Characterization of Polymer Deformation and Fracture

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I. Kinetic Models of Polymer Fracture ........................................ 207
II. ESR Observations of Stress-Induced Bond Rupture in Polymers .... 209
   A. Fundamentals of ESR Spectroscopy .................................. 209
   B. Studies on Drawn Fibers ............................................. 210
   C. Other ESR Fracture Studies ........................................ 215
   D. Limitations of the ESR Method .................................... 215
III. Associated Studies .......................................................... 217
    A. Gel Permeation Chromatography .................................. 217
    B. Infrared Spectroscopy .............................................. 218
    C. Small-Angle X-Ray Scattering .................................... 218
    References ....................................................................... 219

I. KINETIC MODELS OF POLYMER FRACTURE

Although several useful phenomenological models of polymer fracture have been developed over the years, the materials scientist is compelled to seek out analyses that treat the fracture process from first principles. As an illustration of the sort of rate-process treatment often attempted, consider a thermally activated, stress-aided first-order process in which the concentration, \( N \), of unbroken main-chain bonds decreases with time according to

\[-dN/dt = KN \tag{1}\]
where the rate constant $K$ is given by the absolute theory of reaction rates [1] as

$$K = \frac{kT}{h}\exp\left[-(\Delta G^\dagger - \gamma \psi)kT\right]$$  \hspace{1cm} (2)

Here $k$ is Boltzmann's constant, $T$ is the absolute temperature, $h$ is Planck's constant, $\Delta G^\dagger$ is the activation free energy for bond dissociation, $\gamma$ is the activation volume, and $\psi$ is the local stress on the bond. Introducing the activation enthalpy and entropy through the familiar relation $\Delta G = \Delta H - T\Delta S$, Eq. (2) can be written

$$K = K_0\exp\left[-(\Delta H^\dagger - \gamma \psi)/kT\right]$$  \hspace{1cm} (3)

where

$$K_0 = \frac{kT}{h}\exp(\Delta S^\dagger/k)$$  \hspace{1cm} (4)

In Eq. (3) the temperature dependence of the preexponential term is usually neglected in comparison with the much stronger temperature dependence in the exponential term.

To proceed, one must now assume some functional relationship between the molecular stress $\psi$ and the macroscopically imposed stress $\sigma$, and then integrate Eq. (1) to the limit of zero surviving bonds in order to predict the rupture time for the polymer. A particularly simple approach would be to assume that the molecular stress is uniform and unchanging, and equal to the imposed stress. The rate constant $K$ is then truly constant, so that Eq. (1) integrates to

$$N = N_0\exp(-Kt)$$  \hspace{1cm} (5)

The mean time to rupture of a given bond in the above kinetic process is easily shown [2] to be just the reciprocal of the rate constant $K$. If one now claims that the time to rupture of the stressed solid is equal to the average time for bond scission, one obtains the useful and well known Zhurkov equation [3]

$$\tau = \tau_0\exp\left[(U - \gamma \sigma)/kT\right]$$  \hspace{1cm} (6)

Here $\tau_0 = 1/K_0$ is close to the period for atomic bond-pair vibrations and the apparent activation energy, $U$, for the fracture process is related to the activation enthalpy for bond dissociation $\Delta H^\dagger$.

The above derivation is wholly unrealistic, of course; one is certain that the molecular stress must vary widely within the material depending on the local morphology, and that it will change with time due to molecular rearrangements and scissions under stress. The parameters $\tau_0$, $U$, and $\gamma$ can be chosen so as to bring Eq. (6) into agreement with creep-rupture data for a wide variety of polymers, metals, and ceramics, but the parameters so
chosen then reflect not only the kinetic properties of the interatomic bond but the morphology of the material as well. The activation volume is particularly structure sensitive. It is a measure of the effectiveness of the stress in overcoming the activation barrier for scission, and is thus strongly related to the stress-concentrating properties of the internal defect structure.

Even though Eq. (6), as well as many other considerably more elaborate rate-process fracture models, can be brought into line with experimental observation, one often feels that this is more a measure of the obliging nature of the exponential rate equations with their several adjustable parameters than any inherent realism of the model. All such models must involve certain assumptions concerning the nature of the bond dissociation process and distribution of molecular stress which until recently have been impossible to verify, and this has prevented the wide acceptance of any of these treatments. Only in the last decade has the missing element—direct experimental observation of the molecular fracture processes—been available to guide the development of more realistic models. Electron spin resonance (ESR) spectroscopy has proven particularly valuable in this regard.

II. ESR OBSERVATIONS OF STRESS-INDUCED BOND RUPTURE IN POLYMERS

A. Fundamentals of ESR Spectroscopy

As the theory of electron spin resonance spectroscopy is extensive and involved, only a brief description of its essential principles can be given here. The book by Poole [4] includes an extensive bibliography of the pertinent literature. ESR is a form of microwave absorption spectroscopy in which transitions are induced between the Zeeman energy levels arising from the interaction of an assemblage of paramagnetic electrons with an externally applied magnetic field. Upon application of a magnetic field of strength \( H \), the normally degenerate spin of an electron is split in two levels separated by an energy difference \( \Delta E \) given by

\[
\Delta E = g\beta H \tag{7}
\]

where \( g \), the spectroscopic splitting factor, is \( \sim 2.0023 \) for a free electron, and the Bohr magneton \( \beta \) is a fundamental measure of the electron's magnetic character. At thermal equilibrium the electron populations of these two energy levels are given by Boltzmann statistics as

\[
\frac{N^+}{N^-} = \exp(-\Delta E/kT) = \exp(-g\beta H/kT) \tag{8}
\]

At ordinary temperatures \( g\beta H \ll kT \), producing a slight excess of electrons in the lower energy state.
The Planck–Einstein relation states:

$$\Delta E = h\nu = g\beta H$$  \hspace{1cm} (9)$$

Transitions between the two energy levels may be induced by incident radiation of frequency $\nu = g\beta H/h$, which is right circularly polarized along the magnetic field axis. These transitions occur in either direction with equal probability but, since the lower state is more densely populated, the upward transitions outnumber the downward. If thermal equilibrium as given by Eq. (8) is maintained by spin-lattice relaxations, some electrons in the upper state may relax to the lower state by giving their excess energy to their surroundings. This produces a net energy loss from the incident radiation, which may be detected and displayed by suitable instrumentation. In practice, ESR spectrometers display energy absorption as a function of magnetic field strength $H$ with the frequency $\nu$ held constant.

In order to exhibit paramagnetic resonance absorption, a solid specimen must contain electrons that are unpaired, i.e., that are not interacting with neighboring electrons to such an extent as to be subject to the restrictions of the Pauli exclusion principle. When homolytic scission of a covalent bond in a polymer takes place, the two electrons that had been paired in the bond become uncoupled, forming two free radicals that can be detected and identified by ESR spectroscopy. The study of free radical chemistry is a very active research area and ESR has become a standard analytic technique in this field. Many different types of degradation processes have been investigated extensively: thermal degradation; ultraviolet irradiation; neutron bombardment; $\gamma$ irradiation; etc.

The single resonance peak predicted by Eq. (9) is often split into a series of peaks known as hyperfine structure, due to the electron’s ability to interact with the magnetic moments of nearby nuclei as well as with the externally applied field. Since this hyperfine structure is characteristic of the particular active nuclei, it provides a “fingerprint” of a free radical’s local chemical environment and can therefore be used to identify the radical.

B. Studies on Drawn Fibers

1. General

A principal requirement for the successful detection of stress-generated radicals is that they be created in sufficient numbers during the fracture process to exceed the sensitivity limit of the ESR spectrometer. In general, this requirement is not met. Polymers with amorphous or spherulitic structures tend to fracture in a localized manner, usually near an internal or surface imperfection that serves as a stress riser. The number of molecular chains
passing through a given cross section is approximately $10^{14}$ cm$^{-2}$, and the number of scissions created by the passage of a planar crack through the section of a typical specimen is generally so low as to escape detection by ESR. Large radical concentrations can be achieved in most polymers by grinding them so as to produce a large amount of fracture surface, but the stress states operative during grinding are very complex and not conducive to analytic modeling.

To date, the material most amenable to ESR analysis during uniaxial tension has been found to be drawn polyamide fibers. The morphology of these materials is one of more or less aligned fibrils, these fibrils being columnar series of relatively rigid folded-chain lamellar fragments connected by molecular tie chains of various lengths [5]. The crystallites act as crack stoppers in a manner analogous to the reinforcing fibers in composite materials, so that the fracture damage occurs globally throughout the specimen rather than being restricted to a single locality. In addition, the extensive hydrogen bonding present in polyamides serves to inhibit interchain separation, forcing the crack to pass through the relatively weak tie-chain regions and cause covalent bond scission.

Figure 1 is a typical presentation of the ESR spectra generated by a series of stepwise-increasing stresses applied to drawn nylon 6 fibers. ESR spectrometers commonly employ phase-sensitive detection as a means of improving their sensitivity, and these spectra represent a derivative presentation of the microwave absorption. The number of radicals contributing to a given spectrum can be computed by a double integration of the derivative presentation, and comparison of the result with that of a standard such as diphenylpicrylhydrazine containing a known and stable number of radicals. The

\[ \text{FIG. 1 Growth of ESR spectra during stepwise loading of drawn nylon 6 fibers Specimen was predesiccated and tested at 40°C in a dry nitrogen atmosphere. (From [13].)} \]
number of radicals created during fracture depends on time, temperature, stress, and many other factors, but the approximate number of spins observed at the time of final rupture of nylon fibers at room temperature is approximately \(10^{18}\) spins/cm\(^3\).

The spectrum of Fig. 1 is identical to that observed in nylon after other forms of degradation, whether thermal, radiative, or mechanical. It has been shown [6] to be quartet arising from the radical —CO—NH—CH—CH\(_2\)— (\(\sim 26\) gauss hyperfine splitting with the one \(\alpha\) and the two \(\beta\) protons), and a superimposed singlet due to —CH\(_2\)—COH—NH—CH\(_2\)—. These radicals are clearly not at the original scission site, but at more stable sites along the chain to which they have migrated. Originally formed radicals in nylon have been observed after grinding at cryogenic temperatures, but the tendency of radicals to undergo transfer and other secondary reactions after fracture is perhaps the most serious limitation of ESR's use in polymer fracture studies.

Unpaired electrons are highly unstable, and seek to form bond pairs either by combination with other radicals or by reaction with other chemical groups. Radical decay occurs by a relatively rapid first-order kinetic process in the presence of excess oxygen, but can be shifted to a much slower second-order process by testing in an inert atmosphere. A typical data acquisition scheme involves determining the appropriate rate constants, and then correcting the observed radical count for any decay that may have occurred. The decay kinetics should be measured with the specimen under load, since the migration and combination mechanisms are influenced by specimen stress.

Data acquisition is made much more convenient by avoiding the need to scan the full ESR spectrum at various times during loading. One often finds that the height of a single selected peak on the derivative presentation is proportional to the second integral of the spectrum, so that the spectrometer is simply tuned to sit on the chosen peak during loading. This peak is then converted to spin count by the experimentally determined proportionality factor. Computerized data handling techniques make the entire process much more efficient.

2. The Lloyd–DeVries Bond Rupture Model

Most of the earlier rate–process polymer fracture models predict an accelerating rate of bond scission under constant stress, since scission of a particular bond serves to increase the molecular stress borne by its neighbors. The ESR observations are in direct contradiction to this prediction, however. As seen in Fig. (2), the rate of bond rupture in nylon fibers under constant stress decreases monotonically with time. DeVries, Lloyd and Williams [7] interpreted the decreasing rate of bond rupture in creep tests in terms of
a tie-chain contour length model, in which those molecular tie chains that are too short to accommodate a given specimen strain rupture, transferring their load to less critically stressed chains.

Pursuing this idea, Lloyd [8] used the ESR spectrometer to count the percentage of total fracture radicals generated during successively larger increments of specimen strain, thus developing a criticality histogram for the material (Fig. 3). The width of this histogram is an important structural parameter, having a strong influence on the ultimate tensile strength of the material. It is a function of the specimen's thermomechanical processing history, and is also influenced by the specimen testing temperature. Based

FIG. 2 Free radical production during a constant stress (690 MPa) test of drawn nylon fibers at room temperature. (From [13].)

FIG. 3 Radical production histogram for nylon 6 fibers from step-strain tests at room temperature. (From [8].)
on ESR measurements of these histograms, Lloyd developed a rate-process model in which the distribution is considered as a large number of discrete subsegments and a rate equation similar to Eq. (1) written for each of them. A computer is then used to tally the extent of bond scission in each subsegment at each of a number of discrete time increments. The resulting model contains a certain number of adjustable parameters chosen so as to bring the predictions of bond rupture into line with selected ESR observations, but once chosen were able to predict the bond rupture kinetics for a wide variety of arbitrary load-temperature histories.

Lloyd's model is noteworthy principally in that it combines the Eyring description of covalent bond dissociation kinetics with an experimentally determined measure of the internal stress distribution of the material. Given the complex nature of even the relatively simple fiber morphology, one is not surprised that a computer treatment of the kinetic equations is necessary. Although developed principally as a means of predicting bond rupture during the loading process, the Lloyd model is also capable of predicting the final specimen fracture. One simply follows the scissions numerically until no unbroken bonds remain in any of the distribution subsegments. The present author recently employed Lloyd's model, along with the numerical parameters chosen by him to fit his "nylon 6 # 1" material, to predict creep-rupture times for a series of constant stresses and temperatures. These data are plotted in Fig. 4, where it is seen that they show the linear variation of log lifetime with applied stress predicted by Eq. (6). Those data permit a selec-

![Graph showing predicted creep lifetimes for nylon 6 fibers using the Lloyd-DeVries bond rupture model.](image)
tion of the parameters $\tau_0$, $U$, and $\gamma$ in Zhurkov's equation, and the resulting expression is then capable of predicting final rupture times for a variety of loading histories.

C. Other ESR Fracture Studies

Although fiber studies of the sort described above have been most influential in leading to improved understanding of molecular fracture processes, much useful though more qualitative information has been obtained by ESR experiments on less tractable systems. Recently reviewed by DeVries and Roylance [9], these have included studies of grinding and abrasion of spherulitic polymers and elastomers, ozone attack on stretched rubber, deformation of precrystallized rubber at low temperature, and location of the fracture phase in thermoplastic elastomers.

D. Limitations of the ESR Method

In spite of the rather extensive use made of ESR in recent years as a fracture analysis tool, and the number of satisfying results claimed by its proponents, the technique does have certain limitations which tend to prevent full confidence in its measurements. It is worthwhile to list the most serious of these:

1. Most polymeric systems do not suffer enough chain scission during fracture to permit ESR monitoring, so general statements about fracture in systems other than drawn nylon are tenuous. In some systems, bond rupture occurs only at a single small region, as discussed earlier. In other systems, fracture may occur largely as a result of large-segment rearrangements with scission playing only a peripheral role, and in still other systems scission may not occur at all.

2. Heterolysis, rather than homolysis, may occur or even dominate during scission. These events would not produce ESR-detectable radicals. Ozone attack in rubber is generally considered heterolytic, for instance, although radicals are observed as well, presumably via secondary reactions.

3. As mentioned earlier, it is common to correct for the ESR radical count for decay by employing appropriately determined kinetic models. However, it cannot be guaranteed that certain decay mechanisms are not operative, because they may be too rapid to be observed by the spectrometer. Radical migration to the stable side-chain position is an example of an extremely rapid radical reaction. If such reactions are involved in radical decay, the ESR spectrometer would underestimate the extent of bond scission.

4. Another form of secondary radical reaction that would lead to underestimation of scission involves not radical decay but rather a radical-induced
rupture of an adjoining chain without the creation of a new radical. Using a main-chain rupture in a polyethylene sequence for illustration, we see:

\[
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{C} - \text{C} \quad \rightarrow \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\end{array}
\]

The active radical may now abstract a proton form an adjoining chain:

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{C} - \text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

+ \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}

The presence of the side-chain radical weakens the main-chain bonds once removed from the radical, since upon rupture one of the newly unpaired electrons may enter into a \( \pi \) bond with the radical:

\[
\begin{array}{c}
\text{C} - \text{C} - \text{C} \\
\text{H} \quad \text{H} \quad \text{H} \\
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{C} = \text{C} \quad \rightarrow \\
\text{C} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \\
\end{array}
\]

The above rupture would be expected due to the weakening of the bond. An ESR spectrometer would see only one scission by counting the radicals formed to this point, while two chains would have been ruptured. The process can continue, with the result being that the spectrometer may underestimate the scissions by orders of magnitude. In fact, Zhurkov [10] has argued that this is in fact the case. Such a conclusion, if thoroughly verified, would clearly undermine the entire applicability of the ESR method.

(5) Even if the above problems are circumvented, ESR is deficient in that it has no ability to tell just where in the material the scissions are occurring. Although it has been possible to place the nylon fracture radical in the amorphous rather than the crystalline portion of the fiber structure, ESR cannot tell whether bonds are being broken at every tie-chain containing region or at relatively more dispersed positions, perhaps at the defects associated with microfibril ends. This is a distinction of considerable importance to the proper modeling of the fracture physics.
III. ASSOCIATED STUDIES

Given the above-mentioned ambiguities in the ESR results, it is not surprising that in recent years attention has turned to associated analytical techniques that can corroborate or modify the fracture models derived from ESR data. Some of the more active of these studies will be mentioned briefly here. The reader is also directed to chapters in this volume dealing with stress-active infrared absorption spectroscopy and mass spectroscopy.

A. Gel Permeation Chromatography

The ESR measurement of approximately $10^{18}$ scissions/gm at high fracture is high enough to expect that a measurable decrease in molecular weight may accompany fracture in nylon fibers. To investigate this possibility, a specimen of nylon that had been loaded to fracture at room temperature was submitted to gel permeation chromatography (GPC) analysis using $m$-cresol at $95^\circ$C as the solvent. The molecular weight distribution was obtained from the elution curve by using the “Q factor” method in reference to a polystyrene calibration. Figure 5 shows the molecular weight distribution of the fractured specimen, as well as that of a virgin specimen that had received no load. A reduction in the high molecular weight component is apparent, and the number-average molecular weight as computed from these chromatograms drops from 34,800 to 30,000. This corresponds to $(6.02 \times 10^{23})(1/30,000) - (1/34,800) = 3 \times 10^{18}$ scissions/gm, in rather good agreement with the ESR.

![Graph](image.png)

FIG 5. Effect of fracture on molecular weight distribution—GPC analysis. ⋯, fractured; ———, virgin.
measurements. This value is also in agreement with viscosity molecular weight measurements by Crist [11]. Such tests lend credence to the ESR values, and provide some assurance that the more serious limitations to the ESR method described earlier are not operative in polyamides.

Although not as sensitive as ESR, GPC is not affected by secondary radical reactions and is thus more definitive. GPC also provides information as to which chains among the molecular weight distribution are broken during fracture, and this information may be of value in future model development.

B. Infrared Spectroscopy

As a result of secondary radical reactions following fracture, chemically distinct end groups may be formed at the scission site. In the earlier discussion of secondary reactions, CH₃ groups and unsaturated bonds were formed; other possibilities exist as well. Zhurkov [10] has reported success in monitoring the accumulation of such scission-induced groups by means of infrared spectroscopy, and some of his data show a large difference between broken bonds and observed radicals in polyethylene. IR shares GPC's advantage of monitoring stable entities rather than the marginally stable free radicals. Like GPC, IR is not as sensitive as ESR in monitoring fracture. However, the greatly enhanced sensitivity of the newly available Fourier Transform IR spectrometers promises to mitigate against this deficiency.

C. Small-Angle X-Ray Scattering

In another of his many pioneering investigations of fracture, Zhurkov [12] has reported success in using small-angle x-ray scattering (SAXS) to monitor the accumulation of microcracks developed during fracture, supposedly as a result of the coalescence of molecular scissions. Since SAXS is able in principle to measure the size, concentration, and spatial orientation of these microcracks, it offers promise of being able to unravel the problem mentioned earlier as to the spatial distribution of scission events. Zhurkov's data indicate that the microcrack concentration is much lower than the radical concentration, approximately 10¹⁵ cm⁻³. This number is approximately equal to the number of microfibril ends in the fiber structure, in support of Peterlin's contention that damage is associated with strain in-homogeneities in these regions. Such a finding tends to weaken the tie-chain contour length models, which states that scission is predicted more uniformly throughout the specimen. The correct balance between these two viewpoints is currently a matter of some controversy, and work is now proceeding aimed at its resolution.
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