# Some consequences of a fracture criterion for oriented polymers based on electron spin resonance spectroscopy

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ABSTRACT

Electron spin resonance (ESR) spectroscopy, which is able to monitor covalent bond rupture during polymer fracture, has provided an experimental basis on which to construct an atomistic fracture model which takes proper cognizance of the distribution of stress over the material's internal structure. Using a computer model developed by DeVries and Lloyd, estimations of times to fracture were obtained for several different temperatures, stresses, and stress rates. The predicted rupture times agreed satisfactorily with experimental observations, which indicates the practical utility of the ESR-based model. Further, the effective activation parameters which result when the Zhurkov macroscopic fracture model is correlated with the ESR predictions provide an insight as to the role of the internal stress distribution in determining the kinetics of the fracture process.

## 1. Introduction

From the earliest days of the science of fracture, investigators have sought to develop theoretical models of the fracture process which are founded directly on hypotheses of the molecular phenomena underlying the fracture process, and which lead to a realistic appraisal of the lifetime of a solid subjected to arbitrary stress histories. This has of course been a most difficult undertaking, given the complexity of the fracture process. Many of the approaches to date have been various forms of the Eyring reaction-rate theory, in which the rate of dissociation of chemical bonds is written as an exponential involving the temperature, the applied stress, and various activation parameters characteristic of the process. The text by Krausz and Eyring [1] describes the method in some detail.

A significant advance in the atomistic approach to fracture was achieved with the availability of experimental techniques which are able to monitor directly the chemical changes accompanying fracture in certain materials – notably oriented polyamide fibers. These techniques permitted the elimination of much hypothesis as to the fundamental kinetics of the process. Although several techniques have proven useful, by far the most valuable to date has been electron spin resonance (ESR) spectroscopy, in which the free radicals generated by homolytic scission of covalent bonds are identified and counted [2]. DeVries and Lloyd [3] used this technique to develop a kinetic analysis of polymer fracture which describes the rates of bond rupture during the pre-fracture phase of the loading process. This paper will describe the utility of this model in predicting the onset of final catastrophic rupture of the specimen.

## 2. The DeVries ESR model

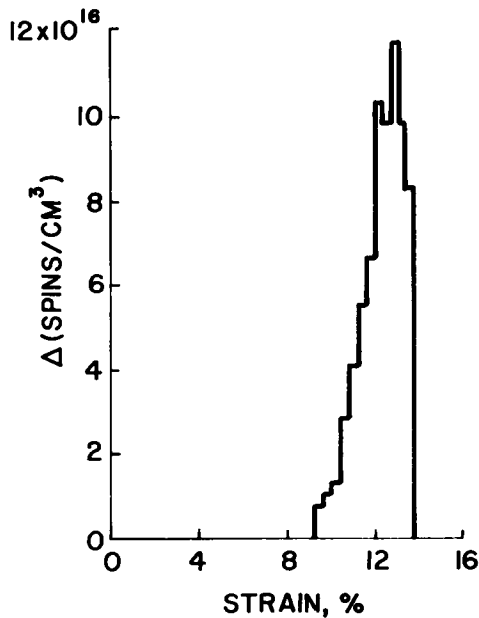Although ESR spectroscopy suffers from several inherent limitations in the study of polymer

Figure 1. Radical production histogram for drawn nylon 6 fibers. Specimens were predesiccated and tested in dry $N_2$ atmosphere at 25 °C. (From Ref. [5].)

fracture, the most serious probably being the possibility of misleading free radical reactions following bond scission, it is much more sensitive than other relevant techniques. In addition, it is able to operate during the fracture process, rather than being limited to a postmortem examination of the ruptured fragments. Measurements by other methods have tended to corroborate the validity of the ESR method, so that the possible limitations which have been noted may not be serious [4].

DeVries and Lloyd [3, 5] performed a series of carefully controlled experiments in which drawn nylon-6 fibers were subjected to various uniaxial tensile stress histories while passing through the microwave absorption cavity of an ESR spectrometer. They were thus able to obtain continuous counts of the number of free radicals created at any time during the loading process. Among the most revealing of the tests performed were step-strain tests, in which the number of radicals created during increments of successively higher specimen strain were recorded. The results could be plotted in the form of a histogram (see Fig. 1), and it was noted that the cumulative extent of radical production versus strain appeared as a straight line on normal probability paper. Based on this observation, DeVries and Lloyd postulated a damage model in which the load-bearing elements within the specimen's microstructure were also distributed normally: some elements would fail at low strain, a larger number would fail at higher strain, and finally the number of elements able to sustain still higher strain would again diminish according to a normal distribution about some mean value. They interpreted this distribution in terms of the contour lengths of intercrystalline tie chains, but this interpretation is somewhat controversial and in fact is not necessary for a kinetic analysis of the data. The hypothesis of failure being associated with the breakage of an ensemble of normally distributed bonds has nevertheless not been completely accepted, even for the drawn polyamide fibers for which such a mechanism seems most possible. (See for example the discussion in *Polymer Fracture*, H.H. Kausch, Springer Verlag (1978).) However, much of the modeling to be presented in this paper would apply to any failure process acting on a

normally distributed ensemble of structural elements, so that the conclusions to be drawn are more general than the bond-rupture model alone.

Briefly stated, the DeVries model follows the Eyring approach and takes the rate of bond rupture to be a first-order kinetic process

$$-dN/dt = KN \tag{1}$$

where $N$ is the concentration of unbroken main-chain covalent bonds, and the rate constant $K$ depends on the stress according to the simple form of a stress-aided thermally activated process:

$$K = K_0 \exp[-(U - \gamma\psi)/RT] \tag{2}$$

In the above equation $K_0$ is a preexponential which contains the entropic contribution of bond rupture and the temperature dependent collision factor. $U$ is the activation energy for bond dissociation, $\psi$ is the local stress experienced by the covalent bond, $\gamma$ is the activation volume, $T$ is the absolute temperature, and $R = 8.314$ J/mole is the Universal Gas Constant. The above relations are common to almost all reaction-rate models of fracture, but in the case of the DeVries model ESR data are used to provide a direct measure of the local stress $\psi$. This represents a substantial improvement over previous approaches, in which arbitrary and often unjustifiable assumptions about the nature of the local bond stress were necessary.

Since the histogram of Fig. 1 represents the variation of various microstructural elements' ability to bear load, it also provides a means of distributing the applied macroscopic stress over the network of covalent bonds. DeVries and Lloyd used ESR histograms to calculate the mean and standard deviation of the distribution of internal stress, and then divided the stress distribution into a large number of subincrements. They then employed an incremental computer model in which a large number of rate equations similar to Eqns. (1) and (2) were integrated numerically. The total extent of bond rupture is then the sum of the ruptures occurring in each of the discrete subsegments of the bond stress distribution, and DeVries showed that the bond rupture kinetics predicted by this model agreed closely with that experimentally observed by the ESR spectrometer.

One of the adjustable parameters in the DeVries model is the fraction of covalent bonds which will eventually break during the loading process. Clearly, in any real material, the initiation and eventual propagation of a fracture surface involves only a small fraction of the molecular bonds in the material, presumably those which are situated more critically than their neighbors with respect to the applied load. These highly stressed sites arise naturally due to the heterogeneous nature of materials. It is this critical fraction over which the Gaussian distribution of stress is applied, while the much larger remainder is said to experience only the average applied stress. Figure 2 demonstrates the stress distribution over the critical subsegment of the microstructure, and in the DeVries model, it is this distribution which is discretized, with a separate bond-rupture equation written for each increment. Due to the exponential dependence of the rupture rate on the local stress, significant rupture occurs only near the right edge of these curves, near what may be termed the theoretical rupture strength of the covalent bond (the stress at which rupture occurs quickly relative to the total time scale of the experiment).

## 3. The DeVries model as a failure criterion

*The Zhurkov equation*

Many researchers have noted the engineering utility of the fracture criterion developed over
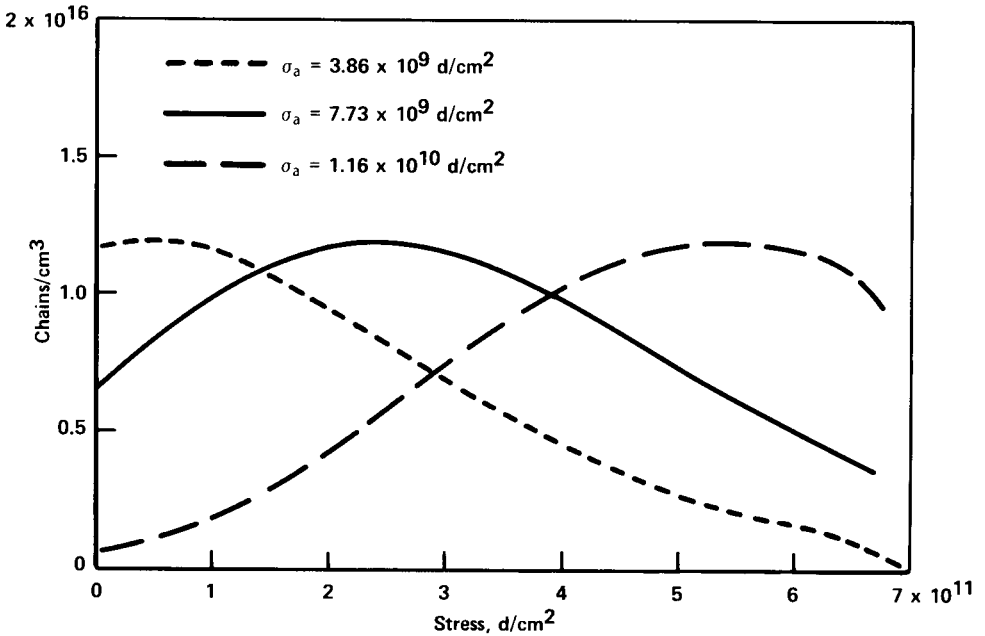
Figure 2. Variation of molecular stress over population of "critically situated" microstructural elements, for various levels of macroscopically applied stress. The lines have been drawn through discrete points representing the molecular stress on the various subsegments of the distribution of critically situated load-carrying elements, and the ordinal values represent the number of elements in each of these subsegments.

many years by S.N. Zhurkov [6], which states that the lifetime $\tau$ of a solid bearing a constant uniaxial stress $\sigma$ is given as

$$\tau = \tau_0 \exp\left(\frac{U_m - \gamma_m \sigma}{RT}\right) \tag{3}$$

Here $U_m$ and $\gamma_m$ are the apparent activation energy and volume for mechanical rupture, and $\tau_0$ is a preexponential factor. This equation may be regarded as derivable from rate-process modeling [4] or as essentially empirical.

For a given temperature, Zhurkov's equation can be written as

$$\tau = \alpha \exp(-\beta \sigma) \tag{4}$$

where

$$\alpha = \tau_0 \exp(U_m/RT) \tag{5}$$

$$\beta = \gamma_m/RT \tag{6}$$

When the stress or temperature vary during the loading process, one may often assume that superposition is possible and write Zhurkov's equation in integral form as

$$\int_0^\tau [\tau_0 \exp\{[U_m - \gamma_m \sigma(t)]/RT(t)\}]^{-1} \, dt = 1 \tag{7}$$

In constant-stress-rate loading ($\sigma = Ct$) at constant temperature, for instance

$$\tau = [\ln(1 + \alpha\beta C)]/\beta C. \tag{8}$$

*Correlation of Zhurkov and DeVries models*

In this present paper, the computer model of DeVries and Lloyd was used to compute the time needed for the entire distribution of load-bearing elements to be ruptured. This time was then taken to represent the creep-rupture time predicted by the DeVries model, and these predicted times were correlated with the Zhurkov analysis.

For the purpose of this correlation, the activation parameters selected by Lloyd and DeVries to fit their "nylon 6 #1" material were used. Lloyd originally chose these constants so as to obtain agreement with ESR results obtained during creep and constant-strain-rate testing. He then showed that the resulting numerical model was capable of predicting accurately the ESR results for several arbitrary stress-temperature-time histories. Lloyd noted that the activation parameters needed to fit the ESR data were generally quite different from the effective values Zhurkov found in fitting (3) to creep-rupture data for similar material. Lloyd determined an activation energy of 282 kJ/mol rather than the 180 kJ/mol found by Zhurkov, and Lloyd's activation volume of $3.0 \times 10^{-6}$ m$^3$/mol (5 A$^3$) was much smaller than Zhurkov's ($1.28 \times 10^{-4}$ m$^3$/mol) (212 A$^3$).

It must be emphasized that Zhurkov's experiments were concerned with the final rupture of the specimen, while Lloyd's were concerned with damage occurring during the specimen loading but not the final rupture point. It should also be pointed out that Lloyd's parameters are closer to what one would expect as atomistic values: his activation energy is close to what molecular orbital calculations predict for the dissociation energy for the critical carbon-carbon bond in polyamides, and his activation volume is very close to the product of the effective molecular chain area and the bond deformation expected at fracture. Zhurkov's values reflect not only the covalent bond properties, but also the defect and stress distribution within the specimen.

Computer creep-rupture experiments were conducted using the DeVries model at several simulated applied stresses and temperatures, and the times to complete dissociation
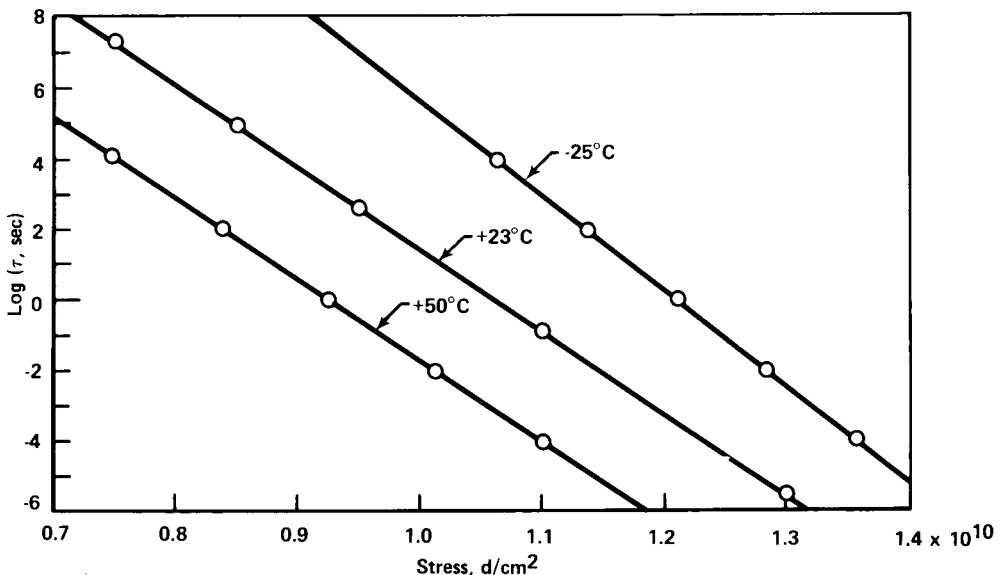


Figure 3. Effect of stress on creep-rupture lifetime as predicted by ESR-based atomistic model.
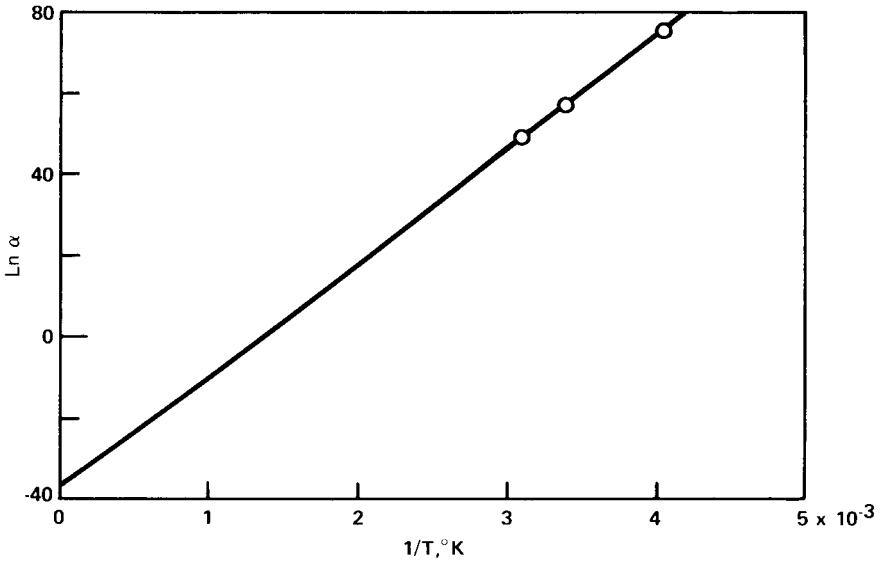
Figure 4. Arrhenius plot to obtain mechanical activation parameters $U_m$ and $\tau_0$.

treated just as experimental creep-rupture data in determining appropriate activation para-meters in the Zhurkov equation. Figures 3, 4, and 5 illustrate the numerical procedure.

Equation (4) predicts that a plot of $\log \tau$ versus stress will be linear, with a slope of $\beta/2.303$ and an intercept of $\log \alpha$. Figure 3 demonstrates that the expected linear relation is obtained; here the individual data are the DeVries-model predictions at various stresses and temper-atures and the solid lines are regression fits to the data. Figure 3 provides values for $\alpha$ and $\beta$ at three discrete temperatures. Equation (5) predicts that a plot of $\ln \alpha$ versus $1/T$ should be linear with a slope of $U_m/R$ and an intercept of $\ln \tau_0$, and (6) predicts that a plot of $\beta$ versus $1/T$ should be a straight line through the origin with slope $\gamma_m/R$. These two plots are shown in
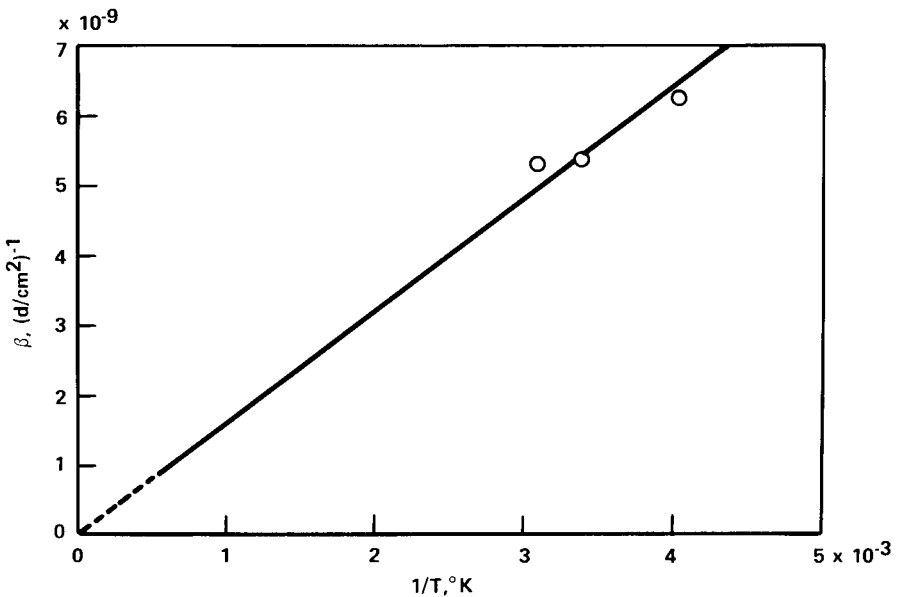


Figure 5. Plot to obtain mechanical activation volume $\gamma_m$.

Figs. 4 and 5 respectively. The data in Fig. 5 show some scatter, and the solid line is a regression which has been forced through the origin. Clearly, more data at other temperatures would be advisable in constructing these latter two figures, but they will suffice for our present purposes. The values of $\tau_0$, $U_m$, and $\gamma_m$ obtained from the above exercise are $1.98 \times 10^{-17}$ s, 235 kJ/mol, and $1.34 \times 10^{-4}$ m$^3$/mol (220 A$^3$) respectively.

These values reflect the defect structure through the incorporation of the ESR-determined stress distribution as well as the inherent covalent bond properties. They are not identical to Zhurkov's values for nylon: although the activation volumes are very close, the activation energy is larger and the pre-exponential factor is four orders of magnitude smaller. These differences may be due both to the lack of precision in the limited number of temperatures included in the computer study and to real differences between the Zhurkov and Lloyd materials.

As a means of assessing the accuracy of the Zhurkov equation with the ESR-derived activation parameters in predicting final specimen rupture of the Lloyd material, (8) was used to predict the time to break in a series of constant-loading-rate tests conducted at various temperatures. These are compared in Table 1 with experimental values obtained by Lloyd, and it is seen that agreement is satisfactory.

TABLE 1
*Fracture times for constant loading rate*

| Temperature | Loading rate | $t_{experimental}$ | $t_{predicted}$ |
|---|---|---|---|
| °C | MPa/sec | sec | sec |
| −25 | 18.7 | 56 | 62 |
| −25 | 5.64 | 188 | 203 |
| 23 | 15.5 | 66 | 67 |
| 23 | 4.66 | 210 | 219 |
| 50 | 12.2 | 70 | 80 |
| 50 | 4.20 | 215 | 227 |

## 4. Conclusions

It is observed that the incorporation of a defect structure into the rate-process models, which is equivalent to using a distribution of molecular stresses in (2), lowers the effective activation energy for mechanical rupture in comparison with the activation barrier for thermal dissociation of the covalent bond. The activation volume, which is a measure of the ability of the applied stress to reduce the activation barrier for scission, is increased. Both of these differences between atomistic and macroscopic activation parameters are to be expected in view of the ability of internal defects to act as stress risers and to place a disproportionate local stress on certain critically situated elements of the microstructure.

## Acknowledgements

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RÉSUMÉ
La spectroscopie électronique à résonnance de spin (ESR), qui est à même d'annoncer des ruptures de liaisons covalentes au cours de la rupture d'un polymère, a fourni une base expérimentale permettant d'élaborer un modèle atomique de la rupture, qui prenne en compte la distribution des contraintes dans la structure interne du matériau. A l'aide d'un modèle de calcul mis au point par De Vries et Lloyd, on a obtenu des estimations des durées à rupture dans le cas de températures, de contraintes et de vitesses de sollicitation différentes. Les durées à rupture prévues sont en accord avec les observations de l'expérience, ce qui indique l'utilité pratique du modèle basé sur l'ESR. En outre, les paramètres d'activation effective qui découlent d'une mise en corrélation du modèle de rupture macroscopique de rupture de Zhurkov avec les prédictions de l'ESR fournissent un éclairage sur la manière dont la distribution des contraintes intervient dans la détermination de la cinétique du processus de rupture.