applied to a structure under plane strain conditions, a deformation zone is produced in the vicinity of the stress concentrators. It consists of coarse fibrils that are oriented in the direction of the applied stress (**Figure 3(b)**). Based on optical microscopic examinations, the deformation zone is illustrated in **Figure 4**. It was experimentally determined by Wang *et al.* [3] [4] that the stress on the boundary of the fibrils is equal to Y .

6) The crack opening displacement [COD] typically increases with time as shown in **Figure 5**, which is based on optical microscopic observations by Lu and Brown [5]. The original microstructure is converted to the deformation zone when the structure is loaded. The first fibril fractures at the time, E . It is important to note that the time to incubate fracture in the first fibril is always a significantly large fraction of the time for the complete failure in the structure. This is a general experimental observation. After the first fibril fractures, there is an acceleration in the rate of increase in the COD because the length of the stress concentrator increases.

The crack propagates by the successive fracture of the fibrils until the remaining ligament fails by yielding.

It is important to determine the stress in the first fibril because that is where fracture initiates. The geometry of the first fibril is illustrated in **Figure 6**. The boundary of the fibrils corresponds to the boundary of the deformation zone where the stress is Y . The area of the boundary of the deformation zone that is occupied by the first fibril is designated by A_o . The cross section area of the fibril is A . The length of the first fibril is the COD. The first fibril evolves from a volume $A_o c$, where c , the sharpness of the stress concentrator, is the thickness of the volume of material from which the first fibril evolves. Conservation of volume gives

$$A_o c = A \text{COD} \quad (1)$$

The validity of Equation (1) is based on the assumption that A is the average cross section area of the fibril and on the facts that the COD is very much greater than c and also that the COD is independent of c .

Stress equilibrium requires

$$A_o Y = A S \quad (2)$$

where S is the stress in the fibril. Combining Equations (1) and (2)

$$S = Y \text{COD}/c \quad (3)$$

It is important to know the morphology of the fibril at the molecular level. Based on the extensive research on the morphology of the fibril by Kieth *et al.* [6], the molecular morphology of a fibril is shown in **Figure 3(b)** where the lamellar crystals are joined together by TM and the thickness of the crystals is the same as in the preloaded state. Also the folded chains are oriented in the direction of the applied tensile stress. Also note in **Figure 3(c)** that the forces, F , that are exerted by the TM, must balance the force exerted by the stress S in the crystal. Therefore

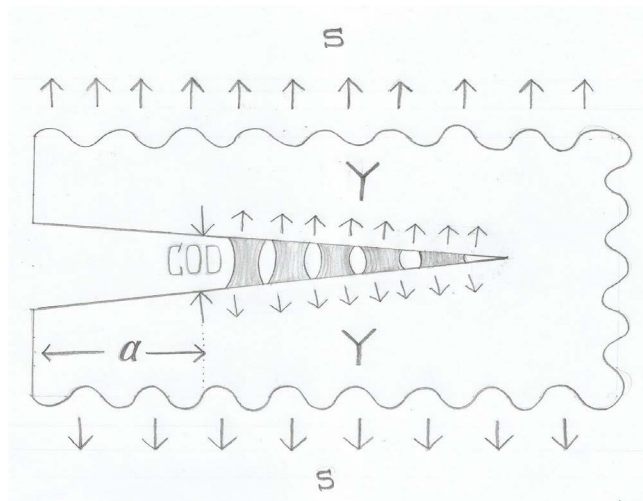


Figure 4. The deformation zone. S is the global stress.

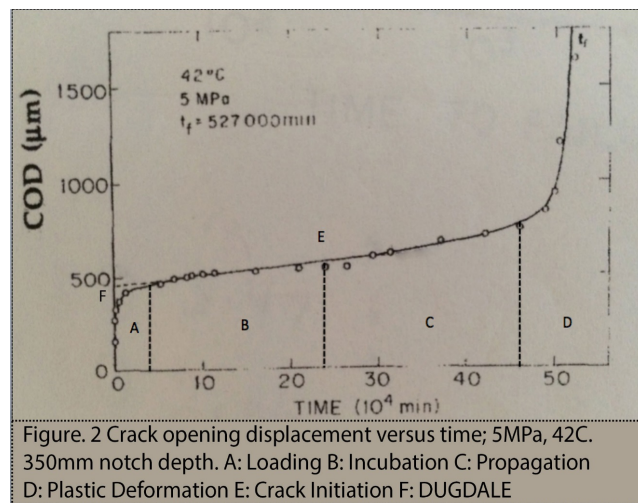


Figure 5. COD versus Time (by Qian and Lu in Reference [10]).

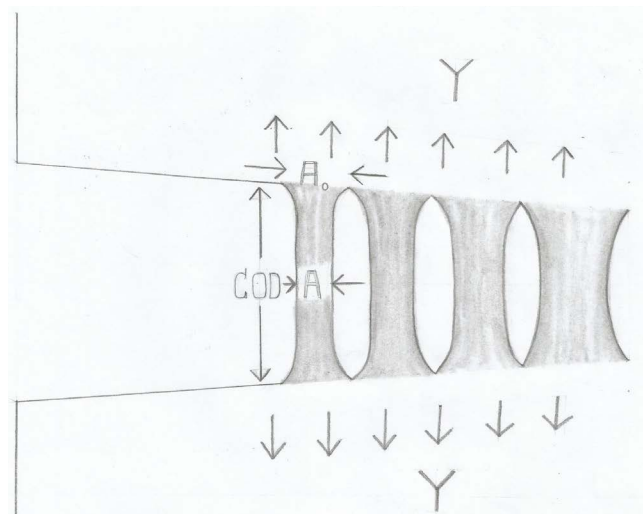


Figure 6. Basis for the analysis of the stress in the first fibril.

$$SA = nF \quad (4)$$

where A is the area on which S acts and n is the number of TM. A is also the area from which the TM emerges from the crystal. By definition, the density of TM is $\rho = n/A$. Combining (3) and (4) gives

$$F = Y \text{ COD} / \rho c \quad (5)$$

In order to better visualize the critical role that F plays in the fracture process, the fundamental morphological unit of the fracture process is exhibited in **Figure 7**, where the TM with the force, F , is pulling on the folded chain and thereby unfolding the chains from the crystal. At the same time the length of the TM between the crystals increases as shown in **Figure 3(c)**. When an entire T is pulled out of the crystal, then TM is eliminated. That event represents the fundamental sub-microscopic fracture process during SCG. It naturally follows that the longer the length of a TM, the longer time it takes to eliminate the TM. When all of the TM in a cross section area of a fibril are pulled out of the crystal, the fibril fractures. The next question is, what is the rate at which the chains are unfolded?

2. Rate of Unfolding the Chains

The rate of unfolding the chains will be derived from the Eyring theory of thermal activation [7]. Follow the theory while focusing on **Figure 7**. The theory begins with the postulate that there is an energy barrier Q that must be overcome in order that a portion of a chain is pulled out of the crystal. The value of Q is the binding energy of a chain to the crystal. The force, F , exerts an energy, Fv , so that the barrier height is reduced to $Q - Fv$. v is called the activation distance. v is the displacement of a chain from its neighbor under the action of the force, F . v is a small fraction of the distance between the chains. The probability of attaining the energy, $Q - Fv$, at the temperature, T is given by the Maxwell-Boltzmann distribution $\exp[-(Q - Fv)/kT]$. Visualize that the TM is undergoing thermal vibrations with a frequency f , which is the frequency at which the force, F , attacks the energy barrier. The frequency at which the barrier is overcome is $f \exp[-(Q - Fv)/kT]$. Every time the barrier is overcome, a length V , of the TM is withdrawn from the crystal. V is on the order of a fraction of a chain length. Thus, r , the rate of withdrawal of a TM from the crystal is given by

$$r = Vf \exp[-Q/kT] \exp[Fv/kT] \quad (6)$$

The value of F from (5) will now be inserted into Equation (6).

$$r = Vf \exp[-Q/kT] \exp[Y \text{ COD} v / \rho c k T] \quad (7)$$

In order to completely know all the parameters that determine r , the basis for determining the COD must be presented. The value for the COD was derived from a theory independently developed by Dugdale [8] and Rice [9] for the stress concentrator shown in **Figure 2** for a material, whose mechanical behavior consists of linear elastic behavior up to the yield point Y followed by no strain

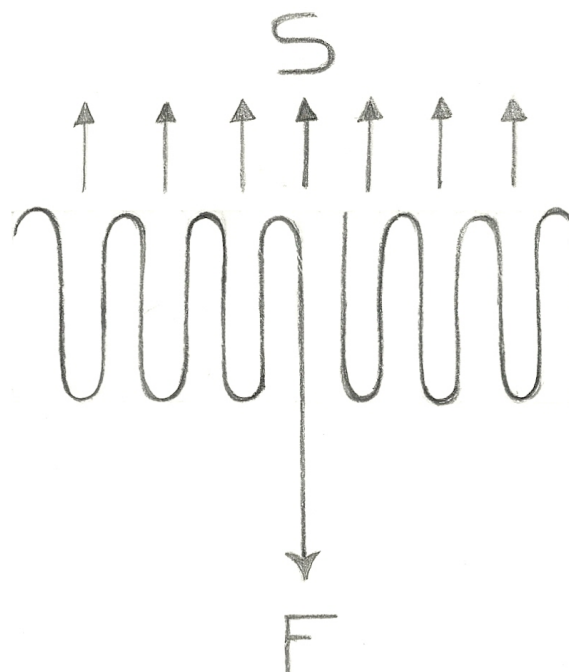


Figure 7. Fundamental process for unfolding Chains from the Crystal. S is the stress in the Fibril. F is the Force acting on a TM.

hardening after the yielding. Since PE only approximates the mechanical behavior of this material, the Dugdale-Rice formula is an approximation to the observed value of the COD. However, the experimental values of the COD vary in tune with the parameters of the Dugdale-Rice formula that

$$COD = K^2 / YE \quad (8)$$

K , the stress intensity, is given by

$$K = gsa^{1/2} \quad (9)$$

g is a geometric factor that depends on the geometry of the stress concentrators, s is the applied stress and a is the length of the stress concentrator. E is Young's modulus.

The experimental values of the COD in PE as measured by Qian *et al.* [10] obey the following equation:

$$COD = Bs^n a^m \quad (10)$$

B is a geometric factor like g . Depending on the resin, n can go from about 3 - 4.5 and m is slightly greater than $1/2n$. The experimental value of the COD approximates the Dugdale-Rice prediction. In order to emphasize the importance of the stress intensity, K , the Dugdale-Rice value of the COD is inserted in [7]. All the factors that determine the rate, r , at which a TM is pulled out of the crystal, are given in Equation (11).

$$r = Vf \exp[-Q/kT] \exp[K^2 v / E \rho c k T] \quad (11)$$

Fracture initiates in the structure when all the TM in a cross section area of the first fibril are pulled out. The time to fracture the first fibril depends on the length average L_z of the longest molecules that contain TM. The time also depends on the rate, r_z that is controlled by the density of TM, ρ_z , whose length is L_z . It is straight forward that the time to initiate fracture can be described by

$$t = L_z / r_z \quad (12)$$

Combining (11) and (12), the time to initiate fracture is

$$t = (L_z / Vf) \exp[Q/kT] \exp[-K^2 v / E \rho_z c k T] \quad (13)$$

After the first fibril fractures, the crack propagates by the successive fracture of the following fibrils. The time to fracture in a fibril is still governed by equation (13) with the exception that K increases because the length of the stress concentrator increases every time a fibril fractures. Thus, the curve of COD versus time in **Figure 2** begins to accelerate after the first fibril fractures. Thus, the crack propagates until the stress in the remaining ligament of the structure increases to the point where final mode of failure occurs by plastic deformation.

3. Experimental Support for the Theory

Equation (13) predicts that t is linearly related to the length of the [TM]. Huang and Brown [11] experimentally confirmed this prediction by experimentally exhibiting that t is linearly related the molecular weight, M_w . Equation (13) indicates that the ultimate limit on the time to failure depends on the ultimate length of the TM. Experiments with ultra high molecular PE were performed that lasted so long that the time of failure could not be measured under the available laboratory conditions.

The introduction of short chain branches [SCB] greatly increases the failure time in copolymers relative to a homopolymer because the density of TM is directly related to the concentration of the SCB. The reason for this relationship is very simple. Direct measurements show that over 90% of the SCB reside in the amorphous region which is the boundary between adjacent crystals (data from Dow Chemical Co. in private communication). Consequently the probability of forming a TM is directly related to the concentration of SCB.

Huang and Brown [12] showed that the log of the time to initiate fracture is a linear function of the concentration of SCB. This result is in agreement with Equation (13) because the concentration of SCB is directly proportional to the density of the TM.

Equation (13) predicts that the high end of the molecular weight distribution is a significant factor. Scholten and Rikjema [13] fractioned 5 resins and measured the concentration of SCB on each fraction. They measured the failure time, t , on each resin. They found that t increased as the concentration of SCB on the highest molecular weight fraction increased. This result confirms Equation (13).

When the specimen is loaded as shown in **Figure 3(c)**, the TM must be longer

than the value of the COD predicted by Equation (8) in order form a bridge between the adjoining crystals. If the length of the TM is below this critical value, the specimen will fail immediately upon loading. Lu *et al.* [14] verified this prediction. They fractionated a copolymer into 5 parts whose molecular varied from about 10^3 to 10^5 gm/mol. They found that the 3 parts whose molecular weight was less than 3000 gm/mol failed immediately upon loading. The other 2 parts with greater molecular weight had failure times on the order of 1000 hr, which is comparable to t for the whole resin.

Huang and Brown [11] measured the failure time as a function of molecular weight. The extrapolation of the molecular weight to $t = 0$ was about 30,000 gm/mol. This result is consistent with the above results by Lu *et al.* [14].

Industry developed resins with a bimodal molecular weight distribution with no SCB on the low molecular weight side of the distribution. If the low molecular weight molecules contained SCB these SCB would be wasted as soon as the structure is loaded. For some application there is a limit on the concentration of SCB because the yield point decreases as the concentration of SCB is increased. When designing a structure, the engineer often optimizes the performance by making a compromise between the yield strength and failure time by SCG.

The inclusion of the notch sharpness factor, c , in Equation (13) is supported by the experimental observation by Lu *et al.* [15] that the notches produced by an ordinary commercial razor results in a failure time that is 10% longer than notches produced by specially sharpened commercial razor blades. The sharpness of the notch, c , is also determined by the speed at which the razor blade produces the notch. It was observed by Lu *et al.* [16] that above a critical speed the time to failure increased because the speed of notching affects the sharpness.

Lagaron *et al.* [16] measured the force, F , on a TM by a combination of optical microscopy and micro Raman spectroscopy. They observed the rate of SCG in several resins and found that F increased as the rate of extension of the fibrils increased. This result conforms with Equation (6).

When a SCG test is measured in an Igepal environment, there is a significant decrease in the failure time (Paper by Ward *et al.* [17]). This effect modifies Equation (13) by reducing the value of Q , the bonding energy of the chains to the crystal, and the remaining terms in Equation (13) are unaltered. Consequently experiments show that the ranking of resins with respect to their failure time is the same whether the test is in air or in any plasticizing agent such as Igepal.

It is also interesting to know why the activation energy is about 100 kj/mol = 1 ev. The activation energy, $Q - Fv$, is largely determined by Q , the bonding energy between a folded chain and the crystal. Although the bonding is based on the Van der Waals bond whose energy is about 0.01 ev, Q is about 1 ev because it is an integration of all the bonds that surround a chain.

It is also interesting to note that whether the chains are regularly or irregularly folded the basic theory is not changed. The only difference is that the Q for irregularly folded chains is expected to be less than that for regularly folded chains.

4. Summary and Conclusions

- 1) The rate of SCG is thermally activated as described by the Eyring theory.
- 2) Equation (13) contains all the quantities that determine the time for the initiation of fracture by SCG in a semi-crystalline polymer. This is the first time that the process of SCG has been completely described by an equation.
- 3) The morphological features of the resin that determine the failure time are L_z , the length of the TM, whose molecular weight is M_z , and the density of the TM, ρ_z whose molecular weight is M_z . These morphological features are controlled by the conditions under which the resin was polymerized.
- 4) The fundamental mechanism of SCG is the unfolding of the chains in the crystal under the action of the TM.
- 5) The time to initiate fracture in the first fibril occupies a major part of the total time for failure by SCG.
- 6) The density of the TM is proportional to the concentration of SCB because over 90% of the SCB are located in the boundary between the crystals.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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