

## Uses of Electron Paramagnetic Resonance in Studying Fracture

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### Synopsis

The uses of electron paramagnetic resonance (EPR) in studying aspects of polymer fracture are discussed. The sensitivity of EPR is such that all phases of fracture are not amenable to investigation by these means. This paper attempts to define those areas where the authors' experience would indicate that success might or might not be expected. A discussion of the difference between the tensile fracture of drawn polymer fibers, in which strong signals are obtained, and cast and molded materials is given.

### INTRODUCTION

The original studies of Zhurkov and his associates<sup>1,2</sup> in the USSR and the later work by Williams et al.<sup>3,4</sup> and Campbell and Peterlin<sup>5</sup> have demonstrated the usefulness of electron paramagnetic resonance (EPR) in studying polymer fracture. At first, this method would seem to open unlimited avenues for research and provide a panacea for fracture studies. There are, however, a number of areas where the authors have attempted to use this technique but have not met with much success. Because a number of groups have expressed interest in conducting studies using these methods, it was thought it might be well to describe the techniques developed. In addition, the areas of fracture research in which the authors' experience would indicate that EPR will or will not be likely to reveal much in the way of quantitative information will be discussed. Since some of these studies (where negative results were obtained) have interesting implications, it was thought it might be well to report some of these findings as well as some limits on the usefulness of the method so as to reduce duplication and repetition of searches along blind paths.

### BACKGROUND

EPR is a form of absorption spectroscopy in which electromagnetic radiation in the microwave region induces transitions between energy levels arising from Zeeman-type splittings in an assemblage of paramagnetic electrons. As such, it deals with systems of elementary particles which

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have a net electronic moment (unpaired electron spins). Thorough descriptions of EPR, its uses, and applications are found in several recent reviews and books.<sup>6-10</sup> In polymer materials, fracture under mechanically applied stress involving molecular bond rupture should result in the creation of free radicals and their accompanying characteristic unpaired electrons; thus, it might logically be studied by this method. An EPR analysis, however, has two practical requirements: sufficient number of free radicals must be produced, and the half-life of the free radicals formed must be long enough to record. The Varian E-3 equipment used in these tests operates in the x-band region ( $\sim 9.5$  ghz) and has a sensitivity of about  $5 \times 10^{10} \Delta H$  ( $\Delta H$ , the line width in gauss) spins under ideal conditions.

If one views a polymer as being composed of long more or less parallel chains looped together in an orderly array, then a polymer having the density and molecular structure of nylon would have approximately  $10^{14}$  chains passing through each square centimeter of area normal to the direction of the chains.<sup>5</sup> Assuming a covalent bond energy of approximately 80 kcal/mole and that a fracture surface can be approximated as a plane of such broken bonds, the theoretical fracture energy per unit area is roughly 250 ergs/cm<sup>2</sup>. Experimental macroscopic crack growth and tearing studies indicate a value more than an order of magnitude higher than this. It would appear, therefore, that fracture is more complex than a simple cleavage of atomic bonds along the fracture surface. Alternately, one can use the tabulated bond strengths along with the number of broken bonds to compute the ideal tensile strength of a polymer. If it is assumed that a few angstroms of displacement is sufficient to separate or rupture a bond, one finds that a polymer should possess a tensile strength of the order of  $10^6$  psi (see the discussion by Peterlin<sup>5</sup>). This estimate is one or two orders of magnitude higher than experimental values. This latter discrepancy might be reasonably attributed to the inhomogeneity of the internal stress field due to such factors as local stress concentrations, interchain entanglements, folds, or alternating amorphous regions between regions of crystallinity. There are several possible explanations for the large surface energy discrepancy. (1) Bonds will be broken throughout the volume of the specimen, not solely on the single plane of major cleavage. Energy is required to rupture these bonds as well as those nearer the fracture surface. (2) Bond rupture or cracks might nucleate at a great many sites but not all of them progress to macroscopic size and subsequent fracture. (3) The true fracture surface might be much larger than the apparent area due to the roughness of the fracture surfaces. (4) Other dissipative functions such as plastic or viscoelastic mechanisms are operative in front of a progressing crack. (5) Secondary (van der Waal) bonds are broken and absorb energy during the untangling of the chains.

It is likely that all of these mechanisms are active to some extent and one might expect the gross behavior to be the summation of simultaneous effects of several phenomena such as chain slippage, viscous energy dissipations, and bond scission. These processes would be expected to vary with poly-

mer type, sample crystallinity, and testing conditions, e.g., strain rate, temperature, humidity, atmosphere. EPR spectroscopy, being able to detect and monitor bond breakage, should be a powerful tool for elucidating the relative importance of these various mechanisms and how they vary with testing or service conditions.

### APPARATUS AND EXPERIMENTAL PROCEDURES

In addition to the Varian E-3 electron paramagnetic resonance spectrometer used in these studies, auxiliary equipment included a variable temperature control unit and a programmed loading fixture. The former maintained the sample at any fixed temperature between  $-180^{\circ}\text{C}$  and  $+300^{\circ}\text{C}$  and permitted control of the atmospheric environment. The loading frame and hydraulic servo system was designed to load the sample at constant stress, strain, strain rate, stress rate, or with relative ease, any reasonable preprogrammed loading.

For sensitivity reasons, the spectrum normally recorded on an EPR spectrometer is the first derivative of the absorption curve. Its second integral is proportional to the number of unpaired electrons in the cavity. In this study this integration was numerically accomplished on a Univac 1108 computer. A comparison of this double integral with that for the "pitch" standards provided by Varian Associates gave a quantitative measure of the free radicals (ruptured bonds) present. It was determined, however,

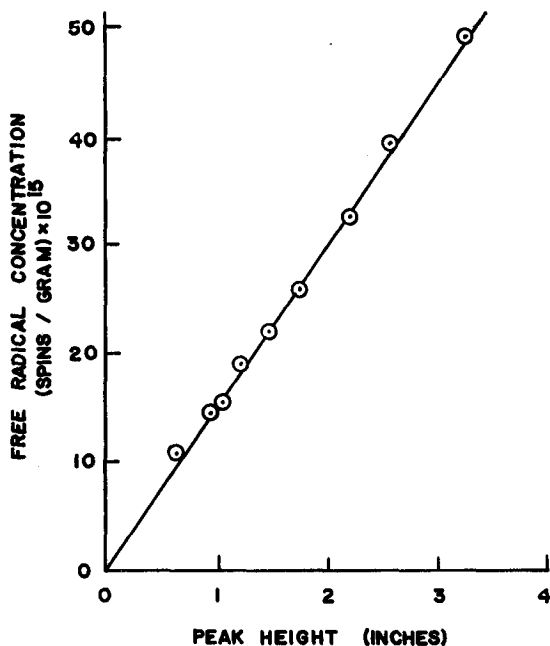


Fig. 1. A comparison of the free-radical concentration (obtained from twice integrating the spectra) with the height of the first peak.

that in some cases this process could be substantially simplified. It can be shown that for a Gaussian or Lorentz distribution, the peak height of the derivative of the function is proportional to the first integral. For polymers with simple spectra it often was possible, through comparison with the double integral, to show experimentally that the peak height of the spectra was proportional simply to the second integral. Figure 1 shows the number of unpaired electrons (spins) determined by numerical double integration versus peak height for nylon 6. Similar results were obtained for nylon 66 and polyethylene. These results greatly facilitate the experimental observations. The rate of bond rupture can as a result be monitored by tuning the spectrometer to the field strength and frequency of one of the spectra peaks and observing its growth as a function of time.

### OUTLINE OF STUDIES

These versatile techniques have been found to be useful in a wide variety of studies of fracture and other types of mechanical degradation or failure. Since the authors began using this tool approximately two years ago, they have begun investigations into: fracture of polymer materials under tensile stress; post-fracture analysis of materials after combined loading; fracture remnants from explosive and impact damaged specimens; fracture surfaces originating from machining, grinding, and crushing operations; cumulative damage in polymers during cyclic and other programmed loadings; the role of environment, such as temperature, humidity, atmosphere (i.e., inert gases, oxygen, and ozone) upon free radical concentrations; the effects of various solvents upon stress crazing in plastics; and free-radical concentration in living tissue, such as collagen.

In addition to studying the results of mechanical degradation processes, certain effects of  $\gamma$ -radiation have also been explored. In this connection it may be observed that a comparatively large amount of work with EPR had been carried out on effects of radiation upon materials. Comparison with these studies permitted a correlation and standardization for our subsequent studies of mechanical degradation because of the similarity in the spectra.

This paper, however, is restricted primarily to discussion of some positive and negative results encountered in attempting to correlate quantitative measurement of free-radical concentration with mechanically induced microscopic flaw formation.

## EXPERIMENTAL RESULTS

### Tensile Fracture

The microwave cavity of the E-3 spectrometer is approximately 1.1 cm in diameter and 2.5 cm in length. The sample itself is usually restricted to less than 0.9 cm in diameter, which corresponds to a cross-sectional area of approximately 0.5 cm<sup>2</sup>. Hence, based on the background discussion above,



Fig. 2. Typical spectrum obtained during tensile loading to fracture of nylon 6 fibers.

one might expect a plane passing perpendicular to the axis of such a cylindrical sample would cut approximately  $10^{14}$  bonds resulting in twice that number of free radicals.<sup>5</sup> Because approximately 1 in. of the specimen length is in the microwave cavity, if bond rupture takes place at points removed from the primary fracture surface or if this surface is very irregular, the free radical concentration could be substantially increased. On the other hand, if untangling rather than fracturing of the chains takes place or if the crack can select a path requiring fewer chain scissions, the number could very possibly be reduced.

Studies were conducted on a variety of polymers in molded, cast, extruded, and drawn fiber forms. Except for the drawn fibers, only barely detectable signals, at best, have been obtained in any of these materials. In these latter highly crystalline and oriented materials, strong signals were

developed by tensile loadings (Figs. 2-5). Such signals were first produced at stresses greater than approximately 60% of the ultimate fracture stress. Figures 2, 3, 4, and 5 show spectra for nylon 6 (drawn 4:1), nylon 66; polyethylene fibers, and polyester fibers, respectively. The nylon 6 was provided by Allied Chemical Company, the Nylon 66 by DuPont, and the

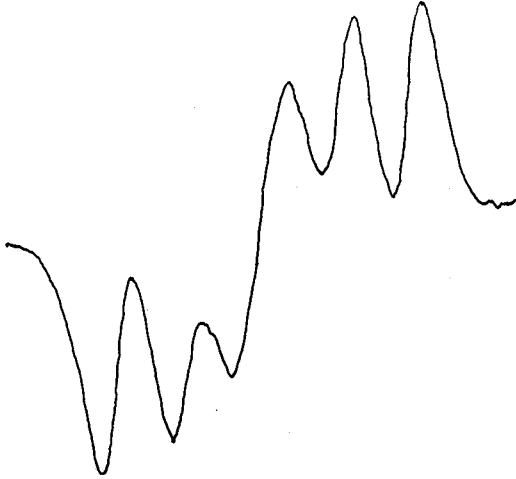


Fig. 3. Typical spectrum obtained during tensile loading to fracture of nylon 66 fibers.

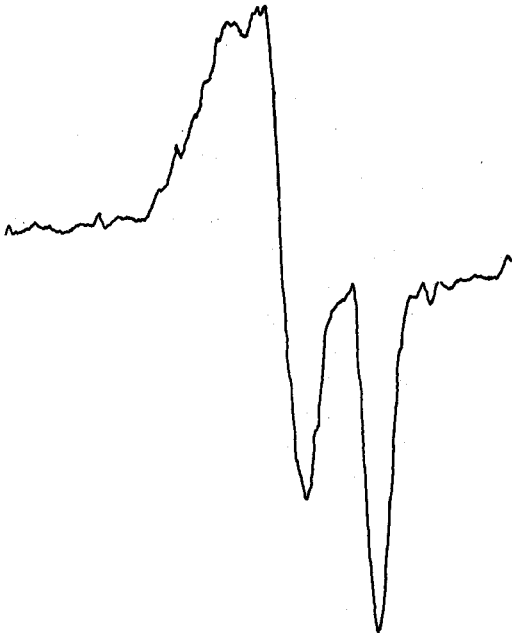


Fig. 4. Typical spectrum obtained during tensile loading to fracture of polyethylene fibers.



Fig. 5. Typical spectrum obtained during tensile loading to fracture of polyester fibers

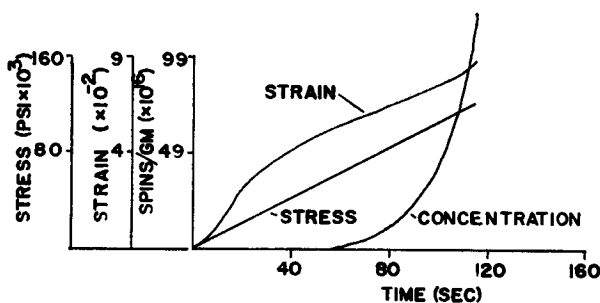


Fig. 6. Computer-reduced data from a constant load rate test of nylon 6 fibers.

polyethylene and polyester fibers by American Viscose Division, FMC Corporation. All were stated by their manufacturer to be of high purity. For example, x-ray fluorescence studies of the nylon 6 fibers indicated that the only inorganic ions present in substantial amounts were copper, 61 ppm; iodine, 0.2%; and all other metals less than 2 ppm. To date, nylon 6 has been studied most extensively. We shall discuss it briefly as being somewhat typical of the behavior of polymeric fibers.

With the current spectrometer sensitivity, the EPR spectra develop at stresses significantly below the fracture stress. At fracture, the nylon 6 samples typically generated  $10^{17}$  free radicals/cm<sup>3</sup> of material in the cavity. Figure 6 shows the increase in stress, strain, and free-radical concentration (obtained from computer reduction of the data) for a constant-stress rate test. The kinetics of the bond-rupture process has been interpreted by Zhurkov<sup>1</sup> in terms of a pseudo-empirical relation in which, at constant temperature,

$$\dot{c} = \beta e^{\gamma\sigma}$$

where  $\dot{c}$  is the rate of free-radical production,  $\sigma$  is the applied (engineering) stress, and  $\beta$  and  $\gamma$  are constants characteristic of the material. As discussed elsewhere,<sup>11</sup> our studies have confirmed this equation only for a constant stress rate loading. For other loadings it leads to discrepancies if

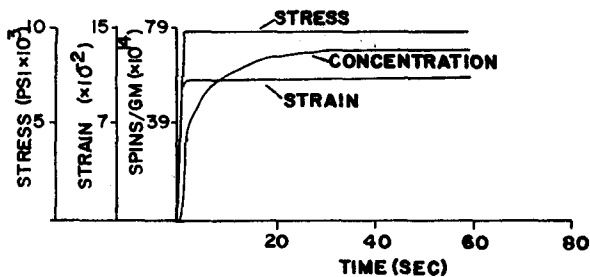


Fig. 7. Computer-reduced data for a creep test of nylon 6 fibers.

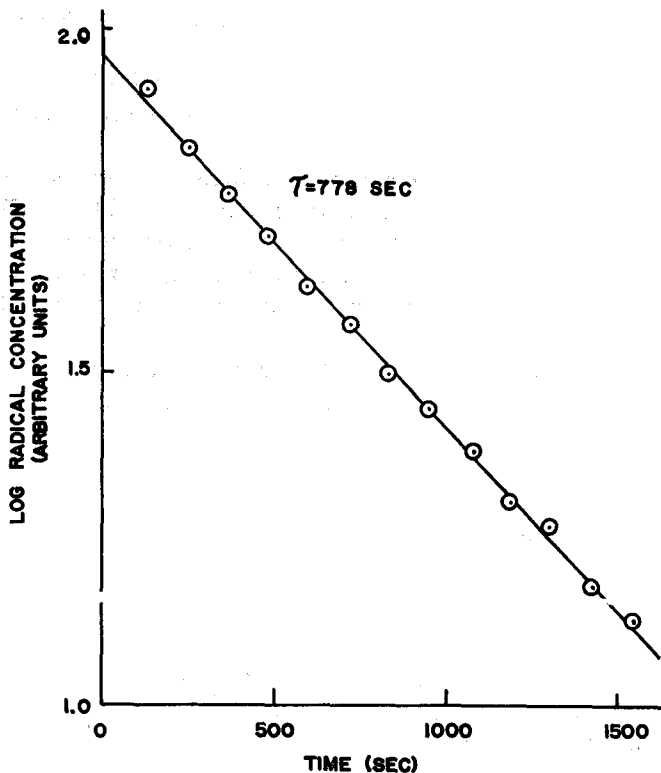


Fig. 8. Decay of EPR signal produced by tension in nylon 6 fibers vs. time.

$\sigma$  is taken as the macroscopic stress and if  $c$  is measured from the time of loading. For example, the Zhurkov relation would predict for constant stress (a creep test) that the free-radical concentration increases linearly with time. Quite obviously, from the data for this loading in Figure 7, this is not the case for the fibers studied. For very high stresses, the rapid increase in concentration of Figure 7 decreased to a quasi-steady-state rate that might be approximated by a Zhurkov-type equation. There appears to be some reason for believing that the behavior can be explained in terms of rate processes and kinetic concepts in conjunction with macroscopic



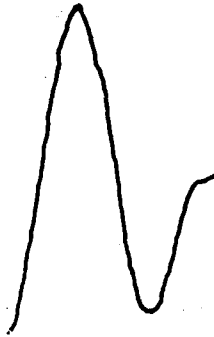


Fig. 9. Very weak EPR spectrum from several pieces of PMMA after fracture.

stress relaxation or random distributions in the tie chains between crystallites. Such a model is being developed but is too involved to be presented here.

For comparative purposes, a variety of different experiments was conducted with molded and cast polymers in an attempt to obtain EPR signals during tensile fracture of PMMA, nylon, PVC, polyethylene, polystyrene, and polyurethane rubber. In all cases, any EPR signal was below the sensitivity threshold of our present equipment for the specimen volume examined.

It was next attempted to increase the fracture surface and hence, the number of newly created free radicals by fracturing the samples before



Fig. 10. EPR spectrum from roughly  $10^{13}$  free radicals in the cavity resulting from  $\gamma$ -irradiation.

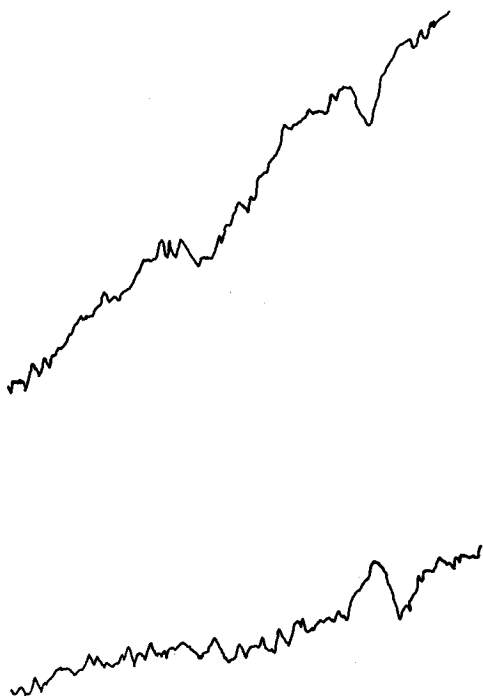


Fig. 11. EPR spectra of fracture pieces of nylon and polyethylene rods. Note gain for these spectra is increased by  $3.2\times$  that for Figures 9 and 10.

inserting them into the cavity, quickly cutting off the fractured ends, and quenching to liquid nitrogen temperature so as to "freeze in" any free radicals formed. At liquid nitrogen temperature, free radicals are very stable and can be kept for days with little if any loss due to recombination, etc. These tensile specimens were rods initially  $3/16$  in. in diameter. The elapsed time from initiation of tensile loading through fracture and quenching was never more than approximately 5 sec. In such a short time, our studies on free radicals formed by other means would indicate that very little of the initial EPR signal should decay. For example, the tests on nylon fibers indicate the decay constant in air at room temperature to be of the order of 800 sec as indicated in Figure 8. This work is further substantiated by  $\gamma$ -irradiation studies on similar materials. One complication here might be that if the newly formed free radicals lie almost entirely at the free surfaces, they might immediately react with oxygen or other agents in the surrounding air, thus substantially reducing this decay rate.

After quenching, the fracture "stubs" were placed in a quartz tube and maintained at temperatures below  $-160^{\circ}\text{C}$  while the spectra were taken. In this way considerably more fracture surface (up to eight or ten pieces) could be placed in the cavity at one time. Also by "freezing" the free radicals, the spectra could be recorded over much longer times with a longer recorder time constant, thereby substantially increasing the system sensitivity and

resolution. Only for PMMA was there then any detectable EPR signal. This result is shown in Figure 9 for six fracture pieces in the 2.5 cm length of quartz tubing. For comparison purposes, Figure 10 shows the spectra (gain and other EPR settings the same as in Figure 9) for approximately  $10^{13}$  free radicals (total number in cavity) induced in nylon by  $\gamma$ -irradiation. Figure 11 shows typical spectra for two other materials treated similarly to that of the PMMA of Figure 9. In this case the gain was increased by a factor of 3; the slope in the curve is due to a background shift at this higher amplification. No obvious free radical signals were present. The same materials were fractured under torsional stresses and similarly treated and observed. The PMMA gave a signal similar to that of tension (still extremely low); all of the others gave negative results.

### Impact Fracture

C. D. Lundergan of Sandia Corporation, Albuquerque, New Mexico, recovered some PMMA samples from an explosive impact test. These pieces, originally in a large flat plate, had a typical volume of 1-2 cm.<sup>3</sup> They were recovered within about 1 min of impact and quickly quenched to liquid nitrogen temperature. Some of the pieces contained visual cracks. By using a 1/8-in. diameter core drill, samples were obtained at liquid nitrogen temperature and at slow speeds to avoid heating. These cores were then studied in the EPR cavity at  $-160^{\circ}\text{C}$ . Once again, little signal above the background noise was present, but those signals which were observed could possibly have arisen from bond scission during the coring operation. In these and other negative studies it might be possible, however, to enhance the signal by using a time averaging computer. Initial attempts along these lines have been encouraging.

### Fracture Due to Machining

Grinding and machining operations also can produce large amounts of new fracture surfaces in comparatively small quantities of material, thus providing another means of generating EPR specimens. Every polymeric material tested, including such materials as collagen, tooth enamel, and dentin produce strong EPR signals after such treatment. (For example, Figure 12 shows a spectrum due to approximately 30 mg of ground nylon 6.) Studies are now under way in which these methods are used to investigate the number of bonds broken per unit area of new surface formed and depth of damage at surfaces as a function of fracturing mode and fracture conditions. Early results in this respect indicate that nylon 6 ground at liquid nitrogen temperature, where it behaves rather brittly, develops between  $10^{13}$  to  $10^{14}$  broken bonds/cm<sup>2</sup> of new surface formed. These studies further indicate that the majority of these broken bonds lie within a few microns of the surface, and that the crack propagates through amorphous regions surrounding the more ordered regions in semicrystalline polymers such as nylon and polyethylene.<sup>12</sup>

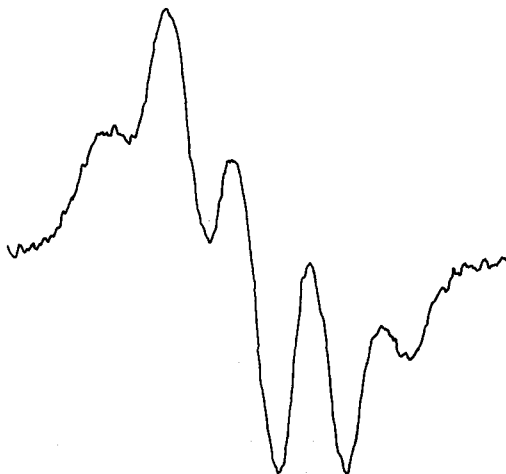


Fig. 12. EPR spectrum resulting from the grindings of 30 mg of nylon 6.

### Fatigue Fracture

Some preliminary results have been obtained by using EPR techniques to study bond rupture under alternating tensile stress. Figure 13 shows the cumulative increase in free-radical concentration when an alternating stress of  $\pm 35000$  psi has been superimposed upon a mean stress of 70000 psi. It is found that in such cases the number of bonds that rupture before final failure is substantially lower than the value for fracture under a monotonically increasing stress. For the case shown in the figure it is reduced approximately by a factor of ten.<sup>11</sup> Efforts to explain the bond rupture in terms of a Zhurkov-type relation<sup>1</sup> with the constants determined from constant stress rate tests did give at least qualitative agreement with the experimental results.

### DISCUSSION

The most unexpected result of these studies was the very large differences in the behavior of the drawn fibers and other forms of the same materials. While the tensile strength of nylon and polyethylene is increased roughly ten times by the drawing operation, the radical concentration at fracture increases from something less than  $10^{11}$ – $10^{13}/\text{cm}^3$  to approximately  $10^{17}/\text{cm}^3$ . This increase of more than  $10^5$  in number of broken bonds might be explained in a number of different ways.

(1) The extent of bond breakage along a fracture surface might be smaller in the cast or molded material than in the fibers. This could be the case if fracture involved a large amount of unraveling of chains rather than their scission. Alternately, the cracks might be able to follow paths where fewer bonds need be broken to fracture the molded samples than in the highly oriented fibers.

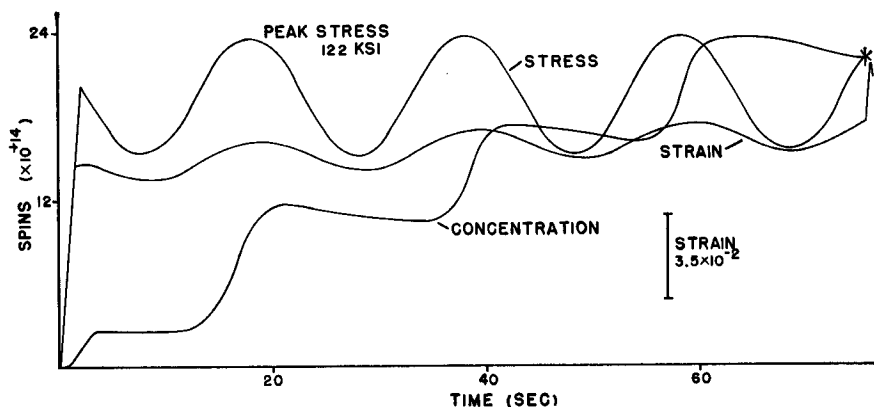


Fig. 13. Stress, strain, and free-radical concentrations as functions of time during cyclic loading of nylon 6 fibers.

(2) Chain rupture might be much more localized in the cast or molded material than in drawn fibers where it is distributed more uniformly throughout the loaded material. Our studies do seem to indicate that in the fibers the free radical distribution is distributed throughout the volume. If this is the case, it might logically follow that what is observed in the fibers is growth of a great many cracks from atomic size until one or more attain a critical (Griffith) size at which failure occurs. Since in most of these studies we are involved with bundles ( $\sim 5000$  one-mil filaments), it is possible that a great many such cracks might be present and growing at a time. The other materials, on the other hand, might fail at pre-existing flaws or have very few microcracks growing at any given time, in which case damage and bond rupture could be confined to a much smaller region of the sample. Even in this case, however, if significant amounts of bond rupture occur along the fracture surface, it should be possible to accumulate enough fracture surfaces to detect the breakage. To date, as previously noted, our attempts with tensile specimens have resulted in, at best, barely detectable signals. Also a few tests have been conducted on larger fibers; bundles of 20 monofilament fibers (each about 0.030 in. in diameter) of nylon and polyethylene exhibited behavior similar in all respects to the smaller fibers. As a result we are led to the conclusion that the size of the fibers is not the most significant factor.

(3) As a final alternative, it could be that a large number of bonds are broken but due to impurities or other causes, the free radicals so formed are so unstable and short-lived that the concentration never attains an easily detectable level. Peterlin<sup>5,13</sup> has reported the presence of an unidentified impurity in some nylon fibers studied in his laboratory which combined with the free radicals formed by fracture, forming a second free radical that is very stable, lasting several days at room temperature. It might be hypothesized that other types of impurities are present in most polymers that can react with the free radicals in such a way as to annihilate them. If such

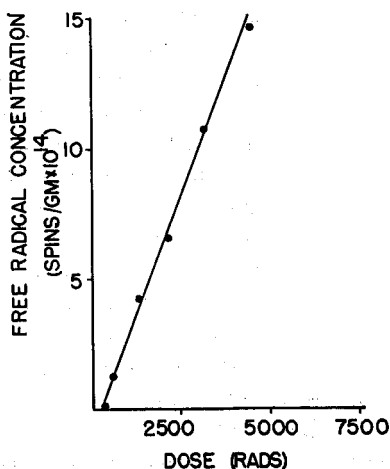


Fig. 14. Free radical concentration vs.  $\gamma$ -irradiation dose in nylon 66.



Fig. 15. Spectra in nylon 66 resulting from  $\gamma$ -irradiation at liquid nitrogen temperatures and then subsequently annealed at room temperature: (upper curve) annealed 1 min; (lower curve) annealed 6 min.

were the case, these impurities need to be present only in sufficient quantity as to annihilate the free radicals formed by tensile fracture but not in too large of concentrations since strong reasonably stable EPR signals are obtained from operations capable of producing large numbers of broken bonds, such as grinding and  $\gamma$ -irradiation. The decay constant of these signals depends on the temperature and atmosphere present but is of the order of minutes or more at room temperature in air. As a partial check of this impurity hypothesis, free radicals, were produced at varying levels of  $\gamma$ -irradiation at liquid nitrogen temperature. The irradiation dosage was varied from 50 to 100000 rad. The number of free radicals

produced for a given amount of irradiation is shown in Figure 14. Within experimental error, the number of free radicals is directly proportional to dosage. No significant difference in behavior was observed between the very low and higher dosage levels. Figure 15 compares the signal for 100-rad irradiation for a nylon 66 sample with a volume of 0.16 cm<sup>3</sup> immediately after irradiation at liquid nitrogen temperature with the same material annealed for 6 min at room temperature. Quite obviously no very rapid decay is apparent. In addition, it is difficult to see why such an impurity would be present in the other forms of all of the materials but not in any of the fibers of some of the same materials that were tested.

A somewhat related possibility is that the free radicals so formed are largely at or near the surface where they can react quickly and combine with agents in the air or testing atmosphere. Quite likely this does take place to some extent and the problem is not easily treated. Our results here are not as conclusive. However, tensile tests were conducted in various inert atmospheres, including helium and oxygen-free nitrogen. The free-radical concentration was still not increased sufficiently to be readily detectable. Another problem with this explanation is that in the fibers a strong EPR signal is present some time before macroscopic fracture is apparent, independent of the testing atmosphere. Once again, it would be difficult to explain why the free radicals are so reactive with the atmosphere in one case but not the other.

It is our opinion that the most likely answer is a combination of (1) and (2) above, i.e., damage is more local, cracks are able to follow paths requiring less bond rupture, and the unraveling of the polymer chains plays a more dominant role in the molded and cast materials than in the fibers. If this hypothesis is correct, it would appear that the materials scientist or engineer might have to use entirely different approaches for different forms of chemically identical materials when attempting to "design" better and stronger materials.

In closing, we might speculate that the ultimate properties of semicrystalline polymers are to a large extent dependent on the character of the regions between the crystallites or micelles. If such is the case, the strength and fracture properties of such a material should be strongly dependent on the number, orientation, and length distribution of the "tie chains" connecting the crystalline regions. It can be demonstrated that a rupture surface by following a path through these "glassy regions" results in the scission of an order of magnitude less bonds than one might expect were it to follow a straight plane normal to the tensile axis.<sup>12</sup> In related but different types of experiments, Peterlin et al. have shown that these regions are significantly changed by drawing and working operations.<sup>13-15</sup> One might then hypothesize that both the difference in tensile strength and the even more drastic difference in the build-up in free-radical concentration before fracture might be explained in terms of these changes. Three changes apparently take place: (1) the size of the crystallites and amorphous regions between them are altered; (2) the orientation and size of the crystallites and possibly

the number, orientation, and length of tie chains are altered; (3) the amount of material in the glassy regions is changed.

Based on these microscopic effects the following alteration in fracture properties might be expected. The fracture strength in drawn fibers would be higher because first, more bonds would need to be broken and second, because of orientation and size effects, it could be more difficult to nucleate a catastrophic (Griffith) flaw somewhat analogous to the effect of grain size on ultimate properties of metals. Third, the orientation and distribution of tie chain effective lengths might be more favorable so that at any given gross load, more of these would actively share the load on the submicroscopic scale. The total number of bonds broken would be higher because more bonds would need to be broken to complete separation. This effect alone could account for perhaps a two- or three-fold increase, but not the observed four to five orders of magnitude change. Also, the distribution of free radicals (broken bonds) would likely be more uniform throughout the sample volume because of arguments similar to the second and third reasons given above.

It is a pleasure to acknowledge the support of the National Aeronautics and Space Administration and the National Science Foundation for major portions of this investigation.

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Received December 18, 1968

Revised July 31, 1969