

## FORMATION OF FREE RADICALS DURING MECHANICAL DEGRADATION OF ELASTOMERS

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) (1,2). In general, two free radicals are generated at the site of a homolytic rupture of a polymeric covalent bond; 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 (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 energy associated with covalent primary bond rupture amounted to only a small percentage of the total energy input required to form new surface area.

It is not obvious, however, whether or not 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 tolylenediisocyanate). The tendency of the cured rubber to contain stable residual free radicals interfered with the EPR measurements produced by subsequent degradation and it was found that the number of these residual radicals could be minimized by 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  $1.30 \times 10^{14}$  radicals per gram.

The sample material was mechanically degraded at temperatures below and above its 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 one-half second 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 decay of

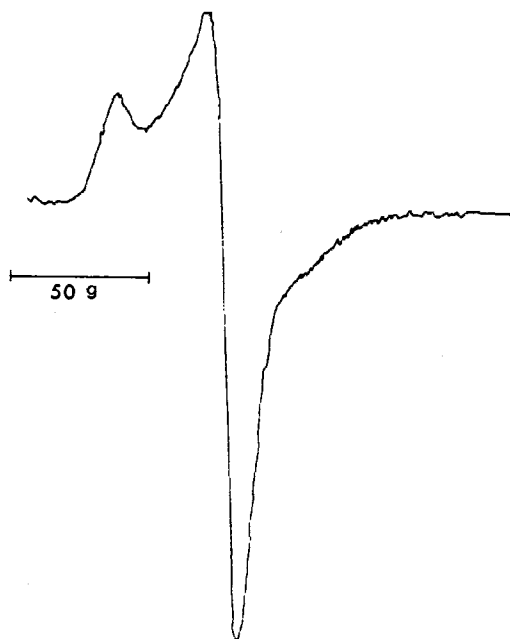


Fig. 1. EPR spectrum resulting from grinding at liquid nitrogen temperatures.

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  $-150^{\circ}\text{C}$ . 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  $-150^{\circ}\text{C}$  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 difference between the spectra of Figures 1 and 2 suggests that different molecular mechanisms might be operative in degradation of Solithane above and below its glass transition temperature or that the free radicals once formed are able to migrate to a different site at the higher temperatures. However, it should be noted that upon warming the low temperature radical did not revert to the room temperature radical but while decreasing in size retained the general shape of Figure 1. For our present purposes, it is sufficient to calculate the

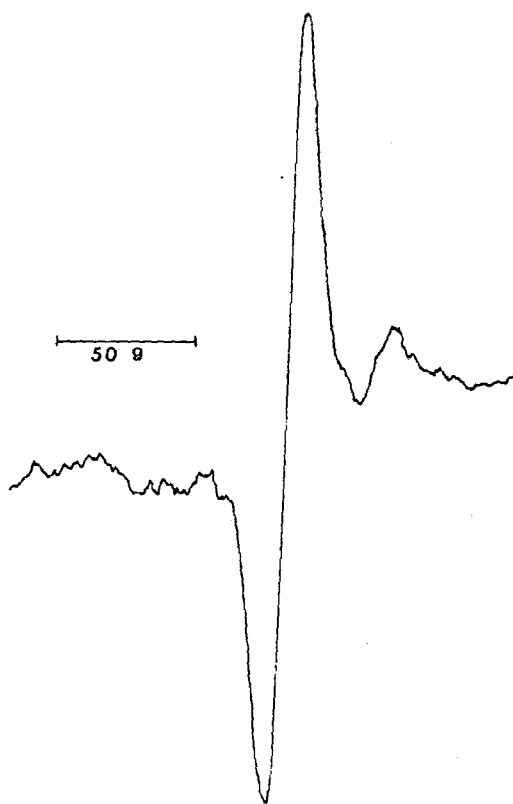


Fig. 2. EPR spectrum resulting from grinding at room temperature.

number of radicals at their final sites and assume that this number is very close to the number of radicals originally formed (for which there is also evidence (2)). After correcting for the residual radicals, grindings formed at room temperature typically contained a radical population of  $6.24 \times 10^{14}$  radicals/g while low-temperature grindings contained  $1.08 \times 10^{16}$  radicals/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 micro-

wave cavity and correspondingly more accurate EPR measurements.

Particles ground at liquid nitrogen temperature differed appreciably from those ground at room temperature; 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  $272 \mu$  with a standard deviation of 23 per cent while the room temperature grindings had a mean diameter of  $154 \mu$  with a standard deviation of only 8.7 per cent. 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  $40.6 \mu$  (14.9 per cent of the mean diameter) with a standard deviation of 30.3 per cent. The corresponding ratio for the room temperature grindings was  $24.4 \mu$  (15.8 per cent of the mean diameter) with a standard deviation of 29.8 per cent.

Based on the above measurements of free radical concentration and particle dimensions,  $4.42 \times 10^{13}$  radicals are created per square centimeter of new surface area formed by mechanical degradation at cryogenic temperature; the corresponding value for room temperature degradation is  $0.155 \times 10^{13}$  radicals per square centimeter.

These values are essentially equal to those found earlier for semicrystalline polymers; in that case we found about  $2 \times 10^{13}$  radicals/cm<sup>2</sup> formed below the glass transition temperature and about  $0.1 \times 10^{13}$  radicals/cm<sup>2</sup> above the glass transition. 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 amorphous phase is available to a fracture path in Solithane. It also appears 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  $2 \times 10^{13}$  bonds per cm<sup>2</sup> ( $< 100$  ergs/cm<sup>2</sup>) is only a small part of the total energy required to form a new surface ( $> 10^4$  to  $10^5$  ergs/cm<sup>2</sup>) as measured by crack and tear growth studies. The major portion of the fracture energy input is evidently consumed by the various viscous dissipation mechanisms. Also, as in 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.

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## References

- (1) K. L. DeVries and M. L. Williams, *Surfaces and Interfaces*, 2, 139 (1968).
- (2) D. K. Backman and K. L. DeVries, *J. Polymer Sci.*, A-1, 7, 2125 (1969).
- (3) K. L. DeVries, D. K. Roylance, and M. L. Williams, *J. Polymer Sci.*, A-1, 8, 237 (1970).
- (4) W. G. Knauss and A. K. Mueller, GALCIT SM 67-8, California Institute of Technology, Pasadena, Calif., 1967.
- (5) A. Peterlin and D. Campbell, *J. Polymer Sci.*, B, 6, 481 (1968).

K. L. DeVries

Dept. of Mechanical Engineering  
University of Utah  
Salt Lake City, Utah 84112

D. K. Roylance

Army Materials and Mechanics Research Ctr.  
Watertown, Massachusetts 02172

M. L. Williams

College of Engineering  
University of Utah  
Salt Lake City, Utah 84112

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