Free radicals and new end groups resulting from chain scission:
2. Mechanical degradation of polyethylene

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The number of chain scissions accompanying mechanical degradation of polyethylene has been estimated from i.r. analysis of new end group concentrations. Polyethylene specimens fractured in tensile deformation and ground under liquid nitrogen were examined. The results are compared to the number of free radicals generated during mechanical degradation and measured by e.s.r. In comparison with previous results in the literature our results are lower by 1–2 orders of magnitude and in better agreement with estimates of the number of chain scissions from viscosity measurements. An ultra high molecular weight polyethylene was examined as a control specimen containing few end groups. The change in the number of vinyl groups resulting from grinding of this specimen were estimated to be at least an order of magnitude lower than that found for lower molecular weight polyethylenes. This finding suggests that large errors may be introduced into the determination of concentrations of end groups through subtraction of relatively intense absorption bands.

Keywords Mechanical degradation; polyethylene; fracture; bond scission; infra-red spectroscopy; electron spin resonance spectroscopy

INTRODUCTION

In a previous paper the authors compared the results of studies by electron spin resonance (e.s.r.) and infra-red spectroscopy (i.r.) on molecular damage in polyethylene resulting from γ-irradiation[1]. It was explained that γ-irradiation at liquid nitrogen temperature facilitates the production of large numbers of free radicals for e.s.r. detection, and on subsequent warming the development of new groups detectable by i.r. without many of the other structural changes associated with mechanical straining and fracture. Since i.r. is sensitive to many of these other changes, such as crystallinity, orientation, surface conditions and sample thickness, it was thought that damage by γ-irradiation would provide a 'cleaner' reference study in which to develop techniques and evaluate their limits of resolution and detectability. Results of the study of molecular changes in polyethylene degraded by mechanical means are presented in this, the second paper of the series.

Investigators in these laboratories, and elsewhere, have been engaged in monitoring the molecular changes associated with deformation and mechanical failure in polymers. To date the major tool has been e.s.r.[1–6] But because of the inherent instability of most organic free radicals resulting from homolytic bond rupture e.s.r. studies have, as a result, been confined to those systems with comparatively stable free radicals and for relatively short-term tests ($\sim$1 h). Due to the particular interest of the role of time in properties of polymers, investigators have searched for other techniques that do not have this inherent limitation. It has been reported that i.r. spectroscopy might be used to detect the new end groups resulting from chain rupture[1,7–12]. Once formed, the new end groups should be quite stable, facilitating studies of long-term properties such as creep and fatigue.

The pioneering work on the use of both e.s.r. and i.r. to study mechanical damage was done by the fracture group at Leningrad under the direction of S. N. Zhurkov. In these initial studies using i.r. it was reported that each free radical might represent a large number of chain scissions[7]. In fact, the number was reported to be several thousand for polyethylene indicating substantially more molecular damage during fracture than generally thought. These reports have stimulated other supplementary studies of bond rupture. The molecular weight changes resulting from fracture have been reported[13,14]. The results of these studies also provided an interesting comparison with e.s.r. *Figure 1* shows the fractional change in the average molecular weight determined by viscosity for nylon-6 at various strains, and *Figure 2* shows the relative changes in molecular weight as a function of the fracture test temperature, as reported by Shen[13]. These curves might be compared with the free radical results for straining and fracture of nylon-6 shown in *Figures 3* and *4*. A quantitative comparison of numbers obtained in the studies is also interesting.

Previous work, in the laboratory at the University of Utah[15], on molecular weight changes is in agreement with a more recent extensive study of viscosity average molecular weight[14]. In both studies it has been reported that the extent of bond rupture as indicated by e.s.r. and *MW* changes differ by a factor of 10 at most if a random-

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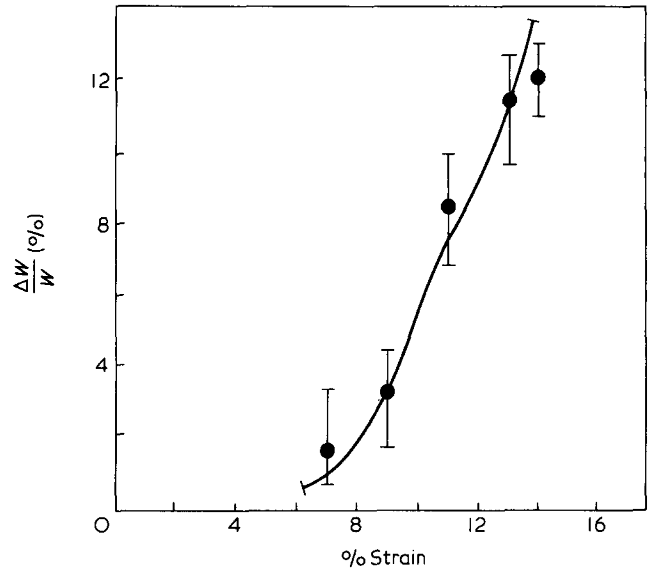

Figure 1 Change in molecular weight *versus* strain for nylon-6 fibres

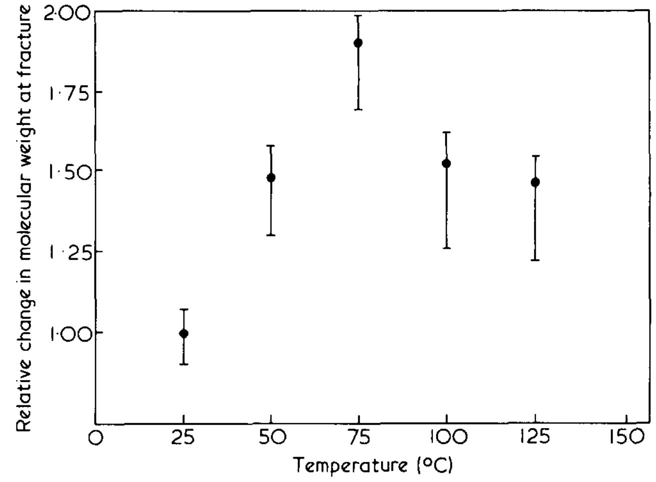

Figure 2 Change in molecular weight as a function of temperature for nylon-6 fibres

scission model is used to determine the extent of bond rupture from molecular weight changes. If one assumes that there is an increased tendency for the larger molecules to rupture over smaller molecules agreement is even better. The difference might also be explained in terms of a rapid free radical decay mechanism in which 90% of the free radicals decay before they can be observed. Perhaps this could occur during the transformation of the primary radicals resulting from chain scission to the more stable secondary radicals that are observed. Stoeckel *et al.*[14] concluded that their viscosity average molecular weight data did not support the conclusion made from the early i.r. results that the extent of bond rupture was more than 3 orders of magnitude higher than the number of free radicals observed by e.s.r.

Our initial efforts to duplicate the i.r. studies were not too promising despite the fact that we used both a dispersive instrument (with sensitivity similar to that used by Zhurkov, *et al.*[7]) and much more sensitive Fourier transform instruments. A major problem encountered in the i.r. determination of new end groups resulting from fracture has been the sensitivity of i.r. measurements to factors other than concentrations of particular groups. Pulling a polymer to fracture affects sample thickness, surface conditions, amount of crystallinity, and chain orientation. I.r. is sensitive to all these factors. In principle, it should be possible to separate the changes in spectra resulting from new end groups from these other factors. but in practice this has proved to be a very difficult task. The potential of the method was thought to be so great that it was essential to explore means of reducing these other effects some of the efforts in this area will be described in this paper.

EXPERIMENTAL

Materials and testing procedures

The primary experimental techniques used in this investigation were electron spin resonance spectroscopy (e.s.r.) and Fourier transform infra-red spectroscopy (*FT*i.r.). The e.s.r. spectra were made on a Varian E-3 instrument.* Infra-red spectra were obtained using a

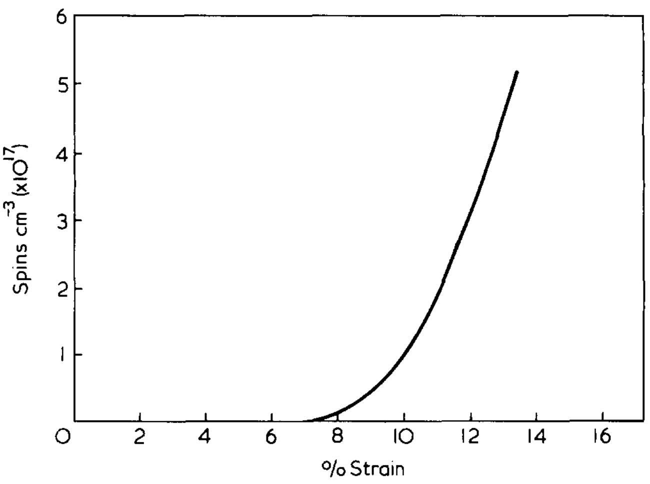

Figure 3 Generation of free radicals in nylon-6 fibres as a function of strain

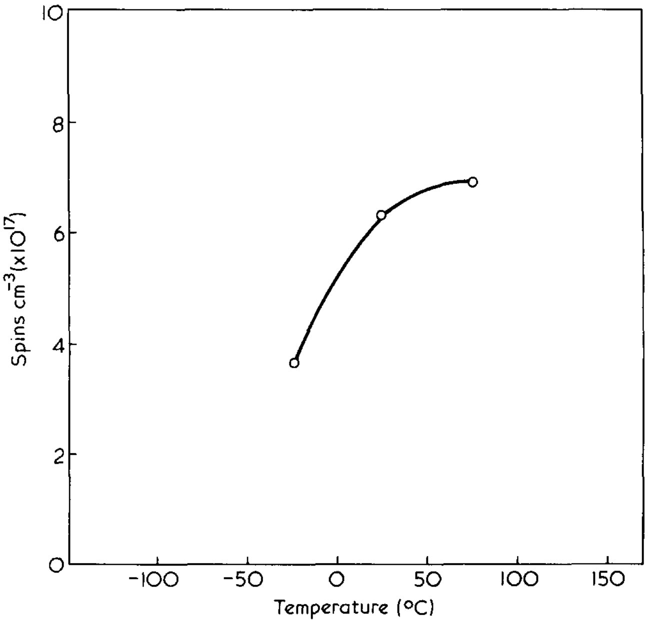

Figure 4 Free radicals concentration just before fracture in nylon-6 fibres as a function of temperature

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* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.

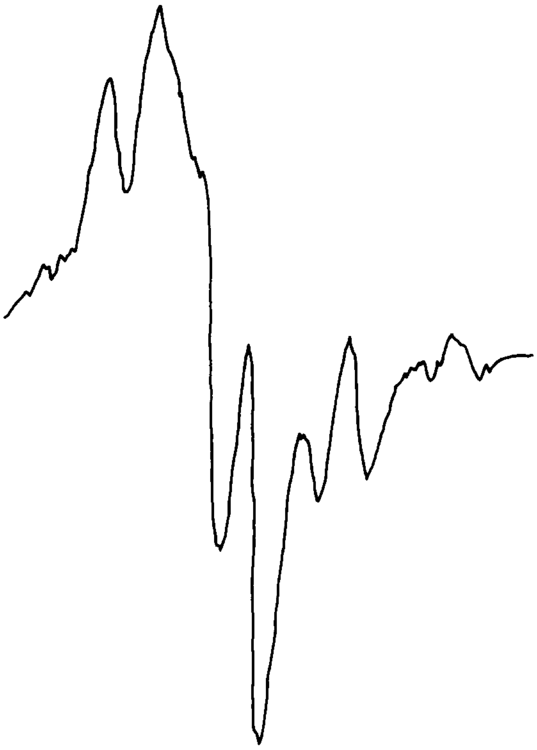

Figure 5 E.s.r. spectrum of tensile-deformed polyethylene fibres. Spectrum taken at −25°C, gain of 8 x 10^5, and near the fracture point

Nicolet series 7000 located at the National Bureau of Standards in Gaithersburg, Maryland.

Linear polyethylene of three types were used in the experiments: 12 mil diameter fibres obtained from W.R. Grace and Co., commercial high density rod $\frac{1}{4}$ inch in diameter obtained from Commercial Plastic and Supply Corp., and rods of a Hercules ultra high molecular weight (*UHMW*) material, Hifax 1900.

The fibres were tested in tensile tests in which the samples were pulled to failure. The commercial and *UHMW* rods were used in studies in which they were ground under liquid nitrogen using a dental burr in a hand grinder. Grinding has proven to be a convenient method of producing large amounts of fracture surface in a small mass of material[6]. Furthermore, the fractured material is produced in liquid nitrogen at which temperature the free radicals have been found to be very stable in most polymers. The material may then be transferred to quartz tubes which are maintained at cryogenic temperatures until tested. If the testing is also conducted at low temperatures, free radical decay is effectively reduced. The grindings are then allowed to warm to, and held at, room temperature for several days. This operation allows the free radicals to undergo chemical reactions to produce stable chemical species for study with i.r.

Films were cast from these grindings by either solvent casting from toluene or by hot pressing. In either case films were produced a few thousandths of a centimetre thick that were suitable for i.r. studies. The fractured fibre segments were processed into films in a similar manner. Reference samples from non-fractured (or unground) material were processed into films under identical conditions. It was noted that in some cases a small amount of non-soluble residue was developed in the fractured fibres. This might be interpreted as a sign that mechanically developed radicals produce cross-linking resulting in some gel formation. This residue was not observed in the case of the non-fractured material. One of the major purposes in processing films in the manner described was to reduce the effects of straining and fracture on the i.r. spectrum other than those changes due to chain rupture. It was thought that a comparison of the i.r. absorption spectra of films processed from fractured specimens with those made from unstressed materials should yield a more direct comparison of the formation of new end groups than by attempting to correct the infrared data for the other stress induced structural changes that may affect i.r. intensities of bands assigned to new end groups.

RESULTS

E.s.r.

Figure 5 shows the e.s.r. spectra from pulling polyethylene fibres at ~0°C in the e.s.r. microwave cavity. This spectrum was taken just before failure at a stress of ~500 MPa. It should be noted that e.s.r. spectroscopy is an 'averaging' technique in that it measures the number of unpaired electrons (in this case free radicals) present in the microwave cavity. For an X-band instrument of the type used in this study the cavity is a chamber ~2.5 cm long and 1 cm in diameter. The concentration of free radicals is obtained by dividing the measured number of free radicals by the volume of the material in the cavity. The spectrum taken by a typical e.s.r. spectrometer is the first derivative of the microwave absorption curve. The number of free radicals is determined by integrating this spectrum twice, with the aid of a computer, and comparing it with a suitable (pitch) standard where care has been taken to keep the experimental conditions (e.g., filling factor) as near the same as possible. Experience would indicate that while the determination of the absolute number of free radicals might be uncertain by as much as a factor of 2 or 3, changes of a few per cent in free radical concentration for a given sample type can be readily detected. As demonstrated in a recent article by Gvozdic and Dole[16], organic free radicals (e.g. alkyl radicals in PE) can exhibit saturation effects at very low power levels. In the results reported here care was taken to account for such saturation effects.

A concentration of 3.5×10^{15} free radicals per gram was determined from e.s.r. spectrum in *Figure 5* and represents the condition just before fracture of the polyethylene fibres. Again, it should be emphasized that this is the average number over the sample volume. The total number of ruptured bonds at or near the final fracture surfaces is undoubtedly higher than this. E.s.r. provides more of a measure of the events leading up to ultimate failure and perhaps the development of critical flaws rather than the growth of the more critical of these flaws to ultimate failure. The i.r. studies were made on films processed from material contained in the microwave cavity and hence provide a similar averaging of events occurring during the deformation leading to fracture. It is felt, therefore, that these studies should provide a valid comparison between the two techniques.

Figure 6 shows the e.s.r. spectrum made at −150°C on grindings of PE fractured under liquid nitrogen. This is a convenient (if somewhat uncontrolled) means of

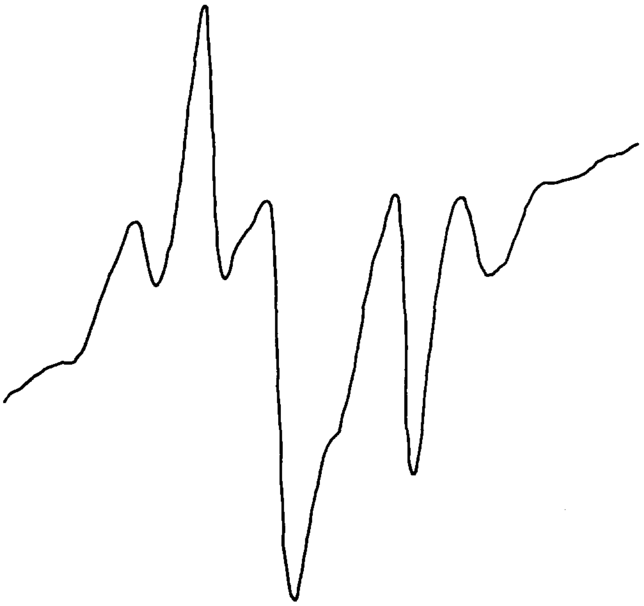

Figure 6 E.s.r. spectrum of ground polyethylene taken at −150°C, and a gain of 1.5 x 10^5

producing a large amount of fracture surface in a comparatively small volume of material. The physical character of these grindings can be seen in the micrographs of *Figure 7*. The concentration of free radicals per gram for the grindings of *Figure 6* was 1.2×10^{16}. The effect of warming these grindings to $-50°C$ for approximately two minutes is shown in the spectrum of *Figure 8*. This spectrum was also taken at $-150°C$. Double integration of the curve in *Figure 8* indicated that it too represented a radical concentration of nearly 1×10^{16}.

Grindings of ultra high molecular weight ($MW = 4 \times 10^6$) material were obtained and studied in order to circumvent the problem of large initial concentrations of end groups which plagued the i.r. studies of lower molecular weight samples. The *UHMW* material was difficult to grind at liquid nitrogen temperatures. Not only did it take extensive grinding to produce much powder but also the powder produced had a strong static charge. The powder therefore adhered tightly to the side of the dewar, drill, etc. Furthermore, this static charge made it difficult to make quantitative e.s.r. measurements. It introduced an extremely large, broad 'base line' drift upon which the comparatively small free radical signal was superimposed. Double integration of the e.s.r. spectrum obtained on the grindings of the ultra high molecular weight material revealed free radical concentration of very nearly $10^{17}/cm^3$. Warming for two minutes to $-50°C$ in air in the variable temperature accessory (actually all transient time) resulted in eventually complete conversion to peroxy radical. Double integration of the peroxy signal also indicated a free radical concentration (within 10%) of $10^{17}/cm^3$.

There was additional incidental evidence for molecular degradation in the grindings. No quantitative measurements were made, but qualitatively it was observed that during the melt casting of films the melt viscosity of the grindings was significantly less than that of the unground material. At a given temperature the material produced from grindings consistently flowed more readily in the mould than did the original polyethylene.

I.r.

Both solvent cast and melt cast films were studied with Fourier transform infra-red spectroscopy. The primary interest of this study was to determine the number of new end groups resulting from chain scission and to compare this with the e.s.r. results. Particular attention was therefore given to the regions of the i.r. spectra assigned to CHO, CH_3, and $CH=CH_2$ groups.

Shown in *Figure 9* are i.r. spectra for high density polyethylene specimen solvent cast from grindings. The top spectrum is from a film of the grindings, the middle spectrum is obtained from the reference film, and the bottom spectrum obtained by digitally subtracting the reference spectrum from the sample spectrum while compensating for the difference in film thickness. The reference film was cast from a piece of polyethylene rod near the point from which the grindings were obtained. Casting and all other conditions with the exception of the grinding operation were kept as nearly identical as possible for the two films. *Figure 10* shows similar spectra for film solvent cast from the polyethylene fibres. In this case the spectrum for a film cast after tensile fracture of the fibres is shown along with that of a reference cast from identical but 'unstressed' fibres and the difference spectrum.

There were perceptible changes between the spectra of

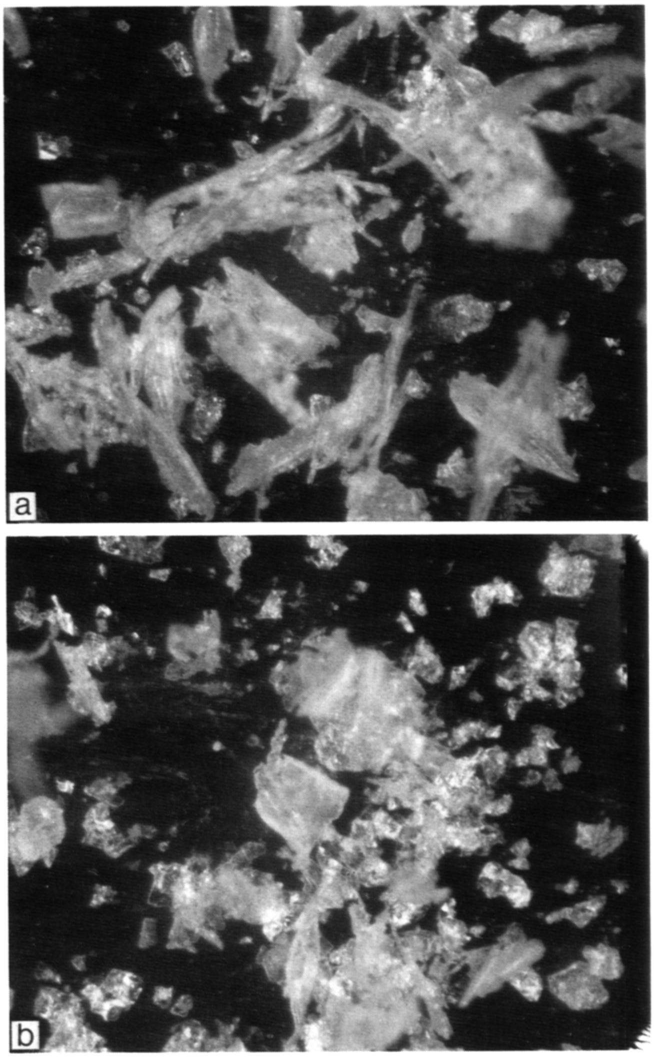

Figure 7 Optical micrographs of ground polyethylene; about 60x. (a) High density PE (b) Ultra high molecular weight PE

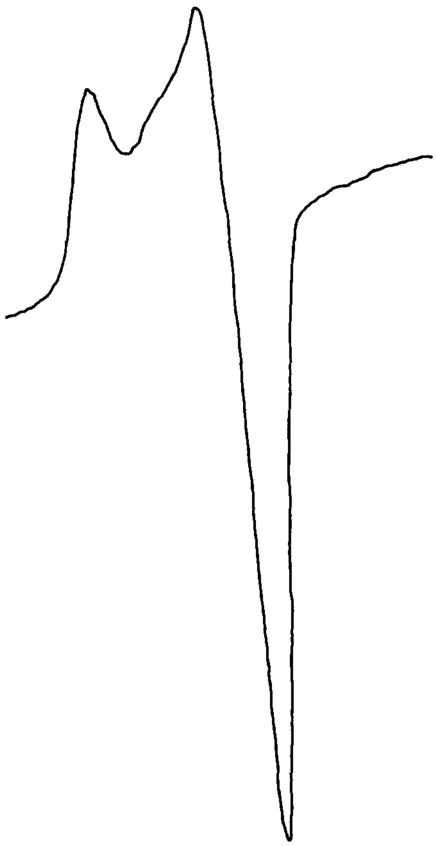

Figure 8 E.s.r. spectrum of ground polyethylene warmed to −50°C

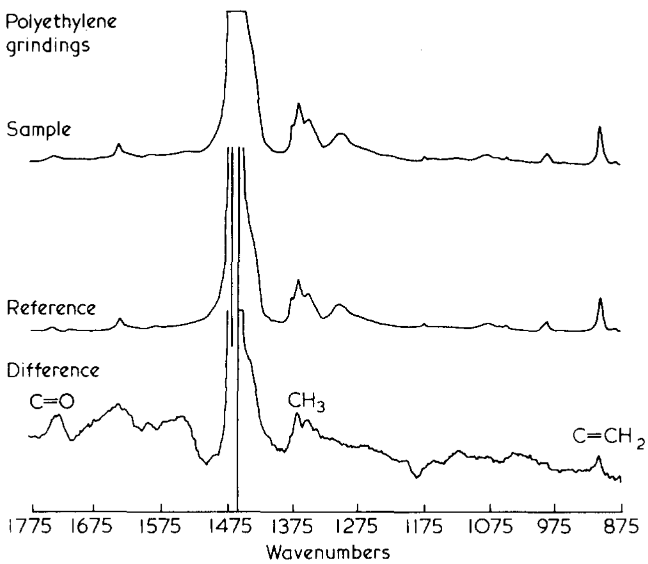

Figure 9 I.r. spectra of ground polyethylene, the reference material and their difference spectrum

the reference and mechanically degraded materials. Significant uncertainties in the quantitative determination of the change in number of new end groups are introduced by the fact that these changes were generally quite small in comparison to the size of the initial absorption bands. The absorption bands at 909, 965, 990, and 1740 cm^{-1} as well as the shoulder at 1370 cm^{-1} are attributed to end groups originally present in the polymers.

Samples of ultra high molecular weight polyethylene were examined in which the initial end group concentrations were extremely low. *Figure 11* shows the spectra from melt cast films of the ground material, its reference, and their difference spectrum. Comparison of *Figure 11* with *Figures 9* and *10* demonstrates that the end group bands are greatly diminished in the *UHMW* PE spectrum which facilitates detection of increased end group concentrations.

DISCUSSION

The results of the i.r. investigation of tensile fractured polyethylene are qualitatively compared to previous studies by Zhurkov and coworkers[7,11] and Tabb[10] in *Table 1*. Spectral changes can be classified as arising from new end groups, vinyl (909, 990, 1642 cm^{-1}), methyl (1370 cm^{-1}), and carbonyl (1717, 1735 cm^{-1}), *trans* vinylene (965 cm^{-1}), and crystallinity bands (1898, 2020 cm^{-1}). As evident from *Table 1* not all investigations have yielded even qualitatively similar data. Zhurkov *et al.*[7,11] reported a significant increase in the *trans* vinylene band at 965 cm^{-1} while neither Tabb[10] nor the present work found any measurable change in this band. It is interesting to note that the i.r. spectrum of the reference polymer of Zhurkov and co-workers[12] showed a

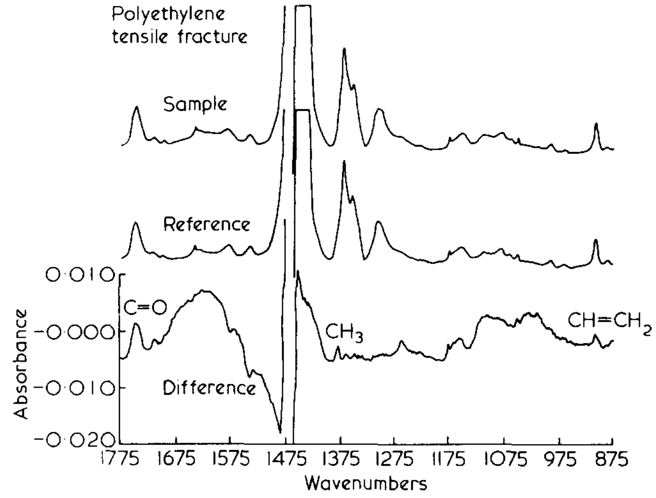

Figure 10 I.r. spectra of tensile fractured polyethylene, the reference material and their difference spectrum

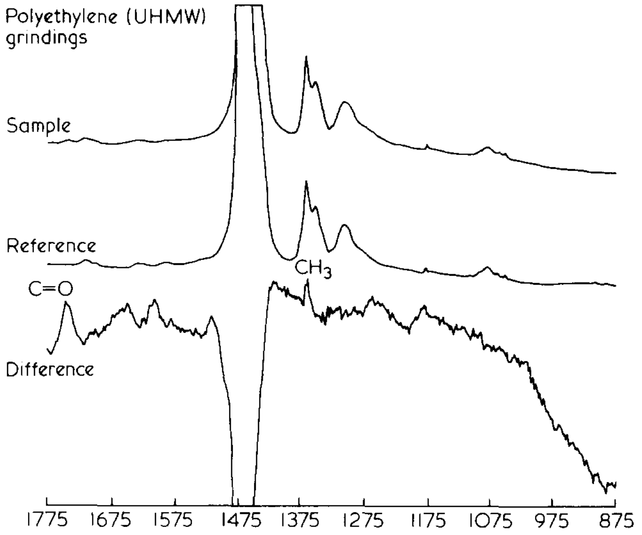

Figure 11 I.r. spectra of ground ultra high molecular weight polyethylene, the reference material and their difference spectrum

significant 965 cm^{-1} band whereas the other polyethylenes investigated had negligible absorption in this region. Incomplete cancellation of the 965 cm^{-1} band may be the origin of this discrepancy.

The terminal vinyl group gives rise to bands at 909 and 990 cm^{-1} with the intensity of the lower frequency band about 3–4 times larger than that of the higher frequency band. We do not observe changes in the intensity of the higher frequency band because on the basis of the observed 909 cm^{-1} band intensity the intensity of the 990 cm^{-1} band would be comparable to the background noise. The 909 cm^{-1} band observed by Tabb[10] is somewhat more intense and, not surprisingly, he observes the 990 cm^{-1} band as well. Zhurkov *et al.*[7,11], however, do not observe the 990 cm^{-1} band even though their 909 cm^{-1} band is more intense, on a relative basis, than that reported by Tabb[10]. The carbon double bond stretching band at 1642 cm^{-1} is also observed in polyethylenes containing vinyl groups with an intensity that is comparable to that of the 990 cm^{-1} band. For our samples the intensities of the 990 and 1642 cm^{-1} bands were such that they could not be differentiated reliably from the background in the difference spectra of *Figures 9* and *10*. For the remaining bands there is a substantial agreement between our results and previous findings[7,10,11]. The only discrepancy is in the 1717 cm^{-1} band which is not reported by Tabb[10], apparently because it is masked by the aldehydic carbonyl band ~1740 cm^{-1}.

Table 1 I.r. spectral changes in tensile fractured polyethylene

Frequency (cm^{-1})	Assignment	Spectral changes* This work	Zhurkov[7]	Tabb[10]
909	$RCH{=}CH_2$	+	+++	++
965	*trans* $RCH{=}CHR'$	–	+	–
990	$RCH{=}CH_2$	–	–	+
1370	CH_3 def. RCH_3	+	++	++
1642	C=C str. $RCH{=}CH_2$	–	NR	++
1717	C=O str. RCOR′	+	+	–
1735	C=O str. RCHO	++	++	+
1898	Combination mode, crystalline	+	NR	+
2020	Combination mode, crystalline	+	NR	+++

* Magnitude of change indicated by number of + signs, the larger the number, the greater the change. No change is showed as – and NR if not reported

From the ultra high molecular weight polyethylene difference spectrum, shown in *Figure 11*, it is evident that the intensity of the 909 cm^{-1} band is greatly diminished compared to the intensities of bands due to the methyl and aldehyde groups. The inconsistency of this result with the difference spectra in *Figures 9* and *10* may also arise from uncertainties in spectral subtraction of relatively intense bands in the lower *MW* polyethylenes. In ultra high molecular weight specimens the number of terminal groups present in the undeformed polymer is very low. Therefore, measured increases in end group concentrations would not be susceptible to errors arising from taking differences in high absorption values. It is evident from visual comparison of the *UHMW* sample and its reference (*Figure 11*) that there is an increase in the concentration of aldehyde groups. The methyl group band near 1370 cm^{-1} in the difference spectrum results from the subtraction of fairly intense bands due to methylene wagging motions of amorphous-phase polyethylene. The change in vinyl group band at 909 cm^{-1} is barely discernible in the background of the difference spectrum and corresponds to a concentration of end groups of at least an order of magnitude less than what we found for lower molecular weight polyethylene.

Concentrations of the new end groups attributable to mechanical degradation and determined from the difference spectra of *Figures 9*, *10* and *11* are presented in *Table 2*. Integrated band intensities were determined by digital integration of the baseline corrected absorption bands. Values for absolute intensities were taken from the literature[17,18] and the Beer's law relationship was assumed. The errors in concentrations are due mainly to uncertainties in the measured integrated intensities and in the values of the absolute intensities taken from the literature. End group concentrations are converted to the number of chain scissions per free radical and given in *Table 3*. The number of chain scissions was estimated from end group concentrations by summation of the number of aldehyde and vinyl groups. Here we intentionally used the same procedure as Zhurkov, *et al.*[7] in order to facilitate comparisons of results. Although Tabb[10] did not discuss end group concentrations in detail he did estimate values

Table 2 Concentrations of chemical groups formed during mechanical degradation of polyethylene

Group	I.r. band freq. (cm^{-1})	Concentrations (No./cm^3 Ground PE Commercial	*UHMW*	Fractured PE	Zhurkov *et al.*[7]
$RCH{=}CH_2$	909	$1.2 \pm 0.4 \times 10^{17}$	–	$1.3 \pm 0.4 \times 10^{17}$	3.4×10^{18}
$RCH{=}CHR'$	965	–	–	–	1.9×10^{18}
RCH_3	1370	$2.2 \pm 1 \times 10^{18}$	$5.6 \pm 3 \times 10^{18}$	$7.3 \pm 4 \times 10^{17}$	11.8×10^{18}
RCHO	1735	$3.7 \pm 0.5 \times 10^{17}$	$1.1 \pm 0.1 \times 10^{18}$	$1.9 \pm 0.6 \times 10^{17}$	4.6×10^{18}

Table 3 Chain scissions per free radical

	Ground PE Commercial	*UHMW*	Tensile fractured PE	Zhurkov *et al.*[7]
No. chain scissions per gram	$5.1 \pm 1 \times 10^{17}$	$1.2 \pm 0.1 \times 10^{18}$	$3.4 \pm 1 \times 10^{17}$	9.9×10^{18}
No. free radicals per gram	1.2×10^{16}	1×10^{17}	3.5×10^{15}	5×10^{15}
Chain scissions per radical	34–50	11–13	68–125	1600

comparable to those of Zhurkov, *et al.*[7]. Our concentrations are lower by approximately an order of magnitude and the resultant number of chain scissions produced per free radical is lower by a factor of 13–145.

The number of chain scissions calculated from our data is much closer to, but still approximately a factor of ten larger than, the values determined from viscosity data[14]. Part of this discrepancy may arise from differences in the initial molecular weights of the polyethylenes used, physical state of the specimens (fibres in our work and films for the viscosity-determined values) and the temperature at fracture. As pointed out by Stoeckel *et al.*[14], deviations from the random chain scission model would have to favour preferential scission of the shorter molecules in order to bring the i.r. and viscosity measurements closer together. This would be most unlikely; in fact, scission of the longer molecules bridging lamellae seems more likely.

Further evidence for the degradation of molecular weight comes from the observed increase in crystallinity of films made from mechanically degraded material. Increases in both the 1898 and 2020 cm^{-1} bands are attributable to slight increases in crystallinity[19].

CONCLUSION

The number of chain scissions resulting from mechanical degradation of polyethylene has been estimated from analysis of end group concentrations. We find that the new end group concentrations are lower by an order of magnitude than the values previously reported[7,10] and that the number of chain scissions per free radical is lower by one to two orders of magnitude. The differences may be attributed to large uncertainties associated with subtraction of relatively intense i.r. absorption bands. For example, the number of new vinyl groups formed as a consequence of grinding ultra high molecular weight polyethylene is at least an order of magnitude less than the value found for a lower molecular weight polyethylene that, according to its i.r. spectrum, contained an appreciable concentration of vinyl groups in the undeformed polymer.

Our estimates of the number of chain scissions is much closer to, although still higher than, values reported from viscosity determinations of the change in molecular weight attendant to mechanical degradation. Possible causes of this discrepancy may be differences in the molecular weight and physical state of the samples used in the two studies.

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