EPR Studies of Mechanically Induced Bond Rupture in Elastomers[*]

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Synopsis

Electron paramagnetic resonance (EPR) spectroscopy was used to compute the surface bond rupture density in polyurethane and to determine the phase experiencing fracture in styrene butadiene block copolymers when these elastomers are subjected to mechanical degradation by grinding. The polyurethane grinding was done at temperatures above and below the glass transition T_g; 0.155×10^{13} radicals/cm² of fracture surface area were formed above the T_g and 4.42×10^{13} radicals/cm² for grinding below the T_g. These values are essentially equal to those found earlier for spherulitic polymers. In all cases the fracture appears able to progress along preferential paths so as to rupture significantly fewer molecular chains than one would expect on the basis of calculations of the number of chains passing through each square centimeter of cross section. Comparison of EPR spectra formed by grinding styrene–butadiene copolymer with those of styrene and butadiene above indicated that at cryogenic temperature, the fracture in the copolymer takes place in the butadiene phase.

Introduction

Electron paramagnetic resonance (EPR) spectroscopy 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 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. In general, two free radicals are generated at the site of a homolytic rupture of a covalent bond in a polymer. The identification of these bonds and the investigation of their kinetic behavior by means of EPR spectroscopy has provided significant new insights into the molecular physics of many diverse aspects of polymer degradation and fracture.[1]

Bond Fracture Density in Polyurethane

Recently the authors have reported success in using electron paramagnetic resonance (EPR) spectroscopy to monitor the formation of free radicals created during mechanical degradation of various spherulitic polymers (nylon, polyethylene, polypropylene).[2,3] From this earlier work it was concluded that fracture in spherulitic polymers takes place along preferential routes which result in the rupture of significantly fewer molecular chains per square centimeter of new surface area than one would expect on the basis of calculations of the number of chains passing through a unit cross section of polymer. In addition, it was found that fewer bonds were ruptured when the sample was degraded at temperatures above its glass transition than at lower temperatures and also that the energy associated with covalent primary bond rupture amounted to only a small percentage of the total energy input required to form new area.

It is not obvious, however, whether the above conclusions would also apply to polymers of other than spherulitic morphology. In particular, the fracture behavior of the amorphous polyurethane elastomer known commercially as Solithane 113 is of considerable interest due to the widespread use of this material as a characterization model for a large class of viscoelastic materials.[4] The Solithane used in the tests reported here was obtained by curing equal proportions of "catalyst" (castor oil) and "resin" (a trifunctional isocyanate manufactured by Thiokol Chemical Corporation by reacting castor oil with toluene diisocyanate). The tendency of the cured rubber to contain stable residual free radicals interfered with the EPR measurements of radicals formed by subsequent degradation, and it was found that the number of these residual radicals could be minimized by
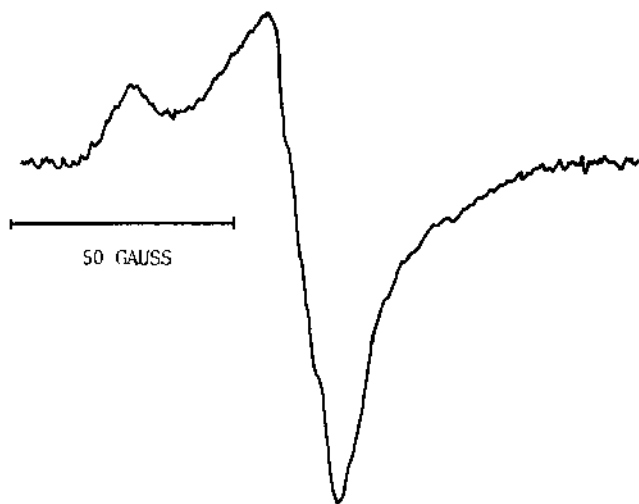

Fig. 1. EPR spectrum resulting from grinding Solithane at liquid nitrogen temperatures.

an appropriate choice of cure time and temperature. Curing for 6 hr and 45 min at 170°F resulted in a residual radical population of 1.30×10^{14} radicals/g.

The sample material was degraded at temperatures below and above the glass transition (namely, liquid nitrogen and room temperature) by grinding it with a small motor-driven rotary burr. The low-temperature grinding was performed with the sample and burr submerged in liquid nitrogen, and the particles formed by room-temperature grinding were quenched in liquid nitrogen within about ½ sec after their formation. The normally short-lived radicals are very stable at cryogenic temperature and samples can be stored in liquid nitrogen almost indefinitely with no appreciable
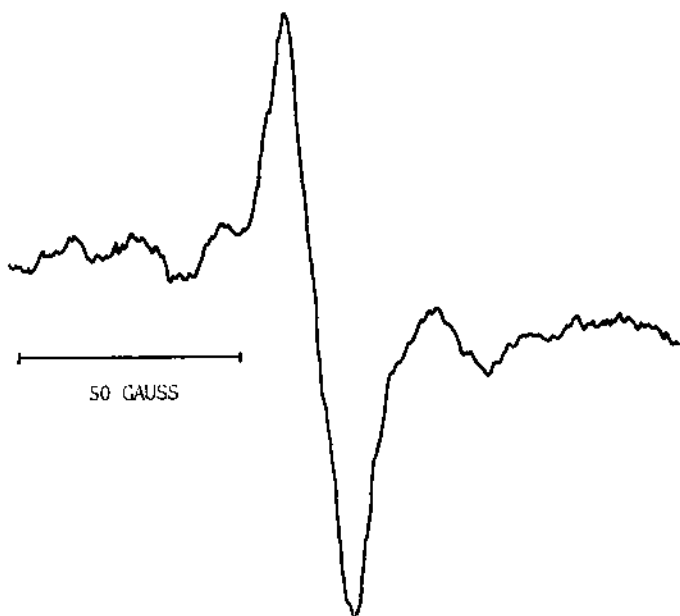

Fig. 2. EPR spectrum resulting from grinding Solithane at room temperature.

decay of the radical population. The grindings formed at either temperature were transferred to a sample tube without leaving the liquid nitrogen bath, and this tube was in turn placed in the EPR spectrometer's low-temperature accessory at −150°C. The EPR spectrum of the ground sample was then recorded and the number of radicals determined by a computer double-integration of the recorded spectrum and a comparison of the resulting value with that of a pitch standard provided by Varian Associates.

Figures 1 and 2 show the EPR spectra generated by Solithane grindings produced at liquid nitrogen and room temperature, respectively. The radicals responsible for these spectra are most likely not those initially formed by the original chain scission since even at −150°C the radicals are mobile enough to migrate very rapidly from the highly energetic chain-ends

to more stable sites along the chain. It is not the purpose of this study to identify either the initial or final radical sites although it should be noted that the marked differences between the spectra of Figures 1 and 2 suggest that different molecular mechanisms might be operative in the degradation of Solithane above and below its glass transition or that the free radicals, once formed, are able to migrate to a different site at higher temperatures. However, it should be noted that upon warming, the low-temperature radical did not revert to the room-temperature radical, but the spectrum, while decreasing in size, retained the general shape of Figure 1. For our present purposes, it is sufficient to calculate the number of radicals at their final sites and assume that this number is very close to the number of radicals originally formed (further evidence supporting this assumption has been given by Backman and DeVries[3]). After correcting for the residual radicals, grindings formed at room temperature typically contained a radical population of 6.24×10^{14} radicals/g, while low-temperature grindings contained 1.08×10^{16}/g.

Statistical calculations of particle size, necessary in the computation of the number of bonds broken per square centimeter of new surface area, are based on photomicrographs of a number of grindings which had been captured without handling on microscope slides during the grinding operations. The projected area and circumference of each particle were measured graphically from the photomicrographs; after correcting for the magnification, the average ratio of the projected area to circumference was taken to approximate the average ratio of the particle's volume to surface area. The use of grinding rather than slicing as a means of mechanically degrading the sample necessitates this statistical rather than direct measurement of fracture surface area, but has the overriding advantage of creating a great deal more surface area per unit volume. This produces larger concentrations of free radicals in the spectrometer's microwave cavity and correspondingly more accurate EPR measurements.

Particles ground at liquid nitrogen temperature differed appreciably from those ground at room temperatures; this also might reinforce the hypothesis of two distinct fracture mechanisms being operative above and below the glass transition temperature. The low-temperature grindings were typically larger and less uniform in size; their mean diameter was 272μ with a standard deviation of 23% while the room-temperature grindings had a mean diameter of 154μ with a standard deviation of only 8.7%. Although different in size, the two types of grindings were about equally irregular in shape. The mean ratio of the photographic projected area to circumference for the low-temperature grindings was 14.9% of the mean diameter (40.6μ) with a standard deviation of 30.3% while the corresponding ratio for the room-temperature grindings was 15.8% of the mean diameter (24.4 μ) with a standard deviation of 29.8%.

Based on the above measurements of free-radical concentration and particle dimensions, 4.42×10^{13} radicals are created per square centimeter of new surface area formed by mechanical degradation at cryogenic tempera-

tures; the corresponding value for room temperature degradation is 0.155 $\times$ 10^{13} radicals/cm^2.

These values are essentially equal to those found earlier for semicrystalline polymers; in that case we found ca. 2 $\times$ 10^{13} radicals/cm^2 formed below the glass transition temperature and ca. 0.1 $\times$ 10^{13} radicals/cm^2 above the glass temperature. Since even the larger (low-temperature) value is much less than the 2.4 $\times$ 10^{14} chains which Peterlin[5] has calculated to pass through each square centimeter of cross section, our earlier paper concluded that fracture must progress along preferential paths through the amorphous phases of the semicrystalline polymer so as to rupture a minimal number of covalent bonds. This conclusion is strengthened by the present study since, of course, only the amorphous phase is available to a fracture path in Solithane. It also appears that the existence of fracture paths in-
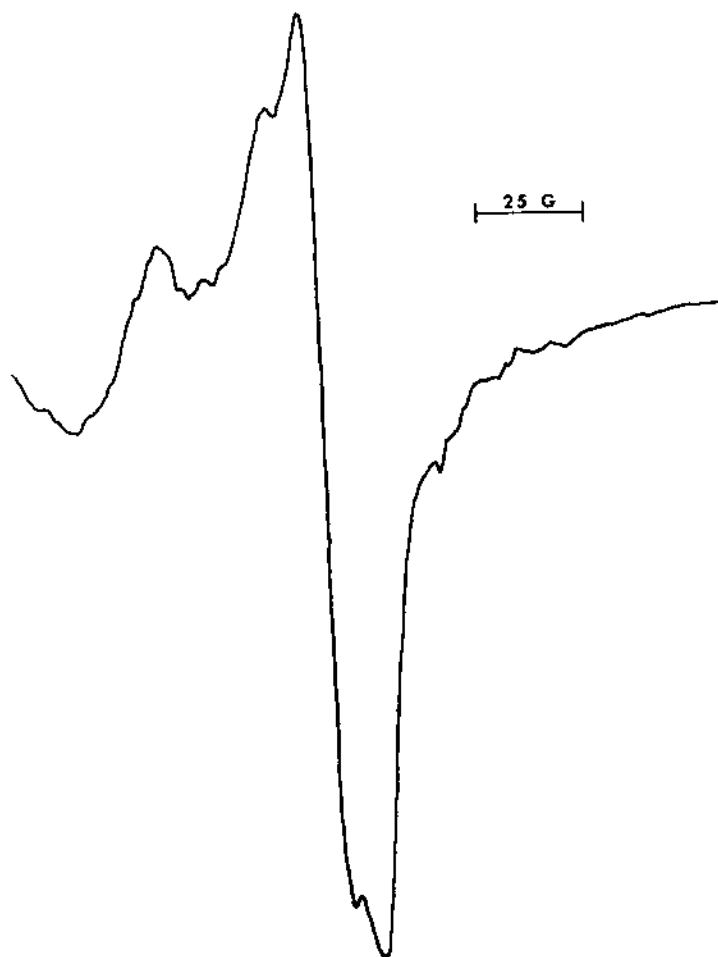

Fig. 3. EPR spectrum of styrene–butadiene block copolymer ground at liquid nitrogen temperature.

volving minimal bond rupture does not require that the existence of fracture paths involving minimal bond rupture does not require the presence of a crystalline phase, and in this regard the mechanism of mechanical degradation is similar in both amorphous and semicrystalline polymers.

As in the case of semicrystalline polymers, we also note that the energy required to rupture 2×10^{13} bonds/cm^2 (<100 ergs/cm^2) is only a small part of the total energy required to form a new surface ($>10^4$ to 10^5 ergs/cm^2) as measured by crack and tear growth studies. The major protion of the fracture energy input is evidently consumed by the various viscous dissipation mechanisms. Also, as is the case of semicrystalline polymers, the reduced density of bond rupture at temperatures above the glass transition is ascribed to greater chain mobility which aids the fracture in picking out more selective paths.

Identification of Fracture Location in Block Copolymers

Block copolymers have been receiving increasing attention in the past several years, owing largely to the ability of these materials to be designed to specific property requirements. Styrene–butadiene block copolymers, for instance, behave as a vulcanized rubber near room temperature but can be processed similarly to a thermoplastic at elevated temperatures (125–225°C). This obviously valuable combination of rubbery properties and thermoplastic processability is generally considered as arising from a molecular structure consisting of rigid polystyrene end-blocks joined by an elastomeric polybutadiene center-block. The polystyrene blocks aggregate together to form small (ca. 200 Å) domains which act as physical crosslinks at room temperature and cause rubbery elasticity but which soften at elevated temperatures to permit plastic flow.

Understanding of the fracture response of these systems depends in large part on identification of the phase, i.e., styrene or butadiene in this case, in which molecular rupture takes place. We have used the hyperfine structure of the EPR spectrum to identify the fracture phase in styrene–butadiene, but two comments should be made concerning the procedure. First, grinding was used as the means of mechanically degrading the samples. This is experimentally convenient, but the very complex stress state at the fracture region should be noted if the results are to be applied to failure by uniaxial tension; it is possible that the failure mechanisms for multiaxial and uniaxial stress states differ. Second, all grinding was done at liquid-nitrogen temperature. This tends to freeze the originally formed radical at or at least near the rupture site, but, of course, both phases are then far below their glass transition temperatures and may fail by different mechanisms than at room temperature. Room-temperature grinding will be done in the near future, but radical migration and decay must then be considered seriously.

Since the identification of a radical by its hyperfine EPR structure alone can be extremely formidable task, we adopted the slightly less conclusive but much more straightforward deductive method of comparing the spectrum of styrene–butadiene block copolymer with those of styrene and buta-
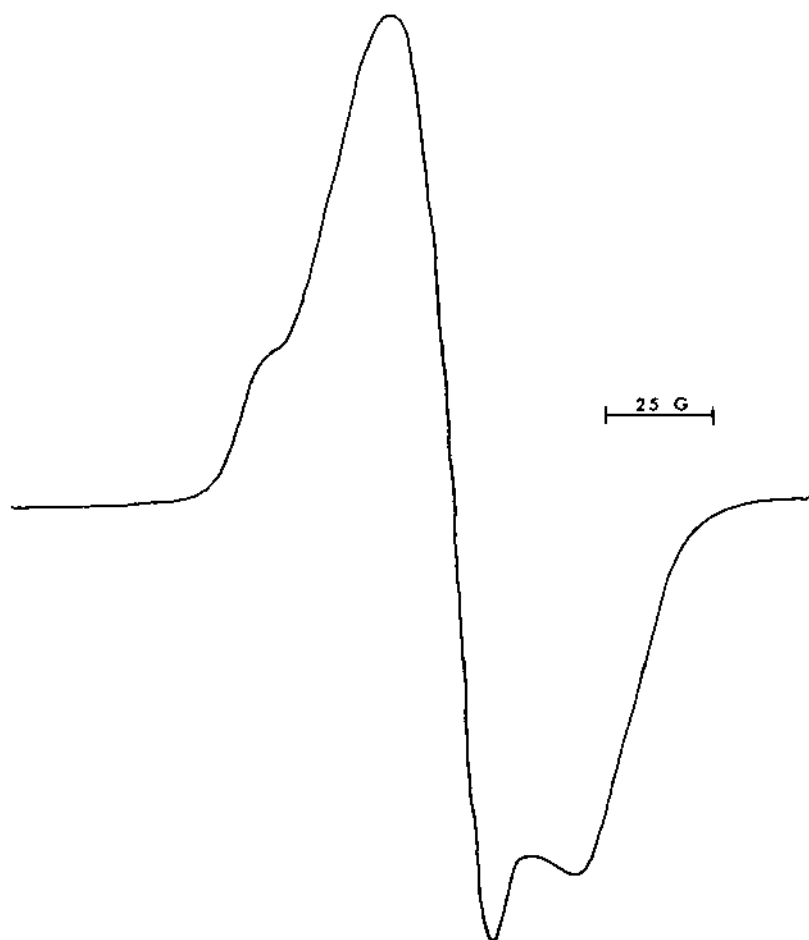
Fig. 4.   EPR spectrum of commercial polystyrene ground at liquid nitrogen temperature.

diene alone.   These spectra are shown in Figures 3, 4, and 5, respectively. They are compared on the basis of shape rather than intensity since intensity varies among other factors with particle size which in turn varied considerably among the three materials.   Although the styrene and the styrene–butadiene spectra both contain lines corresponding to a peroxy radical—a contaminant which can arise in many systems[2]—the styrene–butadiene radical contains all the lines of the butadiene radical but not of the styrene radical.   We feel this justifies assigning the radical in the styrene–butadiene system to the butadiene phase.

This result is somewhat contradictory to observations that mechanical properties in styrene–butadiene copolymers are strong functions of the properties of the styrene phase but not of the butadiene phase.[6]   In addition to our earlier comments on possible differences in fracture mechanisms between cryogenic grinding and room-temperature uniaxial tension, we can note that fracture can take place in the butadiene phase and still
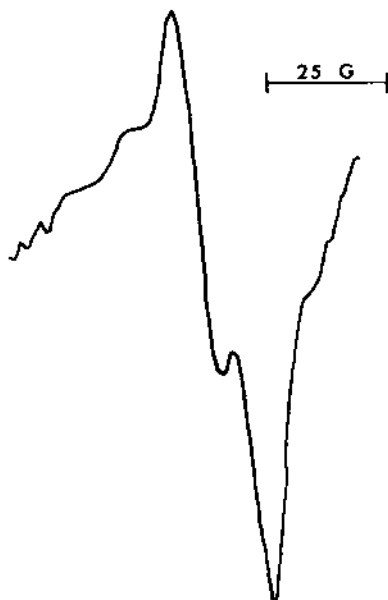
Fig. 5.   EPR spectrum of butadiene rubber ground at liquid nitrogen temperature.

be controlled in large part by the rigid styrene phase via such mechanisms as crack arrest and energy absorption by plastic deformation.

Conclusions

Although the results obtained in these tests are in some cases rather preliminary, they indicate the usefulness of EPR in elucidating the basic mechanisms of mechanical degradation in elastomeric systems.   The work on block copolymers is being extended to other temperatures and to include the styrene–isoprene system.

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