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Fracture Surface Energy of Highly Oriented Polymers

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A Monte Carlo technique is used to estimate the fracture surface energy of highly oriented polymers ruptured under conditions at which the contribution of plastic deformation in front of the propagating crack is small compared with the energy required to form new surfaces at the tip of the crack. The effects of molecular weight, cohesive energy, and breaking energy of the polymer chain are discussed for the cases where: (1) all molecules are fully extended and (2) chain folding occurs at random.

With the extended chain model the fracture surface energy increases monotonically with the molecular weight and approaches asymptotically its maximum value NQ_b . (N = number of polymer chains per unit area and Q_b = energy required to break the polymer chain.)

The cohesive energy, while not contributing substantially to the fracture surface energy at high values of the molecular weight, strongly affects the width of the molecular weight range in which fracture surface energy shows a pronounced molecular weight dependence. The lower the cohesive energy of a polymer, the higher must be the molecular weight to utilize a given fraction of the potential offered by an isolated polymer chain.

For the systems where chain folding occurs at random, the model predicts a maximum in fracture surface energy at a value of number average molecular weight (M_n) corresponding approximately to the number average molecular weight between the folds. For higher values of M_n the fracture surface energy first decreases and then assumes a near constant value. This decrease is attributed to the weakening of the structure through chain folding while the effective length of the molecules remains unchanged.

INTRODUCTION

The expressions for the rate of crack growth, strength, time to rupture, etc., contain three parameters which depend on the molecular structure: modulus, activation energy associated with the process involved in the growth of the crack, and fracture surface energy (FSE).¹⁻⁸ For highly oriented polymeric systems with which this paper is concerned, moduli and activation energies

can either be measured or calculated using measurable molecular parameters. The corresponding values have been determined for almost all polymers of interest. Much less information is available about the magnitude of FSE in oriented polymers. In a few isolated studies, where the effect of molecular orientation has been examined, the level of orientation was too low to be applicable to highly oriented fibers.⁹

The knowledge of FSE and its dependence on molecular weight, rate of loading, and temperature, is essential for a meaningful interpretation of the performance of a polymer.

FSE is complicated to measure, especially in the direction perpendicular to the orientation. In the absence of systematic data allowing generalization, it was desirable to develop a method for calculating FSE from known molecular parameters.

In this paper we consider perfectly oriented systems ruptured under conditions at which the energy effects associated with the plastic deformation in front of the propagating crack are negligible compared with those involved in the formation of new surfaces at the tip of the crack. The emphasis is on the effects of variables which are difficult to control experimentally such as molecular weight distribution, degree of polymerization, degree of chain folding, etc.

THEORY

In polymeric systems, the fracture surface can be formed either by chain scission or by slippage of polymer chains past one another. It is expected that the formation of cracks by chain slippage is favored in systems in which the inter-molecular forces and molecular weight of the polymer are low, while in polymer systems having high intermolecular forces the fracture would proceed predominantly by chain scission. It should be noted that experimental conditions such as temperature and the rate of loading have a pronounced effect on the mechanism of failure.

It should also be pointed out that, in a general case, the fracture surface energy determined experimentally involves, according to Orowan,¹⁰ Irwin¹¹ and Berry¹² two terms, one related to the plastic flow occurring in front of the propagating crack and the other related to the actual process of formation of new surfaces. It will be obvious from the description of the model below, that these calculations are applicable only to the conditions where the effects of plastic flow are small compared with those associated with the process of the opening of the crack. Such conditions are expected to be encountered in highly oriented systems ruptured at very low temperatures and fast rates of deformation.

In the calculation it is assumed that: (a) all the molecules are perfectly aligned in the direction of the applied stress with their ends and folds distributed randomly in the volume of the specimen, (b) the fracture surface can be formed either by chain slippage or chain scission, depending on which is energetically more favorable in a particular volume element, (c) the path of the crack is such as to give the lowest possible value of fracture surface energy and (d) chain end interactions are negligible.

Initially, a two-dimensional array of molecules was used with each molecule being cohesively bonded to four "neighbors". Under these conditions, the programming of all possible fracture paths became very complicated with the introduction of chain folding. In order to facilitate the calculation, we then simplified the model by using a single row of molecules only. A comparative study on a system containing no chain folding showed that the "four neighbor" model and the "two neighbor" model lead to essentially the same results provided the value of specific cohesive energy is adjusted according to the number of "neighbors".

The constructed row of molecules can be visualized as occupying a region of space bounded above and below by an infinitely strong matrix. The "strength" of the bonding of the molecules to the matrix corresponds to the cohesive energy of the system considered. Under these conditions, the crack propagates perpendicular to the orientation which is consistent with experimental observations.

The calculating procedure is as follows. A number of molecules sufficiently large to characterize the distribution is stored in the computer memory in locations designated according to their sizes. Usually 10^4 to 10^5 molecules are used. After a small volume element represented by a short row of molecules is constructed all possible paths are examined and the energetically most favorable one is selected to determine the rupture coordinate at the last molecule in consideration. In the next step a new set of molecules is selected, placed randomly and the calculating procedure carried out as before. The calculations are terminated when a high percentage (80–90%) of the total stored molecules have been used. With the structure containing chain folding our program includes molecules with up to three chain folds. If the random sampling indicates more than three chain folds, the molecule is rejected. In the discussion we shall limit our considerations to cases where, at the end of the calculations, the amount of rejected molecules does not exceed 25 percent by weight. The details of the calculating procedure are described more fully in Appendix I.

Values of Q_b , q_c and N for a given polymer system are usually estimated without difficulties. Values of Q_b are equal to the values of bond energies of the weakest bond in the polymer chain which is most likely to undergo chain scission in the process of crack growth. In cases where chain scission leads to

side reactions (e.g. polyvinyl chloride, polyacrylonitrile, etc.) the energy involved in the entire process must be taken into account.

Values of cohesive energies (q_c) may be estimated by additive systems based on the properties of substances composed of small molecules in which a definite increment is associated with each functional group. Several schemes have been proposed in the past and values relevant to some of the most important systems have been tabulated by Mark *et al.*¹³ and Bunn.¹⁴ The number of molecules per cross-sectional area is calculated from the x-ray data. (See Appendix II.)

It should also be noted that the results of this study are applicable to considerations of strength. It can be shown that the strength of an oriented polymeric system is related to the FSE by the following approximate relationship.

$$\text{Strength} \approx (\text{FSE})^{0.83}$$

RESULTS AND DISCUSSION

The results of the calculations are plotted in dimensionless form as reduced fracture surface energy (ρ_r) versus reduced chain length (L_r). The reduced fracture surface energy is defined by

$$\rho_r = \rho/\rho_{\max}$$

where

$\rho \equiv$ fracture surface energy

$\rho_{\max} \equiv$ maximum fracture surface energy
 $= NQ_b$

$N \equiv$ number of molecules per unit area

$Q_b \equiv$ breaking energy per chain.

The reduced average chain length is defined by

$$L_r = L/L^*$$

where

$L \equiv$ number average molecular weight in repeat units

$L^* \equiv 2Q_b/q_c$

$q_c \equiv$ cohesive energy per repeat unit.

L^* is measured in number of repeat units and represents the critical chain length above which chain breakage occurs. The value of L^* (i.e. $2Q_b/q_c$) is obtained as follows. In the case of an isolated molecule inserted a distance L into a matrix of the same cohesive energy as an ensemble of molecules, the

energy to remove the molecule is given by Lq_c . In order for breakage of a molecule in an ensemble to occur, it is necessary that both ends of the molecule be located at a distance greater than $L^*/2$ from the fracture plane. Thus, $L^*/2q_c = Q_B$ or $L^* = 2Q_B/q_c$.

a) Responses of extended chain systems

Figure 1 illustrates the dependence of reduced fracture surface energy (ρ_r) on the reduced average chain length ($\langle L_r \rangle$) for the extended chain model in which a "most probable" molecular weight distribution was employed. The reduced fracture surface energy increases monotonically with the reduced length and approaches unity asymptotically. For this case, the fracture surface energy and hence, the strength are relatively independent of cohesive

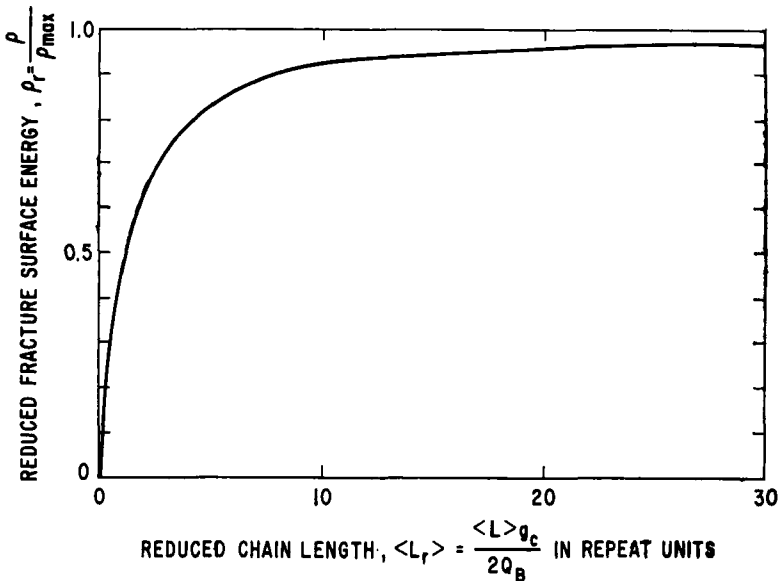


FIGURE 1 Reduced fracture surface energy versus reduced chain length—extended chain model.

energy if the molecular weight is sufficiently high. For example, suppose the ratio of breaking energy to specific cohesive energy is 25. Then, for average chain lengths of say 500 we have $\langle L_r \rangle = 10$; i.e. we are at the flat portion of the curve. Here a twofold increase in cohesive energy (i.e. a twofold increase in $\langle L_r \rangle$) yields a negligible increase in fracture surface energy. On the other hand, cohesive energy has a strong effect on fracture surface energy in the low molecular range. This effect is conveniently illustrated by comparing

the molecular weight necessary to achieve a given fraction of the maximum FSE at different number average molecular weights. For example, with a low cohesive energy system where $Q_b/q_c = 100$ a DP of ~ 800 is required to achieve 80 percent of the theoretically possible fracture surface energy given by NQ_b while with a high cohesive energy system of $Q_b/q_c = 10$ a DP of 80 is sufficient to obtain an equivalent effect.

Consequently, a high cohesive energy is a very desired property despite the lack of a strong effect on FSE and strength in the range of high molecular weight, since it allows the utilization of low molecular weight materials to achieve a high degree of the theoretical strength. This offers both processing and economic advantages. In addition, the cohesive energy affects the width of the molecular weight range where the strength is molecular weight dependent.

We should also consider the shape of the curves at very low molecular weights. If one assumes that a certain minimum strength is required to process the polymers, then these data indicate that the cohesive energy is of utmost importance in determining the minimum molecular weight required to achieve a required level of "processibility". Strictly speaking, the processibility is a phenomenon related predominantly to the melt strength. Nevertheless, the analogy between the solid state strength and that of the melt in this case is justified since in both cases the rupture is a result of chain slippage and not chain rupture. There are ample data on hand supporting the responses predicted by this model. For example, it is well known that strong fibers and films can be produced from low molecular weight polyesters and polyamides. With polyolefins on the other hand, a much higher molecular weight is required to obtain a similar performance. The minimum molecular weights required to produce fibers were studied by Mark and in Table I we present this data along with estimated cohesive energies. The experimentally

TABLE I

Minimum molecular weights required for fiber processing and estimated molar cohesive energies for various polymers

	Minimum molecular weights	Cohesive energy K cal/mole
Nylon-6	6000	9200
Nylon-6,6	6000	9200
Polyethylene terephthalate	8000	11,000
Polyvinyl alcohol	15,000	5800
Polyvinyl chloride	25,000	2600
Polystyrene	60,000	4000

determined values of molecular weights agree well with the trends expected on the basis of the corresponding cohesive energies.

This and many other examples have been found where the calculations based on our model exhibit the observed trends. Thus establishing the adequacy of this model, we can proceed with the study of responses which for one reason or another cannot easily be analyzed by experiment.

b) Effect of random chain folding

The molecular weight–fracture surface energy relationship becomes more complicated when chain folding is taken into account. A considerable amount of work has recently been devoted to the study of the morphology of oriented systems and an overwhelming amount of data has been accumulated which indicate that the chains are not fully extended but that they fold in a similar way as observed in single crystals and spherulitic structures.¹⁵ The frequency of folding and its regularity is expected to decrease with increasing orientation. Thus, the conclusion derived from a model where the folds are distributed randomly are not expected to differ appreciably from the observations obtained with a real highly oriented polymeric system.

Figure 2 shows a plot of reduced fracture surface energy (ρ_r) versus reduced

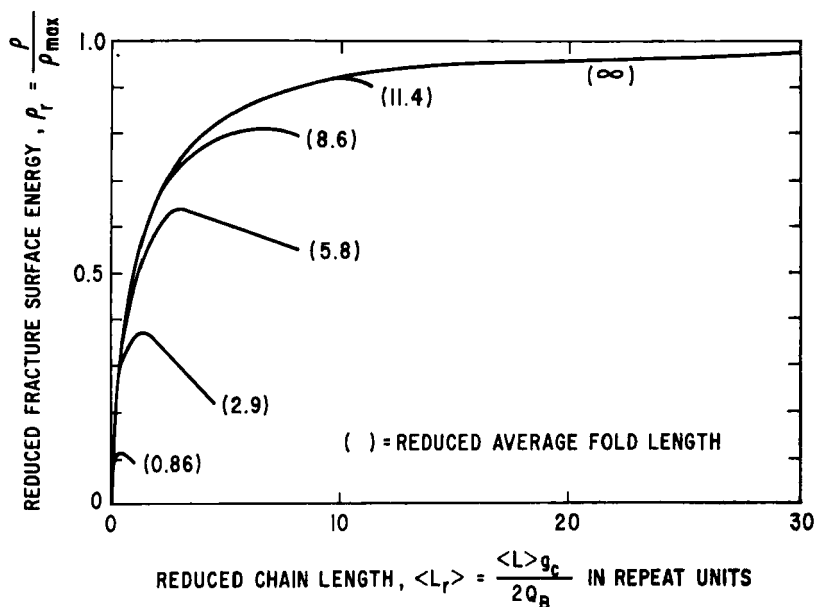


FIGURE 2 Reduced fracture surface energy versus reduced chain length for various degrees of chain folding.

average chain length ($\langle L_r \rangle$) for various degrees of chain folding including the extended chain model. The degree of folding is expressed as the reduced average length between the folds ($\langle L_{fr} \rangle$) which is defined by

$$\langle L_{fr} \rangle \equiv \langle L_f \rangle / L^*$$

Here, $\langle L_f \rangle$ is the average length between folds, in repeat units, and L^* is as before, $2Q_b/q_c$. In contrast with the extended chain model, where the fracture surface energy increases monotonically with the molecular weight, the model with chain folding predicts a maximum in strength near the value of reduced average chain length ($\langle L_r \rangle$) corresponding to the reduced average length ($\langle L_{fr} \rangle$) between the folds. This behavior can be understood if one considers that according to the present model the degree of chain folding increases with the molecular weight and the formation of a fold in a highly oriented structure eliminates the contribution of two adjacent molecules.

The effect of cohesive energy on fracture surface energy for the folded model can be illustrated using Figure 2 as follows. Assume an average length between folds of 150 repeat units, an average chain length of 200 and constant breaking energy Q_b . Then, for a high cohesive energy system (e.g. $Q_b/q_c = 12.5$, i.e. $L^* = 25$, $\langle L_r \rangle = 8$ and $\langle L_{fr} \rangle = 6$) the reduced fracture surface energy ρ_r is about 0.58. A lower cohesive energy system (e.g. $Q_b/q_c = 25$, i.e. $L^* = 200$, $\langle L_r \rangle = 4$, and $\langle L_{fr} \rangle = 3$) would have a reduced fracture surface energy of about 0.25. The corresponding values for the extended chain model would be 0.90 and 0.80 respectively. By comparing the values for the extended chain and folded chain models, it is apparent that in addition to exhibiting lower fracture surface energies, the folded model is much more sensitive to changes in cohesive energy than the extended chain model. This result is very important because it shows that the degree of chain folding could be estimated from the effects of temperature on strength. It can be assumed that in a highly oriented system the effect of temperature is primarily on modulus (which can be measured independently) and the cohesive energy. Based on the above results it is to be expected that the strength of highly oriented systems with a high degree of chain folding should be more sensitive to variation of temperature than those containing a lower degree of chain folding.

Furthermore, it should also be noted that with extended chains a deficiency in cohesive energy can be (at least theoretically) compensated by increasing the molecular weight. With the folded chain model, on the other hand, this holds only when the molecular weight is lower than the molecular weight between the folds. If, however, the molecular weight of the polymer is greater than that between the folds, the effect of an increase of the molecular weight is opposite, i.e. an increase in the molecular weight leads to a decrease in FSE and strength.

c) Contributions of chain breakage and chain slippage

According to this model, the FSE is a sum of two contributions, one associated with the breakage of primary bonds and the other associated with the breakage of secondary bonds. This latter contribution represents the fraction of the FSE due to chain slippage.

Figure 3 shows the relative contribution of chain breakage (expressed as the ratio of fracture surface energy due to chain breakage to total fracture surface energy) as a function of reduced length for various degrees of folding. Considering the curve for the extended chain model, the predominant effect at low reduced lengths (less than 1 say) is that of chain slippage. As the length

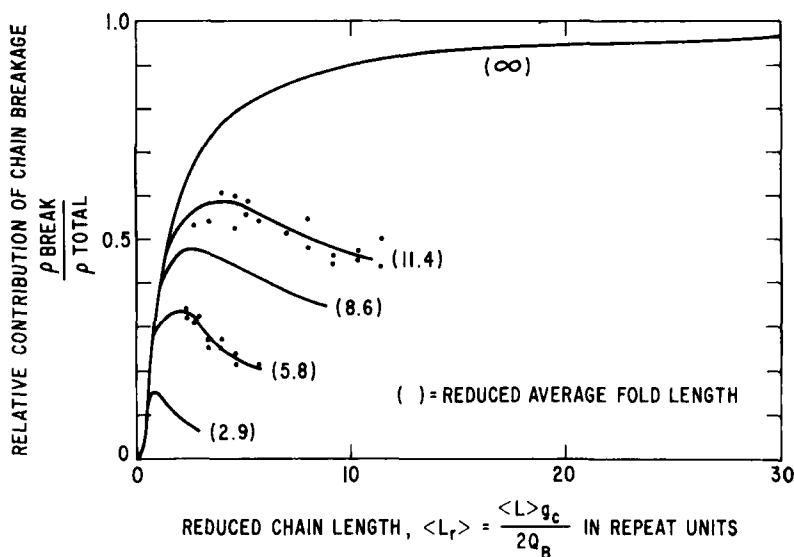


FIGURE 3 Relative contribution of chain breakage to fracture surface energy versus reduced chain length for various degrees of chain folding.

(molecular weight) is increased, the contribution of chain breakage to the total energy increases monotonically. At a value of $\langle L_r \rangle$ approximately equal to 1.6, the contributions of the two mechanisms are equal; at higher lengths, the contribution of breaking predominates approaching unit asymptotically. As with total fracture surface energy, the extended chain models exhibit maxima in breaking contribution and, for a given molecular length, (breaking and cohesive energies being constant) the breaking contribution decreases monotonically with decreased average fold length (i.e. with increased folding). The maxima in breaking contribution occur at values of reduced length equal to about one-half that of the corresponding maxima in

fracture surface energy. Thus, if a given fiber is in a region of decreasing fracture surface energy, then the breaking contribution is also decreasing with increasing molecular weight.

This last observation, namely, that the contribution to chain scission decreases with molecular weight in the region of decreasing FSE is of great importance because it provides the possibility of distinguishing a decrease in strength due to chain folding from that associated with other effects by measuring the concentration of free radicals formed during straining of specimens by EPR techniques.

CONCLUSIONS

The presented model explains the behavior of oriented polymeric systems below the glass transition temperature in a wide range of experimental variables. The described calculations can be applied to establish the potential of a polymer in a highly oriented state and to predict the changes in the mechanical responses resulting from structural modifications, provided the basic molecular parameters are known. The model is particularly suitable for the study of the effects of changes in the molecular weight distribution and for determination of the molecular weight ranges required to achieve a desired performance. One problem that has not been discussed but is readily amenable to a quantitative analysis by this method, is the study of effects associated with the presence of various amounts of monomers and/or cyclic oligomers, a phenomenon encountered in many polymerization processes.

Several implications derived from the presented studies cannot be verified at present. The main difficulty is the lack of information regarding the chain folding in non-equilibrium highly oriented systems, and the uncertainty about the values of specific cohesive energies in oriented polymers. The most interesting result of these calculations, the prediction of a maximum strength in the low molecular weight range, will have to wait for verification until more experimental data, using carefully characterized specimens, become available. Although the existence of an optimum performance in a low or medium molecular weight range appears to be in disagreement with the general experience, there are experimental data where such trends have been observed. However, these trends have usually been attributed to the increased difficulty of achieving structural perfection and high orientations as the molecular weight is increased.

In view of the data presented, the experimental results indicating a maximum in strength in the low molecular weight range offer the opportunity for interesting studies with regard to the structure, provided the analysis is supported by necessary x-ray, electron microscope, I.R., etc. data.

Another phenomenon which should be mentioned in connection with this work is the loss in strength occurring on annealing of highly oriented polymers. It has been observed that heating of such systems can lead to a substantial loss in strength without producing any significant changes in the wide angle x-ray scatter. The most conspicuous effects noted in these cases is the increase in the intensity of the low angle x-ray scatter¹⁶ and an increase in the intensity of IR absorption bands attributed to the vibrations in the folds.¹⁷ The interpretation put forward on the basis of these observations was that the annealing or controlled thermal contraction leads to an increase in chain fold density.^{18,19} It is hoped that an analysis of such data using the presented model would contribute both to the understanding of the phenomenon and to the elucidation of the structure. The indication that a folded chain structure should be more sensitive to changes in cohesive energy than the extended chain structure suggests numerous possibilities for structural analysis.

APPENDIX I—CALCULATING PROCEDURE

The calculations involve three phases: storage of molecules; construction of the array of molecules in the fracture plane; and calculations of fracture surface energy.

Input data consists of the selection of the number average degree of polymerization \bar{P}_n and the degree of polymerization distribution function $f(P)$. The distribution is divided into F intervals having the width ΔP . F is chosen to be sufficiently large to characterize the distribution. In our calculations, F was chosen to be 200.

For practical polymerization processes and conditions involved in specimen preparations, it appears necessary to disregard very long molecules which have a small chance to survive severe processing conditions without breakage. In the absence of reliable data regarding the maximum expected chain length we assumed in our calculations that

$$P_{\max} = 10 \cdot \bar{P}_n$$

Thus, the width of an interval is given by

$$\Delta P = 10 \cdot \bar{P}_n / F$$

Each interval of the distribution is assigned a subscript K (K ranges from 1 to F in steps of 1; the interval $P = K\Delta P$ to $P = (K + 1)\Delta P$ has index K) and two arrays of length F are defined by the average length or degree of polymerization (P_K) and the number of molecules within the interval (N_K).

In the case of the most probable molecular distribution, the distribution function is given by²¹

$$f(P) = y^2 e^{-yP}$$

where

$$y = 1/\bar{P}_K.$$

For this distribution, the average length P_K is given by

$$P_K = \frac{\int_{K\Delta P}^{(K+1)\Delta P} P f(P) dP}{\int_{K\Delta P}^{(K+1)\Delta P} f(P) dP}$$

clearly $K\Delta P \leq P_K \leq (K+1)\Delta P$.

It is assumed that there are N molecules in each interval at the beginning of the experiment (i.e. $N_K = N$ for all K).

A one-dimensional array of molecules intersecting the fracture line is constructed by means of the following Monte Carlo technique. First, a random value of the interval index K is chosen. A second random number (*PROB*) taking values between 0 and "a", is then chosen and compared to the probability ($g(P_K)$) of finding a molecule of length P_K at the fracture plane, ("a" is chosen as the maximum probability ($g(P_K)_{\max}$) for reasons of sampling efficiency). If

$$PROB \leq g(P_K)$$

the operation is successful, and a molecule of length P_K is drawn. If

$$PROB > g(P_K)$$

the operation is considered a failure and another K is randomly selected and the decision process repeated.

The probability of finding a molecule of length P_K at the fracture plane is proportional to the size of the molecule (P_K) and to the number fraction of such species present. That is

$$g(P_K) \sim P_K(N_K/\Sigma N_K).$$

Normalizing the distribution to unity, i.e. imposing the requirement that

$$\Sigma g(P_K) = 1$$

implies that

$$g(P_K) = (P_K N_K / \Sigma P_K N_K).$$

To insure that the array of molecules used in computing the fracture surface energy represents the original molecular distribution, selection of molecules by

the above scheme is made without replacement and the routine is terminated when a large fraction (e.g. >80%) of all the molecules have been selected. Thus, the selection criteria distribution $g(P_K)$ changes due to the unit decrease in N_K resulting from the selection of a molecule from the K th interval.

After the selection of a particular molecule of length P_K , it is positioned with respect to the fracture plane by the selection of a random variable (POS) between 0 and 1. The position above the plane is given by P_K times POS and below by P_K times ($POS - 1$).

In the absence of experimental data regarding fluctuations in the length between folds, a Gaussian distribution characterized by the average length between folds λ , and the standard deviation σ was assumed. That is, the distribution of fold lengths was assumed to be

$$f(l) \equiv \frac{1}{\sqrt{2\pi}\sigma} \exp - \left(\frac{(l - \lambda)^2}{2\sigma^2} \right)$$

where l = length between folds. As with the molecular distribution described above, we set

$$\lambda_{\max} = 10\lambda$$

and divide the interval ($l = 0$ to 10λ) into 200 parts, i.e.

$$\Delta\lambda = (\lambda_{\max}/200) = (\lambda/20).$$

The average length between folds in the J th interval ($l = J\Delta\lambda$ to $(J + 1)\Delta\lambda$) denoted l_J , is given by

$$l_J = \frac{\int_{J\Delta\lambda}^{(J+1)\Delta\lambda} f(l) dl}{\int_{J\Delta\lambda}^{(J+1)\Delta\lambda} f(l) dl}$$

Selection of fold length is made by comparing a random number (LAM) between 0 and $[f(l)]_{\max}$ with $f(l_J)$, J being selected at random between 1 and 200. If $LAM \leq f(l_J)$, then the length of the fold is set at l_J . If $LAM > f(l_J)$ another selection is made.

Construction of a folded molecule proceeds as follows: the length (P_K) and the position of one end (P_K times POS) are determined as in the construction of the extended chain array. A fold length l_J is then randomly selected as described above and compared with the total molecular length. If $P_K > l_J$, a fold segment of length l_J is constructed from the end of the positioned molecule. If $P_K \leq l_J$, the molecule appears in extended chain form. If folding occurs, the selection of the second fold length proceeds using the remaining length of

APPENDIX II—FRACTURE SURFACE ENERGY OF VARIOUS ORIENTED POLYMERS

For a quantitative interpretation of strength of uniaxially oriented fibers and films it is necessary to know the FSE of such systems. The results of this study show that this property can be calculated if we know the number of molecules intersecting a unit cross-sectional area N , the energy required to break the weakest bond in the polymer chain, and the cohesive energy per unit length of polymer chain. In this section we derive values of FSE for a series of polymers which are frequently used in our laboratories.

From the mechanical point of view, one would expect that the breaking energy Q_b for a given polymer chain is related to the energy of the weakest bond in the chain. This hypothesis has been verified experimentally by Zhurkov *et al.*²⁰ by measuring the activation energies associated with the mechanical breakdown. In Table II the values of activation energies obtained

TABLE II
Activation energies for mechanical and thermal breakdown
(Kcal/mol)

	Mechanical	Bonds involved	Thermal
Polytetrafluoroethylene	75	C—C	76–80
Polyethylene	—	C—C	72
Polypropylene	56	C—C	55–58
Polystyrene	54	C—C	55
Polyacrylonitrile	48	C—C	31
Polyester	—	C—O	38
Nylon-6	45	C—N	43
Polyvinylchloride	35	C—C	32

from mechanical experiments with the bonds involved in rupture are listed. These values correspond to values of Q_b used in our calculations. For comparison, Table II also includes the values of activation energies associated with thermal degradation. Inspection of the data shows that the mechanical and thermal activation energies are of the same magnitude, thus indicating the similarity between these two types of polymer ruptures. In connection with the calculation of FSE, where Q_b appears as an overriding factor, the data in Table II provide the explanation for the close relationship between the mechanical strength of a polymer and the energy of the weakest bond in the chain.

Values of specific cohesive energies (per polymer chain repeat unit) of several polymers are listed in Table III. The factors affecting the cohesive energy, such as: intermolecular hydrogen bonding, dipole interaction, dispersion forces, chain packing, are well understood. Several schemes have

TABLE III

Values of specific cohesive energy and number of molecules/cm² for various polymers (10⁻¹³ ergs/repeat unit)

	Specific cohesive energy	Number of molecules/cm ²
Nylon-6	6.4	5.65
Nylon-6,6	6.4	5.72
Polyethylene terephthalate	7.7	4.90
Polyethylene	0.95	5.50

been proposed to estimate the cohesive energy from known molecular parameters.

The number of molecules intersecting a plane perpendicular to the polymer chain can best be estimated from x-ray data. Values of N for several polymers are also listed in Table III.

As discussed in the main body of this paper, the FSE, when plotted as a function of reduced chain length, exhibits maxima as the degree of folding is varied. This behavior is illustrated in Figure 2. Since we would like to compare the behavior of different materials at corresponding fold lengths, a plot of maximum reduced FSE versus reduced fold length is shown in Figure 5. We

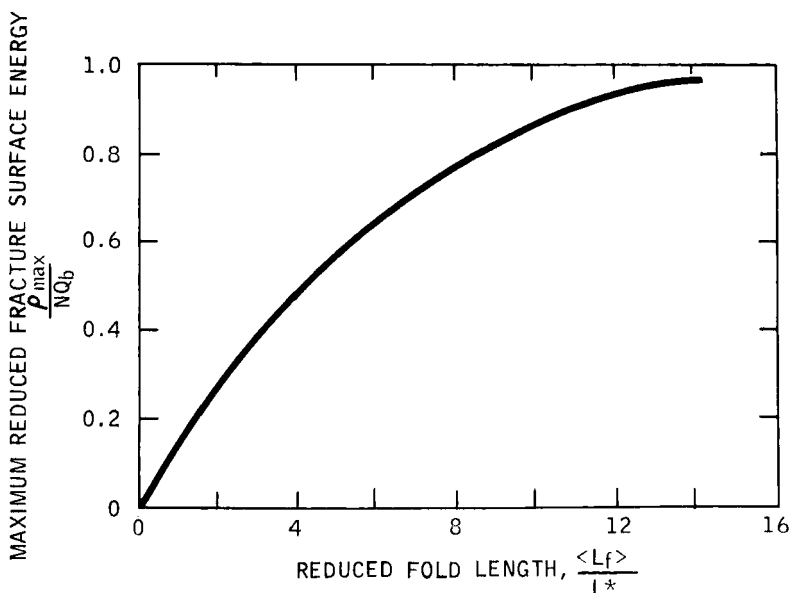


FIGURE 5 Maximum reduced fracture surface energy versus reduced fold length.

may use this figure to obtain the maximum FSE at various fold lengths by knowing N , Q_b and q_c since from these we may determine the maximum FSE in the absence of folding ρ_{\max} (given by NQ_b) and the length normalization factor L^* (given by $2Q_b/q_c$). Then, given an average fold length $\langle Lf \rangle$ we may determine ρ/ρ_{\max} from Figure 5 and thus the corresponding maximum fracture surface energy ρ for that particular level of folding. Results of such calculations for Nylon-6, Nylon-6,6, Polyethylene terephthalate, and polyethylene at fold lengths of 50, 200 and 1000 Å are presented in Table IV.

TABLE IV

Values of maximum fracture surface energy in ergs/cm² for various polymers at various degrees of chain folding

	Average fold length = 50 Å	Average fold length = 200 Å	Average fold length = 1000 Å	No folding
Nylon-6	138	566	1650	1770
Nylon-6,6	139	573	1670	1790
Polyethylene terephthalate	116	464	1260	1290
Polyethylene	41.4	290	1300	2760

References

1. A. A. Griffith, *Phil. Trans. Roy. Soc.* **A221**, 162 (1921).
2. E. Orowan, "Fracture and strength of solids", *Report on Progress in Physics, Physical Society of London* **12**, 185 (1949).
3. G. R. Irwin, "Fracture dynamics in fracturing of metals", A.S.M. 149 (1948).
4. T. Yokobory, *J. Phys. Soc. Japan* **10**, 368 (1955).
5. J. J. Gilman, *Fracture Proceedings of an International Conference on the Atomic Mechanisms of Fracture*, Swampscott, Massachusetts, Wiley, New York (1959).
6. J. P. Berry, *J. Mech. Phys. Solids* **8**, 194 (1960).
7. D. C. Prevorsek and W. J. Lyons, *J. Appl. Phys.* **35**, 3152 (1969).
8. For additional references see—"Physical Basis of Yield and Fracture", Inst. of Physics and Physical Society, 1966 Conference Proceedings.
9. L. J. Brautman, MIT Report R63-35, July 1963.
10. O. K. Felbeck and E. Orowan, *Welding J. Research Suppl.* **39**, 5105 (1955).
11. G. R. Irwin, J. A. Kies, and H. L. Smith, *ASTM Proc.* **58**, 640 (1958).
12. J. P. Berry, *J. Polymer Sci.* **50**, 107 (1961); **50**, 313 (1961).
13. H. Mark and A. Tobolsky, *Physical Chemistry of High Polymeric Systems*. Interscience Publishers, Inc., New York, Second Edition p. 150 (1950).
14. C. W. Burn, *J. Polymer Sci.* **16**, 323 (1955).
15. A. Peterlin, *The Role of Chain Folding in Fibers, Man-Made Fibers*, H. I. Mark, S. M. Atlas, and E. Cernia, Eds., Wiley-Interscience, New York (1967).
16. P. F. Dismore and W. O. Statton, *J. Polym. Sci.* **B2**, 1113 (1964); **C13**, 133 (1966).
17. J. L. Koenig and M. J. Hannon, *J. Macromol. Sci. (Phys.)* **B1**, 119 (1967).
18. W. O. Statton, J. L. Koenig, and M. Hannon, *J. Appl. Phys.* **41**, 4290 (1970).
19. D. C. Prevorsek and J. P. Sibilia, *J. Macromol. Sci. (Phys.)* **B5** (3), 671 (1971).
20. S. N. Zhurkov and S. Abasov, *Vysokomolek. Sojed.* **3**, 441 (1961).
21. P. J. Flory, *Principles of Polymer Chemistry*, 319, Cornell University Press, Ithaca, New York (1953).