

The Quantitative Detection of Free Radicals on Mechanically Formed Polymer Surfaces

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Synopsis

Mechanochemical reactions are becoming increasingly important; yet, quantitative data on mechanoradicals are sparse. A study was undertaken to determine the surface concentration of free radicals which are available for reaction when chemical bonds are broken by mechanically forming fresh polymer surface. Polyethylene and polypropylene were cut under a benzene solution of the free-radical scavenger diphenylpicrylhydrazyl, using countersinks as the cutting tools. Accurate surface area measurements of the polymer shavings were made. Surface free-radical densities up to $2 \times 10^{13}/\text{cm}^2$ for polyethylene and $9 \times 10^{13}/\text{cm}^2$ for polypropylene were determined. The physical conditions of the test and of the cutting tool were found to have an effect on the results, but not as profound as that of base polymer.

INTRODUCTION

The application of mechanical energy to high polymers can cause chain rupture and subsequent formation of two free radicals called mechanoradicals, or macroradicals. The stability of these macroradicals will depend upon their environment as well as the structure of the polymer in question. The macroradicals formed can participate in a wide variety of reactions to form new terminal groups, compounds, or copolymers. The plasticization of rubber by mastication has been a widely used industrial process for many years. Early experimenters attributed this plasticization to the action of oxygen, thermal degradation, electrical discharges, or to the destruction of "globular" structures.¹ In the early 1930's, Staudinger alone categorically asserted that the plasticization was due to the breaking of chemical bonds of long chain-like molecules.^{2,3}

The development of the theory of rubber mastication, particularly in Russia, began to make the mechanism of mechanodegradation clearer.⁴ The first definitive work in the Western world was accomplished by Watson et al.⁵ who, in 1952, showed that masticating rubber broke chemical bonds forming free radicals. More recent work has followed this same qualitative approach with emphasis on newer methods of analysis.

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Bresler et al.^{6,7} were the first to obtain electron spin resonance spectra of freshly milled polymers. They milled polyethylene, polycaprolactam, poly(methyl methacrylate), polystyrene, polyisoprene, and polyisobutylene with a conical bit at various temperatures. They found that in milling at room temperature in vacuo they could detect no radicals in polyethylene and polycaprolactam, but could detect radicals in the case of poly(methyl methacrylate) and polystyrene. On the other hand, when the milling occurred under liquid nitrogen, they observed radicals in all cases, the life of the radicals depending upon their structure. A "calculation" of the surface area of the poly(methyl methacrylate) turnings, compared to the number of radicals they found, enabled Bresler to estimate that essentially 100% of the chains exposed by the cutting process ruptured to form free radicals.

Others⁸⁻¹⁷ have presented strong evidence of mechanoradical formation in polymers. Results have been mostly qualitative and semiquantitative. Uncertainty exists concerning the position of the radicals in the substrate polymer, as well as difficulty in the precise measurement of the number of radicals. The results presented are subject to large discrepancies in measurement or calculation. Quantitative results may be presented as a percentage of chemical bonds broken (% BB) of those that theoretically could have been broken, i.e., those that intersect the new surface. Thus, Pazonyi⁸ claims 35% to 120% bonds broken; Bresler,^{6,7} 100%; Campbell and Peterlin,^{9,10} from 0 to greater than 100%, depending upon polymer orientation; and Backman and DeVries,¹¹ 0.3%.

These large discrepancies are due to several factors. Inaccurate measurement or approximation of the surface area produced has heretofore been a universal problem. Additionally, work done with ESR necessarily includes radicals formed deep in the polymer substrate which may have no relation to the area produced. This work includes accurate measurement of surface area with detection of only surface radicals, thereby producing meaningful values of radicals produced per unit area produced. These are, of course, the only radicals that are potentially useful for surface reactions, initiation, etc.

EXPERIMENTAL

Equipment

In order to accurately determine those macroradicals that might be useful in a subsequent chemical reaction, i.e., those on the new surfaces, the physical equipment and processes must be chosen such that a measurable amount of surface area is produced and a chemically detectable number of radicals is produced. Both conditions are necessary; neither alone is sufficient. It was found that a drilling operation using a three- or four-fluted countersink met these requirements.

The equipment used in this investigation is shown in Figure 1. A drill press was equipped with a $1/2$ -hp variable-speed, reversible, remote-control

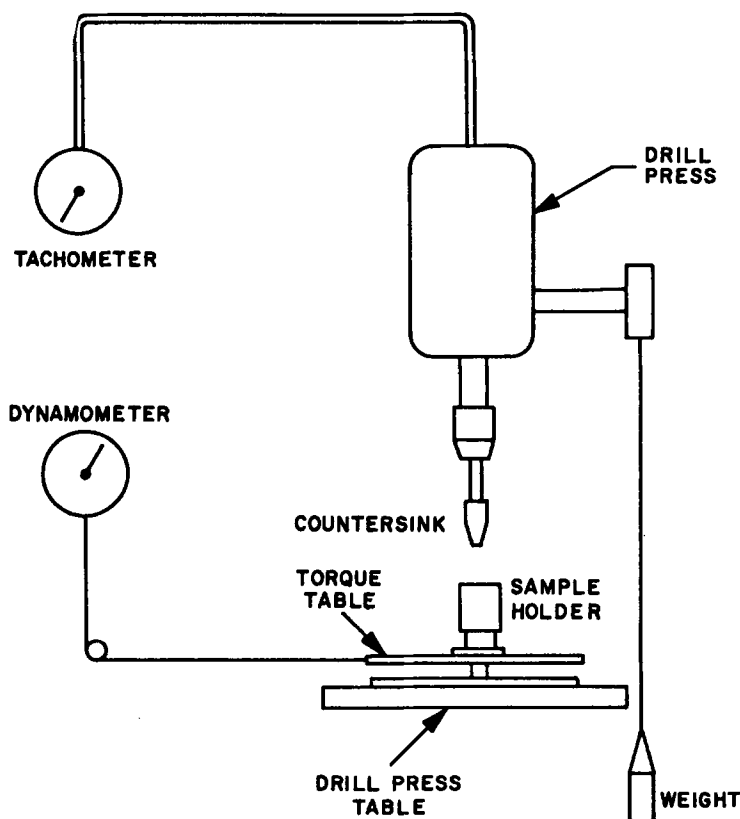


Fig. 1. Schematic drawing of equipment used.

motor. Spindle speed could be varied from 300 to 3000 rpm unloaded. A flexible coupling was inserted directly into the top of the drill press spindle, and the other end was attached to a wall-mounted tachometer.

A torque table, which consisted of an $\frac{1}{8}$ -in.-thick, 12-in.-diameter aluminum plate mounted on a thrust bearing mounted on a second aluminum plate, was bolted to the drill press table. This arrangement allowed the torque table to rotate freely. The sample, placed in a holder, was bolted to the torque table. A 40-lb test nylon monofilament line attached the torque table to a dynamometer. The dynamometer measured the force required to prevent the torque table from turning while a sample was being drilled. This force, multiplied by the radius of the torque table, yields the torque applied to the sample by the drill press. The product of the torque and the spindle speed is the power input to the sample. The product of the power input and the duration of the drilling, measured on a separate electric timer, is the total energy input to the sample.

The spring return on the drill press quill was removed and a 6-in. diameter pulley attached to replace the feed handle. Weights were hung

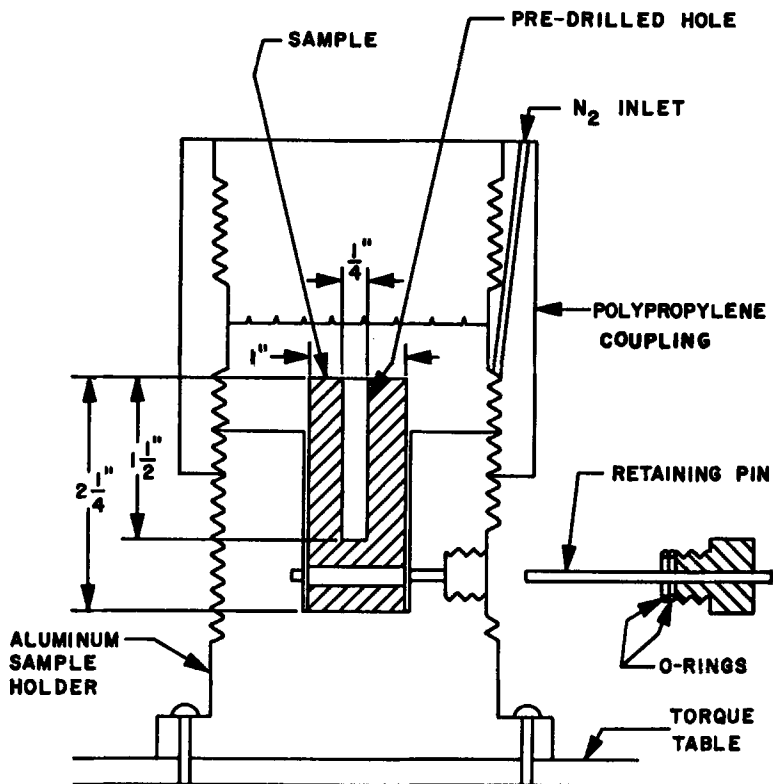


Fig. 2. Cross-sectional view of polymer sample in sample holder.

from this pulley to adjust the force of the cutting bit on the sample. By proper adjustment of the weight and the motor speed settings, the spindle speed and the dynamometer reading could be varied independently.

Figure 2 shows a cross-sectional view of the sample in the holder. The samples were made from commercial 1-in.-diameter extruded rod. Each sample was $2\frac{1}{2}$ in. long and was machined flat on both ends to fit the holder. A $\frac{1}{4}$ -in. hole was predrilled axially to a depth of $1\frac{1}{2}$ in. from the top of the sample. A $\frac{3}{8}$ -in. hole was drilled through the sample about $\frac{5}{16}$ in. from its base to accommodate a $\frac{1}{8}$ -in. retaining pin, which was inserted through the sample and served to prevent the sample from rotating within the sample holder during drilling. The top of the sample holder was threaded to accept a standard 3-in. polypropylene pipe coupling. This created a cavity to hold the chemical detector solution. A hole drilled through the coupling wall, slightly off from the vertical, provided a passage-way to introduce nitrogen gas into the solution to purge dissolved oxygen.

Countersinks, 1 in. in diameter, were used as the cutting tools for this investigation. They could be obtained with three or four flutes and with included angles, i.e., the angle of the tip, of 60° to 120° . The three-flute type has the cutting edges formed by slight hollowing of the conical tip

in front of each edge; the four-flute countersink is quite different, as the cutting edges are built out from a central core so that only the cutting edges contact the polymer. The sharpness of the cutting edge is an important consideration in the plastic cutting process. The sharpness or dullness of the bits used was determined by microscopic examination at $120\times$. If, under this magnification, the cutting edge appeared to be a line, the bit was declared to be sharp. If the cutting edge appeared rounded, with definite shadows, the bit was declared dull. These terms are, of course, relative and only imply that, for a given type of bit, a "sharp" condition is clearly sharper than a "dull" one.

Procedures

The sample was placed in the sample holder and the retaining pin passed through a predrilled hole in the sample and secured. Fifty milliliters of a standard solution of diphenylpicrylhydrazyl (DPPH) in benzene was pipetted into the sample holder. The holder was then bolted to the torque table and the nitrogen purge started. The desired values of speed and torque were set by simultaneously starting the drill press and timer and in the first few seconds adjusting the motor speed and weight on the feed pulley. The length of time of any run varied from 2.5 to 20 min and was continued until sufficient shavings were produced to give a total surface area that could be measured. Temperatures of the benzene solution and three locations in the polymer near to the drilling surface were measured with thermocouples and on certain runs continuously recorded. The thermocouple wells were predrilled into the polymer from the outside surface. The highest temperature was always attained in the benzene solution and for a run of at least several minutes duration typically reached 70°C . At this temperature, which is approximately 10°C below the boiling point of benzene, the vapor pressure was sufficiently high to cause vaporization of enough benzene to remove the heat generated. Even in much longer runs the temperature remained essentially constant. Since the benzene solution is in intimate contact with the newly formed surface, a temperature of 70°C could be reported for this mechanochemical reaction. Thermocouples in the wells in the polymer sample indicated temperatures up to 40°C but were necessarily separated from the cut surface by a thin section of polymer. Temperature is defined, of course, for an appreciable mass of molecules and, as measured, is not useful to describe the energy considerations of a molecular chain as it is severed.

To determine how much DPPH had been consumed by reacting with free radicals during the drilling, it is necessary to determine the concentration of the solution after the run is completed. Because of solvent evaporation and clinging of more depleted solution to the shavings, it was found that a withdrawn sample was not representative. All the remaining DPPH had to be recovered and the final resultant diluted solution used to determine the total unreacted DPPH. The combined washings and shavings were filtered with an asbestos mat prepared using only benzene. The

washed shavings were retained for the surface area measured by nitrogen sorption.¹⁸ This technique was especially developed for measuring surface areas of polymer shavings. Total surface areas of 0.2 to 3 m² are accurately determined by this modified BET method for samples of shavings of 1 g or less. The filtered washings are diluted to 250 ml, and a 50-ml sample is centrifuged at 3000 rpm for 3-5 min. This centrifuged sample was used for measurements of DPPH concentrations photometrically. The calibration curve for DPPH on the photometer used, a Fisher electrophotometer II, is linear so that the dilution of the DPPH solution recovered is accounted for by a factor equal to the ratio of final to initial volumes.

This procedure was checked for possible losses of DPPH due to other than mechanochemical reaction in several ways. A solution of DPPH in benzene was refluxed for 30 min and had no measurable change in absorbance, indicating stability of the free radical under measurement conditions. A blank was established for the reaction of DPPH with polymer surface when no mechanochemical reaction was conducted. Fine shavings of polyethylene and of polypropylene were prepared on an ordinary lathe. Samples of the shavings were washed and then immersed in DPPH solution. Surface free radicals are not present after the newly formed surface has been briefly exposed to the atmosphere. In this manner, the reaction of DPPH with any impurity remaining in the polymer can be detected. The extent of such immediate reaction with the polymers used in this study is so slight that it has negligible effect on the results of the mechanochemical reactions. Also, three control experiments were conducted to determine the recovery of DPPH with no mechanochemical reactions occurring. The experiments were conducted identically with all others, except that the countersink bit never came into contact with the polymer sample. Shavings formed by drilling in air were added to simulate the recovery procedure. The recoveries averaged 99.8%, with deviations of only a few tenths of a per cent. Again, such small losses of DPPH do not affect the results appreciably.

In these recovery experiments with polymer shavings and in actual runs, the absorbance of the DPPH solution continued to slowly decrease due to some secondary reaction. The DPPH consumed by a secondary reaction was not counted in determining the number of free radicals produced on the surface since the extent of only the very rapid free-radical reaction on the surface is desired. The time from the start of a run to the first absorbance measurement after filtration and recovery of all benzene solution was 20-35 min. Therefore the absorbance was measured as a function of time and extrapolated backward to the experimental run time, t_r , to determine the absorbance of the DPPH solution immediately after the run ceased. As an example, Figure 3 shows the log of DPPH concentration versus time for a particular polypropylene run. Note the linearity of the extrapolation of the log of the absorbance of DPPH to t_r . The decrease in concentration of DPPH from time 0 to t_r is due to mechanochemical

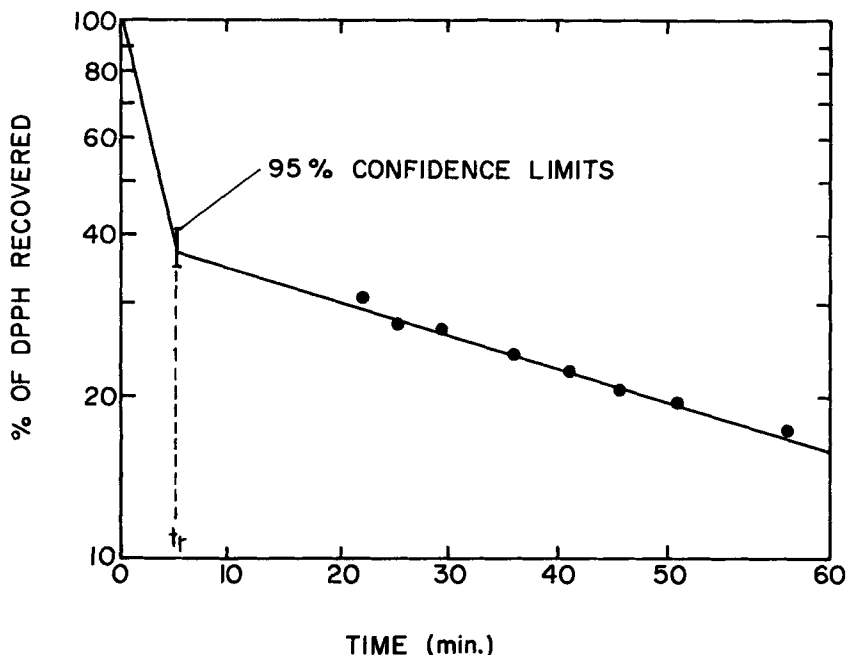


Fig. 3. Typical absorbance data showing extrapolation to end of an experimental run.

reaction. In this run, 63% of the DPPH reacted with surface free radicals during drilling; less than 20% additional consumption occurred during the hour that followed. Also shown are 95% confidence limits on the extrapolated absorbance at t_r , as determined from statistical calculations based upon the linear relationship. From initial and final concentrations, the amount of DPPH consumed in the reaction is determined and can be related to the number of radicals produced in that run.

The maximum number of chains that could intersect a unit area in a perfect crystal can be calculated from the chain packing of the crystalline form with the assumption that the aligned chains are perpendicular to the area. A correction is made for the lower density of the sample compared to that of the crystal. For each run the area of the polymer shavings is measured by the technique previously mentioned and is used to calculate the maximum number of chains that could be theoretically severed. The number of radicals found in an experiment may then be converted to bonds broken by dividing by two. This number of bonds can be conveniently expressed as a percentage of those that could theoretically be broken (termed % BB). The percentage reported is a minimum, since the number of chains actually intersected by cutting will be considerably less than calculated for cut normal to the chain axes in a perfect crystal. However, % BB is proportional to the number of active reaction sites per unit area produced and offers a convenient basis for comparing the extent of the surface reaction.

Experimental Design

The factors investigated include the operating conditions of the experiments, speed, and cutting torque, as well as the four basic characteristics of the countersinks used. These characteristics and their values are as follows: number of flutes, three or four; angle of the tip or included angle, 60° or 120° ; sharpness, sharp or dull; rake angle, 0° or -30° . Rake angle is measured between the forward surface of the blade and the normal to

CONDITION OF BIT		SHARP		DULL	
		0°	-30°	0°	-30°
INCLUDED ANGLE	RAKE ANGLE				
	FLUTES				
60°	3	SHAVINGS TOO LARGE	SERIES 3	COUNTER SINK WILL NOT CUT POLYMER	
	4	SERIES 4	SERIES 7	SERIES 2	SERIES 6
120°	3	SHAVINGS TOO LARGE	SERIES 5	COUNTER SINK WILL NOT CUT POLYMER	
	4	THIS COUNTERSINK NOT AVAILABLE			

Fig. 4. Overall experimental design.

the plane of the polymer surface being formed. The negative angle means that the forward surface of the blade above the cutting edge is ahead of the cut. These four factors form a 2^4 factorial design of 16 possible blocks of experiments. The factors of speed and torque were investigated within each block.

Figure 4 shows the overall possible 16 blocks, or plots, and the series numeration for those blocks that were run. The blocks that were deleted from the design had practical problems rather than theoretical problems associated with them. A four-fluted countersink with an included angle

of 120° is not available commercially, which eliminates the bottom row of four blocks from consideration. The three-fluted countersinks contact a sample on an entire surface rather than only on an edge, rendering them essentially useless when dull. The three-fluted countersinks with a 0° rake angle cut shavings that were too large to be packed into the surface area sample holders. The six remaining blocks represent the limited design used for high-density polyethylene. Additionally, series 8 was run to determine the effect of different polymers, namely, low-density polyethylene and nylon, and a duplicate of series 2 was run on polypropylene and designated series 9.

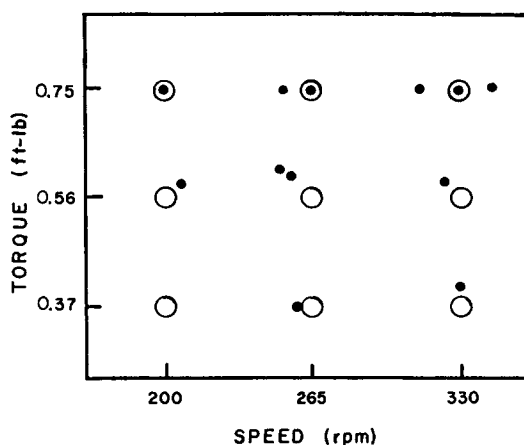


Fig. 5. Experimental design within a single block.

Figure 5 shows an example design within a block for series 2. The circles represent the designed conditions of speed and torque, while the dots represent the actual conditions at which the runs were made. The design within each block was orthogonal with respect to speed and torque, but difficulties in attaining exactly predetermined values of speed and torque caused the discrepancies between designed and actual conditions. Series 2, 3, and 9 were designed for nine runs, all others for four runs.

The extent of reaction for series 9 was much greater than for the other series. This resulted in almost complete exhaustion of the DPPH solution, even when the area produced was not particularly large. To insure that DPPH would always be in excess, which was necessary for good extrapolations, series 9 was made with a higher concentration (0.30–0.33 g/l.) than were the other runs (0.016–0.018 g/l.). Absorbances were then measured in 4-ml electrophotometer cells rather than the standard 23-ml cells. This resulted in a lessened sensitivity which was acceptable owing to the greater amount of reaction. In all other respects, the polypropylene runs of series 9 were run identically to the polyethylene runs of series 2.

RESULTS AND REGRESSION ANALYSIS

The values of the per cent bonds broken (% BB) for the runs made on polyethylene were mostly in the range of 0.5–1.5%, while the values for polypropylene were 10–20%. Estimates of the experimental error calculated from duplicate runs for polyethylene and polypropylene varied with the magnitude of % BB when either % BB or $\log(\% \text{ BB})$ was used as the dependent variable, but showed no such trend with $(\% \text{ BB})^{1/2}$ as the dependent variable. Therefore, in order to obtain a single regression equation with uniform variance for both polymers, $(\% \text{ BB})^{1/2}$ was used as the dependent variable in the analysis.

The major variables regressed were speed, torque, sharpness, rake angle, number of flutes, included angle, polymer used, power, and total energy input. In addition, all possible and plausible two-factor interactions were added as well as second-order terms of speed, torque, and power to provide 40 possible items. To avoid computational problems, the main variables were coded about their means. Table I lists the coding for the discontinuous variables of polymer, sharpness, rake angle, flutes, and included angle.

TABLE I
Coding Used for Discontinuous Variables

Variable	Coding	
	-1	+1
Polymer	polypropylene	polyethylene
Sharpness	dull	sharp
Rake angle	0°	-30°
Number of flutes	3	4
Included angle	120°	60°

tinuous variables of polymer, sharpness, rake angle, flutes, and included angle. A stepwise forward-selection regression¹⁹ was used to build the "best" model using the results from 56 runs.

Analysis showed significance (95% level) of the polymer term and the coefficient b_{12} of the speed (Sp) \times sharpness (Sh) interaction. Since the variables were coded about their mean values (designated by bars over the variable), the interaction term was actually of the following form:

$$b_{12}(Sp - \bar{Sp})(Sh - \bar{Sh}) = b_{12}Sp \times Sh - b_{12}Sp \times \bar{Sh} - b_{12}\bar{Sp} \times Sh + b_{12}\bar{Sp} \times \bar{Sh}.$$

Thus, in addition to the speed \times sharpness interaction, the regression equation necessarily contains linear speed and sharpness terms since the average values are merely preselected constants. In order to obtain the best coefficients for each of these terms, linear speed (not significant) and sharpness (significant) were forced into the regression equation. This provides a somewhat better fit to the data and does not add to the complexity of the regression equation. With both linear speed and sharpness

TABLE II
Summary of Regression Analysis for (% Bonds Broken)^{1/2} with
Combined Polyethylene (44 Runs) and Polypropylene (12 Runs) Data

Source	Degrees of freedom	Sum of squares	Mean square	<i>F</i> -ratio	Critical value <i>F</i> _{0.95}
Regression	5	79.579	15.916		2.90
Residual	50	4.429	0.089		
lack of fit	35	3.479	0.099	1.41	2.22
error	15	0.945	0.063		
Term of Equation		Coefficient		<i>F</i> -ratio	<i>F</i> _{0.95}
Constant		1.3345			
Polymer		-1.3856		794.0	4.54
(Speed/100) × sharpness		0.3029		23.4	4.54
Speed/100		0.0946		2.28 ^a	4.54
Sharpness		-0.1231		5.69 ^a	4.54
Flutes		-0.1246		5.30	4.54

^a These terms were required in the equation since they enter via the interaction (see text).

terms forced into the regression equation, the number of flutes on the countersink adds significantly to the prediction of bonds broken. No other terms of the remaining 35 are then near this significance level. Table II shows the analysis for the final regression equation. Note that this equation is a statistically adequate fit of the data as its "lack of fit" is clearly not significant. When decoded, the prediction equation for the combined data becomes the following:

$$\begin{aligned}
 (\% \text{ BB})^{1/2} = & 1.911 + 0.00084 (\text{speed}) - 1.062 (\text{sharpness}) \\
 & + 0.00303 (\text{speed}) \times (\text{sharpness}) - 0.125 (\text{flutes}) - 1.386 (\text{polymer})
 \end{aligned}$$

where speed is in rpm and other factors are as defined in Table I. Prediction curves with 95% confidence limits plotted from the above equation are shown in Figure 6 for polyethylene and in Figure 7 for polypropylene. Actual data points are included for Figure 7 for polypropylene and are shown in Figures 8 and 9 for polyethylene.

The most striking effect noted is that of polymer; polypropylene yields about ten times as many radicals as does polyethylene under similar conditions. It was not possible to extend the polypropylene data by using sharp countersinks, as they gave thinner shavings that tended to string together as opposed to polyethylene whose thicker shavings tended to break up. This "hinge" property of polypropylene is well known; it has been used commercially to produce molded articles with built-in hinges.

The effects of sharpness of the cutting edge, speed of cutting, and the number of cutting edges on the countersink are interrelated. From Figure 6 it can be seen that for polyethylene, a sharp, three-flute countersink produces over 1.5% bonds broken at speeds in excess of 400 rpm. At lower

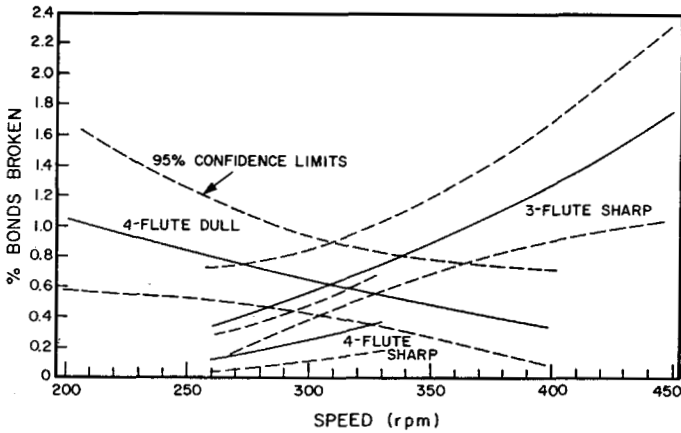


Fig. 6. Prediction curves and 95% confidence limits for high-density polyethylene.

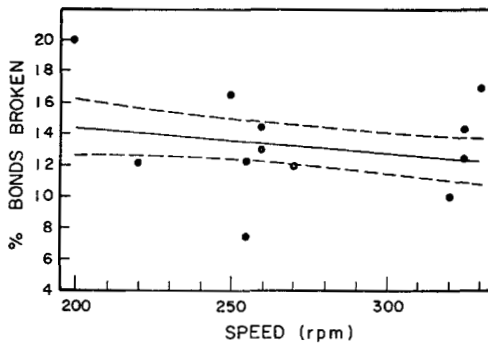


Fig. 7. Prediction curves with 95% confidence limits and data points for polypropylene using dull four-fluted countersink.

speeds, below 300 rpm, the response drops below 0.5%. The sharp, four-flute countersink produces even fewer bonds broken over the limited range of speeds at which it could be successfully used in these experiments. However, the dull four-flute countersink gives the opposite effect of speed. One per cent bonds are broken at 200 rpm, and this response drops to 0.4% at 400 rpm. Note from Figure 6 that the confidence limits are wide due to the scatter of data as shown on Figures 7, 8, and 9. Nevertheless, the trends are real as established by the statistical analysis.

The three- and four-flute countersinks cut by different mechanisms owing to their different contact with the polymer sample. The three-flute countersink does more parallel-type cutting as it slides along a surface, while the four-flute countersink does more scraping as only the thin, protruding cutting edges contact the sample. The difference in % BB may be due to a greater ability of the polymer to fracture along crystalline boundaries when scraped than when cut. A cutting operation sets up stresses along planes which produces smooth surfaces. Scraping produces a rougher surface. On the other hand, the three-flute countersink may in some way

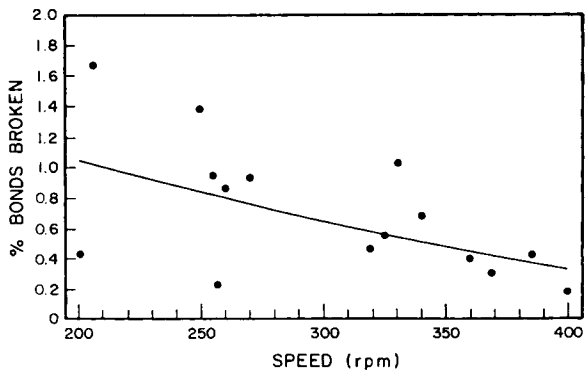


Fig. 8. Prediction curve and data points for high-density polyethylene using dull countersinks.

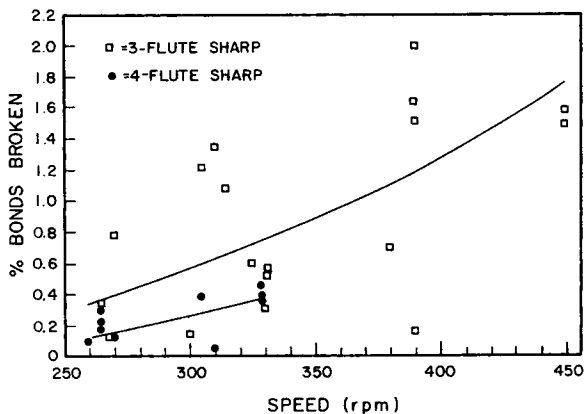


Fig. 9. Prediction curves and data points for high-density polyethylene using sharp countersinks.

be activating the surface by the continuous rubbing of its more extensive contact surface. It must also be noted that it is not possible to guarantee that equivalent degrees of "sharpness" and "dullness" were achieved for the various countersinks. This, the effect of flutes could be fortuitous, stemming from this possible inequality of sharpness; but in any case, the sharpness of the cutting edge is an important factor in the mechanochemical production of free radicals.

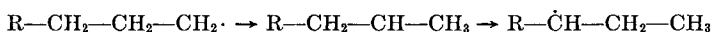
The effect of the speed of the operation depends upon the sharpness of the countersink. For sharp countersinks, greater speeds produce more radicals; while for dull countersinks, lower speeds produce more. The greater number of radicals produced at higher speeds for sharp countersinks may be due to the shorter time allowed for stress relaxation. The opposite effect for dull countersinks may stem from a tendency for the countersink to slide over the sample and fail to cut continuously at higher speeds. The exact nature of this relationship remains undetermined.

The included angle of the tip of the countersink and rake angle of the blade face to the normal of the surface had no significant effect on the bonds broken.

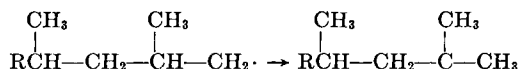
One might reasonably expect that, when cut, a polymer would tend to fracture along crystalline boundaries and not break any bonds at all. Given a perfectly crystalline polymer and an infinitesimal cutting rate, this would probably be true. However, real polymers are not perfect crystals with regular faces as they contain tie molecules as well voids. As many as 20% of the chains of a polymer mass may be tie molecules.^{20,21} It is impossible to avoid rupturing at least the bonds in the tie molecules during cutting or fracture.

Furthermore, predominantly amorphous polymers might be expected to have more bonds ruptured than predominantly crystalline ones under similar conditions. In this work, such a trend between limited data on low-density (more amorphous) polyethylene and these extensive results on high-density (more crystalline) polyethylene was not found. However, with the large scattering of results involved in these experiments, the number of runs made with low-density polyethylene are not sufficient to draw valid conclusions concerning the effect of crystallinity. The large response of polypropylene cannot be explained by crystallinity alone. An explanation can be based upon the physical property differences of polyethylene and polypropylene. The rigidity of the polypropylene molecules in their matrix is greater and not able to bend or give to applied stresses as easily, they rupture to a greater extent. While other differences in morphology do not seem to be sufficient alone to account for the much greater extent of surface reaction measured with polypropylene, they undoubtedly contribute to some degree.

However, a more fundamental understanding of the macroradicals formed by the mechanochemical process leads to an important difference between polyethylene and polypropylene that likely accounts for much of the great difference in results. The formation of radicals on newly formed polymer surfaces is at best momentary. If no reactant chemical species is immediately available to the radical, it will migrate into the polymer interior by hydrogen transfer. Once away from the surface, the free radical is more stable due to the absence of species with which it can react. Migration of the free radical in polyethylene to the interior is much more likely than with polypropylene. The individual steps of migration from carbon to carbon in the polyethylene chain are simply the repeating of the same general reaction which results in the migration of a secondary free radical:



In polypropylene, however, the more stable free radical shown in the following reaction is formed:



The continued process of free-radical migration is not favored for polypropylene because of the stability of the tertiary free radical. This leaves the free radical at the surface and available for reaction and offers an important mechanistic reason why the extent of surface free-radical reaction is an order of magnitude greater for polypropylene than polyethylene.

The nature of the study of macroradicals depends upon the use to which the information obtained will be put. In measuring the degradation of a polymer mass, a pertinent response to measure would be the total number of radicals formed by the process in question. For purposes of evaluating possible useful surface reactions, only those radicals on the surface should be counted. Thus, the methods used in this research provides the first quantitative data on surface radicals potentially available for reaction.

COMPARISON WITH OTHER WORK

The quantitative determination of the active free radicals on newly formed polymer surfaces has been attempted previously. Backman and DeVries¹¹ sliced polymers with a plane, quickly quenched the free radicals in liquid nitrogen, and measured the total radical content of the sample by electron spin resonance (ESR). All radicals formed, not just those on the surface, are counted by ESR. The radical densities determined by Backman and DeVries are reported to depend upon the temperature at which the polymer sample was cut. Of course, this is the ambient, and the temperature in the immediate vicinity of the cut is likely to be higher and very difficult to even approximate. Therefore, we have not reported a single temperature for our work but the readings of thermocouples counted in the polymer adjacent to the cut (max. 50°C) and the temperature of the solution in intimate contact with the surface (max. 70°C).

Table III compares the radical densities obtained in this work and the maximum values reported by Backman and DeVries for polyethylene, nylon, and polypropylene. For polyethylene and nylon, their maximum values are within the ranges we obtained. Since we found the free-radical density to vary with sharpness of the blade and the speed of cutting, agreement of their ESR results with our DPPH results is feasible. The sharpness of the blade of their plane and speed of cutting are not reported, so a

TABLE III
Free-radical Surface Densities Compared with the
Maxima Obtained by Backman and DeVries

Polymer	Radical density, $\times 10^{-13}$	
	This work ^a	Backman and DeVries
Polyethylene	0.1-2	0.6
Nylon	0.5-4	1.5
Polypropylene	7-9	0.7

^a Based upon the range of predicted values over cutting conditions employed.

more detailed comparison is not possible. The maximum free-radical density they obtained for polypropylene is an order of magnitude below our range. Our higher results could be due to the differences in mechanical procedures, with polypropylene results being exceptionally affected by the differences. However, Backman and DeVries discuss the possibility that free radicals are formed in much larger concentrations than they observe, but have a lifetime much too short for observation by their technique. By slowly grinding polymers at liquid nitrogen temperature and then warming, they did not find radical decay reactions. Thus, Backman and DeVries assume that it is possible to neglect radical decay in the $1/2$ sec between cutting and quenching in liquid nitrogen.

This is contrary to Bresler's^{6,7} contention that macroradicals could not be detected at all at room temperature. In fact, he found that polycaprolactam ground in liquid nitrogen gave macroradicals that lasted but for a minute or two even at this low temperature. Polyethylene ground under similar conditions gave no primary radicals at all. In addition, Peterlin and Campbell⁹ could not detect macroradicals during the fracture of nylon 6 or nylon 66 rods at room temperature. Had they obtained the same radical density achieved by Backman and DeVries, they would have produced approximately 2×10^{12} radicals in their single fracture. This is about an order of magnitude greater than the sensitivity of the Varian ESR spectrometer and therefore should have been detectable.

DeVries, Roylance and Williams²² report similar findings to those of Campbell and Peterlin. Therefore, we conclude Backman and DeVries results are likely to be low due to radical decay. Their temperature effect on free-radical density might well include the effect of temperature on radical decay as well as the polymer rigidity, and they recognized this possibility. From the previous discussion of migration of the free radicals, greater loss of at least the original polypropylene free radicals would be expected since they do not migrate to the interior as readily as polyethylene radicals. Therefore, Backman and DeVries could have had a much greater loss of the free radicals with polypropylene leading to their values being near the polyethylene ones they determined.

It should also be noted that Backman and DeVries used the surface area calculated from the dimensions of the individual slices, assuming planar surfaces to report radical densities. They recognize that the new surfaces are formed along paths of least resistance, which are not planar. Thus, their estimate of area is likely to be in error by a significant factor which differs for various polymers depending upon the smoothness of the surfaces formed when sliced. They did determine one area with a commercial sorptometer. For nylon ground with a rotary file under liquid nitrogen, they report 0.3 to 0.7 m²/g, but comment that this equipment is accurate for surface areas above 10 m²/g. Our specially developed surface area measurement equipment and method enabled us to obtain meaningful surface areas for polymer samples in the low specific surface area range found with polymer shavings.

Pazonyi et al.⁸ also investigated mechanoradicals with the use of DPPH. They sliced polymer into an alcoholic solution of DPPH and allowed it to age for 24 hr before absorbance measurements were made. We found that DPPH reacts with compounds having active α -hydrogen atoms, including alcohols, much too quickly to be used to quantitatively determine the extent of mechanochemical reaction. Their explanation that the DPPH takes time to "diffuse" into the polymer is difficult to accept, as there is no substantiation in the literature that DPPH can diffuse significantly into an unswelled polymer. We found experimentally that DPPH reacts with polymer surfaces at varying rates. This reaction with fine poly(tetrafluoroethylene) shavings results in colorless solutions in 10 min, while fine polyethylene shavings can discolor a DPPH solution in several days. Thus, reactions of DPPH with the alcohol and with the nonfree-radical polymer surface consume the reagent and give the excessively high results for surface free-radical density in the work of Pazonyi et al. Further, the surface area produced by Pazonyi in slicing was approximated by the physical dimensions of the slices. As just discussed, this does not lead to good approximations and is likely an additional reason that they report more free radicals than the maximum calculated for complete bond cleavage.

SUMMARY AND CONCLUSIONS

It has been found that diphenylpicrylhydrazyl, in a proper solvent, can be used to quantitatively determine the number of macroradicals present on newly formed polymer surfaces. Coupled with accurate area measurements of the surfaces formed, this method has been used to determine that the number of free radicals formed is $2 \times 10^{13}/\text{cm}^2$ of new surface for polyethylene and $9 \times 10^{13}/\text{cm}^2$ for polypropylene. Thus, at least several per cent of the exposed polyethylene bonds are broken and are available for surface reaction. The corresponding figure in the case of polypropylene is much higher, 20% or more. The likely explanation is that migration of the free radical along the chain to the interior of the polymer occurs readily for polyethylene, but the more stable tertiary free radical which results from severing polypropylene remains available at the surface. The physical condition of the cutting is important as both the sharpness of the blade and the speed of the cutting procedure affect the percentage of the exposed bonds that are broken.

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