

## An Experimental Investigation of Some Models of Polymer Fracture\*

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### ABSTRACT

It has recently been shown that the techniques of EPR spectroscopy can be used to monitor atomic bond rupture during fracture of polymeric materials and thus provide important new insights of the molecular mechanisms of fracture in these materials. In particular, this method can be used as a fundamental check of the several atomistically-derived theories of polymer fracture. In this paper such a check is made of two representative such theories, those of S. N. Zhurkov and W. G. Knauss. It is shown that these theories do not provide physically realistic models of the fracture mechanisms in oriented polymeric fibers and it is suggested that their lack of relevance is due to the unique morphological structure of highly oriented polymers.

### 1. Introduction

The formulation of valid theoretical models which can describe the molecular response of a polymeric solid to fracture stresses has long been hindered by the lack of experimental observations of these processes. The development of a tractable molecular fracture theory of necessity involves many simplifications and assumptions and the validity of these assumptions is generally difficult to ascertain. The "material constants" inherent in these theories are usually chosen to bring the model into quantitative agreement with time-to-break data and the existence of the agreement is often suggested as validation of the model. Such an agreement, however, may be fortuitous arising from the freedom given by several undetermined constants in a rather general mathematical expression; independent experimental data on the molecular mechanisms is really needed to resolve the question.

Recent works [1-4] have demonstrated the applicability of electron paramagnetic resonance (EPR) spectroscopy to the study of the submicroscopic fracture mechanisms operative in polymers. EPR techniques provide direct observations of molecular bond rupture in polymers; these observations provide basic checks of present atomistic theories of fracture and are of use in the formulation of still more physically reasonable models.

EPR is a form of microwave absorption spectroscopy in which radiative transitions are induced between the Zeeman energy levels of an assemblage of unpaired electrons. Whenever unpaired electrons (free radicals) are present in the EPR spectrometer's absorption cavity in numbers greater than a sensitivity limit of approximately  $10^{12}$  radicals, a spectrum can be produced whose intensity is a measure of the number of radicals present and whose shape (the "hyperfine structure") is a measure of the local chemical environment of the radical. Since homolytic rupture of a covalent polymer bond generates two free radicals, EPR provides—at least in principle—an experimental means of determining how many of which bonds are broken during polymer fracture, and monitoring their number as a function of time.

### 2. Experimental

A Varian E-3 EPR spectrometer was employed in these studies. It was used in conjunction with a servo-operated hydraulic loading system capable of producing any desired loading program: constant stress or strain, constant stress or strain rates, cyclic loading, etc. The equipment

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included a variable temperature controller capable of maintaining stable sample temperatures over the range from  $-165^{\circ}\text{C}$  to  $+300^{\circ}\text{C}$  and permitted the tests to be conducted in a variety of atmospheres. Load, displacement, and EPR signals were recorded on magnetic tape as functions of time during the tests so as to allow data reduction and model fitting on a Univac 1108 digital computer with digital plotting capabilities.

Although in principle EPR can be used to monitor bond rupture in any polymer, drawn polyamide (nylon) fibers have proven particularly amenable to this technique in that their mechanical breakdown generates high concentrations of free radicals. This paper presents data taken on drawn multifilament polycaprolactan (Nylon 6) fibers kindly provided by Allied Chemical Corporation. X-ray fluorescence spectra obtained by the manufacturer indicated that the only inorganic ions present in substantial amounts were copper (61 ppm) and iodine (0.2 per cent); all other metals were less than 2 ppm. X-ray diffraction and lustron characterization indicated the morphological orientation and mechanical properties characteristic of drawn nylon fibers.

### 3. Results and Discussion

#### *EPR Measurements*

An easily detectable stress-induced free radical spectrum was generated in the nylon fibers at stresses greater than approximately sixty per cent of the fracture stress. The intensity of the spectrum was monitored continuously during the loading along with the signals from the load and displacement transducers. The computer-reduced data from two particularly interesting loading modes, constant stress and constant stress rate, are shown in Figs. 1 and 2.

#### *The Zhurkov Thermo-Fluctuation Model of Fracture*

Most atomistic theories of polymer fracture regard the phenomenon of catastrophic rupture as the end result of a gradual accumulation of broken bonds, i.e. bonds are ruptured throughout the loading history and not solely at the time of the catastrophic failure. Indeed, this behavior is

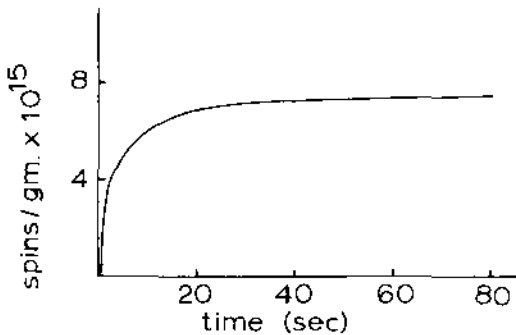


Figure 1. Free radical generation in drawn Nylon 6 fibers at constant stress (100 ksi).

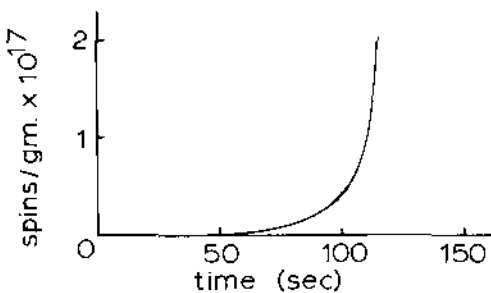


Figure 2. Free radical generation in drawn Nylon 6 fibers at constant stress rate (1050 psi/sec).

demonstrated directly by Fig. 1. The primary tasks of the atomistic theories are (1) predicting the relation between the applied stress and the bond rupture rate and (2) predicting the accumulation of broken bonds at which catastrophic rupture will occur.

S. N. Zhurkov [5], noting that the creep lifetime of most solids varies exponentially with the applied stress, has proposed a general theory of fracture in which bonds are ruptured by a thermally activated, stress-aided process which continues until there are insufficient bonds remaining to maintain the specimen's structural integrity. Zhurkov's equation for time-to-break  $\tau$  under a constant external stress  $\sigma$  takes the form of an Arrhenius relation:

$$\tau = \tau_0 \exp \left\{ \frac{U - a\sigma}{kT} \right\} \quad (1)$$

where  $\tau_0$ ,  $U$ , and  $a$  are material constants,  $k$  is Boltzman's constant, and  $T$  is the absolute temperature. The novelty of this formulation lies in the numerical values found for the constants  $\tau_0$  and  $U$ ; these were found to be close to the natural period of lattice oscillations and interatomic binding energy, respectively, for almost all materials. Zhurkov felt that this correlation was not fortuitous but rather an indication that stress-induced thermal bond dissociation is the controlling factor in fracture with such mechanisms as chain conformational change and internal stress relaxation playing secondary roles which do not effect the material's lifetime under stress. The constant  $a$  in Equation 1 was interpreted as a measure of the "effectiveness" of the stress in overcoming the bond activation barrier  $U$ ; as such,  $a$  is a stress-concentration factor related on the internal stress distribution in the material. The thermofluctuation model, then, involves the breakage of bonds under the influence of an applied stress at a rate which varies exponentially with the magnitude of the stress.

Such a hypothesis is readily checked by EPR spectroscopy and in fact Zhurkov reports [1] that EPR tests have corroborated the constant-temperature relation

$$dn/dt = \alpha \exp(\beta\sigma) \quad (2)$$

where  $\alpha$  and  $\beta$  are constants and  $dn/dt$  is the rate of free radical production.

However, we were able to obtain strict agreement with this equation only for the constant load rate loadings of the type reported here in Fig. 2. Numerical differentiation of this data up to within about 95% of the stress to fracture gave an approximate exponential relation between the rate of bond breakage and the instantaneous engineering stress. It appears that equation 2 is valid only for select loading modes and must in general be applied with care. At constant stress and temperature, for instance, equation 2 predicts a constant rate of bond breakage: Zhurkov's data for Nylon 6 [6] predicts that  $6.3 \times 10^{15}$  bonds will be ruptured per second at room temperature and 100 ksi stress, in marked contradiction with Fig. 1, which shows an approximate asymptotic curve rather than a straight line for this temperature stress state. Careful investigation reveals that the shape of the asymptotic part of this curve is roughly exponential with stress at high stress levels.

It should be mentioned that EPR data should not be left uncorrected for such effects as free radical decay, which occurs continuously throughout the loading test. Careful tests, however, show conclusively that the rate of bond rupture varies widely throughout a constant-stress test. The bond breakage decays monotonically from an initial value of approximately  $10^{15}$  bonds/second to nearly zero as seen in Fig. 1. Roylance *et al.* [3] have demonstrated that the quasi-steady state value of the free radical concentration shown in Fig. 2 is exponential in the stress. Indeed, the authors suspect that this result might also be what Zhurkov *et al.* have reported. In reference [7] they imply that their results are not of the radical formation rate per se but of the radical concentration two minutes after application of a stepwise load. Therefore, their data might also be interpreted as concentration of radicals instead of formation rate. The decrease in bond rupture rate during the creep test of Fig. 2 is likely due to stress redistributions caused by changes in morphology, molecular bond rupture, deformation, etc. In addition, there is increasing evidence that the bond rupture rate rises markedly just prior to catastrophic rupture of the sample. Such observations are clearly not in accord with equation 2.

### The Knauss Fracture Model

There have been several attempts over the past several decades to apply the theory of reaction rates to molecular bond rupture in polymers [8–10]. Such models generally assume that bond rupture obeys first order kinetics (rate of rupture proportional to number of bonds remaining) where the rate constant varies exponentially with stress and temperature in a manner similar to equation 1. These analyses are capable of considerable elaboration; such effects as chain orientation and bond recombination can be included and a good many material constants inevitably appear in the formulation. Perhaps the most problematical aspect of these theories

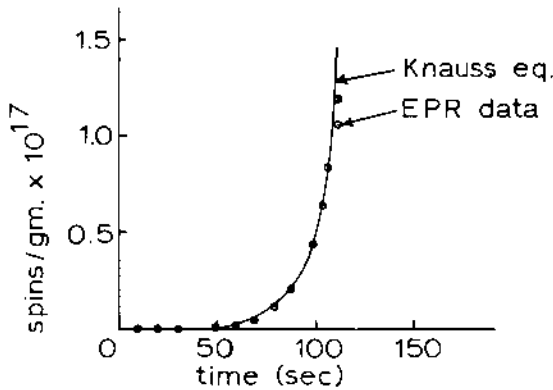


Figure 3. Knauss equation and EPR data for constant stress rate test (1050 psi/sec).

is the description of the stress actually experienced by the chemical bond and the relation between this atomic stress and the external macroscopic stress. Of the several rate-process fracture models available, that of W. G. Knauss [11] was selected for discussion here since his formulation of the rupture kinetics is representative and his solution of the atomic stress distribution problem is novel and promising.

The Knauss formulation is a blend of atomistic and continuum theories in which bond rupture is described by reaction-rate theory and the critical accumulation of broken bonds at which catastrophic fracture occurs is governed by the familiar Griffith–Rivlin–Thomas criterion. The resulting equations involve three material constants and Knauss found that these constants could be chosen so as to bring his theory into agreement with the failure envelope of the SBR rubber he was investigating.

Although the rubbery amorphous polymer to which Knauss applied his model and the highly oriented drawn fibers from which the EPR data were taken differ greatly in morphology, the Knauss model is sufficiently general that a direct EPR investigation of its atomistic facet is quite revealing. In the atomistic part of his theory, Knauss postulates the existence of certain inherent “weak” regions in the polymeric solid in which bond rupture occurs preferentially. The chemical bonds in this region are characterized by a statistical distribution of strengths and the probability of single-bond rupture or deformation is written in terms of the elastic energy stored in the bonds rather than the difficult-to-determine local stress. The statistical distribution of bond strengths may allow for (time-independent) morphological chain orientation and the stored-energy approach allows for time-dependent viscoelastic loading histories. The theory leads to a bond rupture rate equation of the form

$$\frac{dn}{dt} = -\lambda \left\{ \frac{n}{\gamma} \cosh \frac{W(t)}{NkT} - \sinh \frac{W(t)}{NkT} \right\} \quad (3)$$

where  $n$  is the number of broken at time  $t$ ,  $W(t)$  is the elastic strain energy per unit volume stored in the chemical bonds at time  $t$ ,  $N$  is the number of bonds per unit volume, and  $\lambda$  and  $\gamma$  are material constants.

The constant stress rate test was chosen for the initial EPR fit. Values of the elastic energy  $W$  were recorded as functions of time during the test by numerical integration of the stress-strain data, corrected for viscous dissipation by loss factors which had previously been determined from hysteresis tests. As seen in Fig. 3, an acceptable fit of the Knauss equation to the EPR data was found for the choice of constants  $\gamma = -1.02 \times 10^{17}$ ,  $\lambda = 7.22 \times 10^{13}$ , and  $NkT = 467$  psi.

The exponential-appearing nature of the EPR curve for constant stress rate tests, however, makes it particularly easy to fit the essentially exponential rate-process models of Zhurkov or Knauss. When the values of the constants chosen above are used with the values of  $W(t)$  corresponding to a constant stress test, the Knauss formula produces the curve seen in Fig. 4.

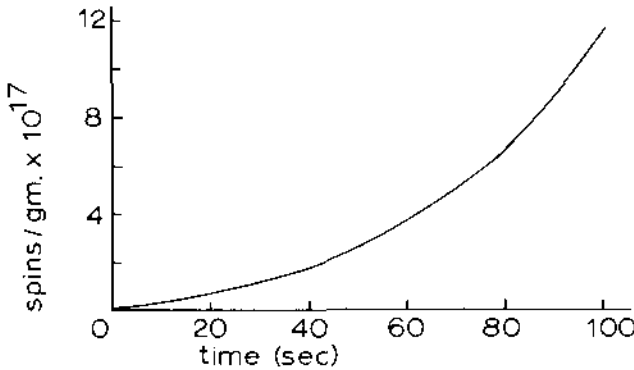


Figure 4. Knauss equation for constant stress test (100 ksi).

Comparison of Figs. 1 and 4 then shows the obvious contradiction, both in numerical magnitude and curve shape, between the model and the experimental data.

#### 4. Discussion

It is evident that neither the Zhurkov nor the Knauss atomistic theories provide a physically realistic model of stress-induced bond rupture for other materials. Since both models are essentially based on the well-established rate process relation giving the probability of thermo-mechanical dissociation of a chemical bond as an exponential in the perturbing force on the bond, their failure in this case is likely due to an incorrect assessment of the atomic stress distribution. Zhurkov's model in effect assumes a uniform stress distribution; Knauss' model permits a statistical distribution of atomic stress but assumes this distribution remains unchanged during the loading history.

It appears then that neither model is consistent with the morphology of drawn fibers where fracture seems to take place in the more or less amorphous "tie chain regions" which connect the folded-chain crystallites [12]. These tie chain regions consist of molecules of various lengths whose ends are fixed in the adjoining crystallites. As the fiber is strained, the shorter tie chains are ruptured first, causing the load to be carried by the larger number of medium-length chains. Under constant stress, the bond rupture rate would then decrease as in Fig. 1; under constantly increasing stress these chains would also be broken, producing an increasing rupture rate as seen in Fig. 2.

Preliminary quantitative results from such a mode, based on the response of a normal distribution of chain lengths to various strain (as opposed to stress) histories, are in essential agreement with the EPR data [13]. This model is being improved and the results will be reported separately.

## Acknowledgment

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## RÉSUMÉ

On a montré récemment que les techniques de spectroscopie électronique à résonance paramagnétique peuvent être utilisées avec succès pour la détection des ruptures des liaisons atomiques au cours de la rupture des matériaux polymères; ces techniques ont permis de jeter de nouvelles lumières sur les mécanismes moléculaires qui interviennent au cours de la rupture de ces matériaux.

En particulier, la méthode permet de procéder à un contrôle, sur une base fondamentale, de quelques théories atomiques de la rupture des polymères.

Dans le présent mémoire, on procède à un tel contrôle de deux théories des plus typiques, celles de Zhurkov et de Krauss.

On démontre que ces théories ne conduisent pas à des modèles physiquement représentatif du mécanisme de rupture des polymères à fibres orientées. On suggère que cette inadaptation résulte de la structure morphologique particulière des polymères à orientation marquée.

## ZUSAMMENFASSUNG

Neuerdings wurde gezeigt, daß die Verfahren der elektronischen Spektroskopie erfolgreich für den Nachweis von Zerstörungen in den atomaren Bindungen während des Zerreißens von Polymeren herangezogen werden können. Sie führen somit zu wichtigen neuen Erkenntnissen über die molekularen Mechanismen der Zerstörung dieser Werkstoffe.

Im besonderen kann dieses Verfahren für eine grundlegende Kontrolle verschiedener atomistisch abgeleitet Theorien über den Bruch von Polymeren herangezogen werden. Im vorliegenden Bericht werden zwei dieser Theorien, nämlich diejenigen von S. N. Zhurkov und W. G. Krauss, überprüft.

Es wird gezeigt, daß diese Theorien kein physikalisch realistisches Modell des Bruchmechanismus von Polymerfasern geben, und es wird vorgeschlagen diesen Mangel an Zutrefflichkeit durch die spezielle morphologische Struktur der streng gerichteten Fasern zu erklären.