An infra-red study of bond rupture during plastic deformation in high-density polyethylene

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The effects of elongation, time and temperature upon the concentrations of carbonyl and vinyl groups formed during the plastic deformation of high-density polyethylene have been studied using infra-red spectroscopy. Samples drawn in various atmospheres are also described. The morphology of lamellar crystallized polymers is now taken to involve both folded chains and those linking adjacent lamellar cores. It is difficult to reconcile this model with the ideas proposed by Peterlin to explain plastic deformation at the molecular level unless one is prepared to accept that numerous chain ruptures occur during the process. We confirm in this paper that this is not the case and hence go on to propose an alternative explanation for the processes that occur when spherulitic materials become oriented and fibrillar. We propose and provide evidence that mechanical work is concentrated into very small volumes in the neck region leading to localized melting and subsequent recrystallization.

(Keywords: polyethylene; infra-red spectroscopy; plastic deformation; chain rupture)

INTRODUCTION

In the late 1960s, Peterlin devised a molecular model to explain the plastic deformation of semicrystalline polymers. He based his analysis, in the case of polyethylene, on the observation that few chains ruptured during the massive reorganization that occurs in converting a chain-folded lamellar–spherulitic structure into an oriented fibrillar polymeric solid. He presumed, on the basis of knowledge at the time, that few chains interlink the lamellae (tie molecules) and that, under stress, the lamellae tilt and partially unfold: this produces microfibres containing small blocks of the original chain-folded lamellae[1,2]. Microfibrils produced from lamellae are connected to their neighbours by very occasional molecules (probably originating in the interlamellar tie molecules referred to above). Further deformations at high strains result in inter-microfibrillar movement and inevitably lead to some molecular rupture.

Recently, it has become clear that Peterlin's assumption that spherulitic polymers consist of sheaves of lamellae each of a chain-folded structure and involving very limited numbers of interlamellar tie molecules is no longer justifiable. Although some doubt still exists on the extent of the interlamellar connection, it is now generally accepted that many of the chains cross the disordered regions between lamellae and link the adjacent crystalline cores[3]. Accepting this new view of lamellar structure, it is difficult to envisage the substantial molecular-level changes that Peterlin described as fibrils formed from spherulites unless one is prepared to accept that massive chain rupture and the generation of new chain ends must accompany the deformation process. Alternatively, there may be a substantially different mechanism involved in the plastic deformation process, as has been suggested by Juska and Harrison[4]. We have therefore reinvestigated the formation of new chain ends during plastic deformation of polyethylene.

Rupture of bonds results in radical formation, a phenomenon first demonstrated, in the present context, by Bressler *et al.*[5] Homolytic breakage leads to the formation of primary radicals ($-\dot{C}H_2$ in polyethylene) and then of secondary radicals by abstraction of hydrogen ($-CH_2-\dot{C}H-CH_2-$ in polyethylene), or reaction with oxygen ($R-O-\dot{O}$). Owing to the high reactivity of the primary radicals, it is often difficult to assess the number originally formed, because several secondary reactions may occur after the generation of one primary radical.

Many studies of the effect of mechanical stress on polyethylene have been undertaken, and infra-red spectroscopy and electron spin resonance (e.s.r.) have been widely used. The molecular-level consequences of mechanical processes such as fracture due to excessive loading (uniaxially stressed to fracture), fatigue fracture (cyclic loading), impact fracture and machining (milling, shaving, grinding) have been studied by e.s.r. spectroscopy[6-8], by infra-red spectroscopy[9-13] and even by viscometry[14]. An e.s.r. study on polyethylene subjected to plastic deformation, covering both the generation and decay of radicals, has also been reported[15].

The estimates of the number of bonds fractured in such situations and derived from three different methods are as follows:

I.r. spectroscopy	10^{18} to 10^{19} broken bonds/cm^3
E.s.r. spectroscopy	10^{16} to 10^{17} broken bonds/cm^3
Viscometry	$\sim 10^{16}$ broken bonds/cm^3

There are considerable experimental problems in the use of e.s.r. spectroscopy. Most of the experiments, e.g.

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Table 1 Characteristics of the high-density polyethylene used for the drawing experiments

Property	Value
$\bar{M}_n$	19 500
$\bar{M}_w$	130 000
Density (g ml^{-1})	0.956

machining and fracture, must be performed at low temperatures (77 K) to preserve any free radicals that are generated. However, plastic deformation experiments must be attempted at ambient temperature, as a consequence of which the number of radicals actually observed is less than the initial concentration, since the primary radicals react rapidly near 300 K. However, according to Stoeckel *et al.*[14], only 10–20 % of the radicals are 'lost'. Nevertheless, this approach must be suspect and there is probably a systematic error that leads to erroneously low values. The viscometric approach also poses problems because it does not measure chain ends directly and the decrease in viscosity consequent upon 10^{16} broken bonds/cm^3 in polyethylene is little greater than measuring errors.

Infra-red spectroscopy should provide the best approach because it measures the final stable products of bond rupture; the uncertainty involved relates to the choice of extinction coefficients for the bands characteristic of the functional groups formed following bond rupture.

Infra-red spectroscopy was therefore chosen as the diagnostic technique for the study now reported. The work relates to bond scission processes in high-density polyethylene (HDPE) during plastic deformation, by determining the concentration of end groups in samples drawn under a variety of conditions.

EXPERIMENTAL

The linear polyethylene used in this study was supplied by the British Petroleum Company plc, and was manufactured by the Phillips process. The salient characteristics are summarized in *Table 1*.

Thin isotropic films of uniform thickness were used for the deformation studies. They were made from the pellet material pressed at 150°C at 5–5.5 MPa for about 5 min; the films were then quenched in iced water.

The films were deformed in a table-model Instron machine (model TML), where a crosshead speed of ~ 0.5 cm min^{-1} was used. An insulated box was fitted to the Instron, to provide a variable-temperature facility and the ability to work with an atmosphere of nitrogen or oxygen. The quality of the moulding proved to be important during plastic deformation. The behaviour of the samples was rather variable; some broke soon after the yield point had been reached, presumably because of defects, e.g. air bubbles, dust particles within the polymer. Consequently only those samples which behaved similarly under stress, as assessed by their decrease of width, formation of a neck and its propagation along the length, were studied further.

Infra-red spectra were recorded on a Nicolet MX 1 Fourier transform spectrometer. Three hundred interferograms were accumulated over a 9 min period and analysed with a resolution of 2 cm^{-1}. These conditions were chosen to obtain an adequate signal-to-noise ratio.

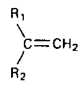
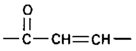
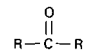
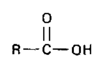
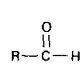
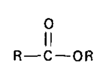
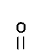
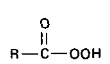
It is known that orientation occurs during the drawing process[16]. Hence polarized infra-red spectra were measured. The total absorbance A_0 is given by the average of the absorbances along three orthogonal axes: A_x, A_y and A_z. For a specimen uniaxially oriented along the y direction, the absorbances measured along the two other axes will be equal[17]. Hence,

$$A_0 = (A_y + 2A_x)/3$$

making it possible to determine A_0 from measurements in two orthogonal directions in the plane of the film. The spectrometer samples a circular area of 8 mm diameter and, since the films are unlikely to be homogeneous or uniform in thickness across this relatively large expanse, they were masked by a 2 × 5 mm slit placed over the specimen and situated in the centre of the spectrometer beam cross-section. For the two directions of the electric vector of the radiation, spectra of the background, together with those of the undrawn and drawn samples, were recorded. The total absorbance was then calculated using the above equation for A_0.

Vinyl and carbonyl groups are the functions most likely to occur as the result of chain scission of polyethylene in air. Both are readily detectable by infra-red spectroscopy, using the characteristic frequencies[18] listed in *Table 2*. In the case of the carbonyl group, it is now well established that the observed peak in the thermally or photochemically oxidized polyethylene is a composite band, probably containing three components specific for the saturated aldehydic, ketonic and carboxylic groups[19]. There is also evidence that the first of these is the least abundant[20,21]. There is a readily detectable shoulder near 1740 cm^{-1} and this has been assigned to ester groups[19].

Table 2 Characteristic infra-red frequencies for functional groups that may be formed in polyethylene by chain rupture

Functional group	Vibrational mode	Frequency (cm^{-1})
CH_3	$\delta(CH_3)$	1370–1380
$R{-}CH{=}CH_2$	$\delta(CH_2)$	910, 990
 $R_1R_2C{=}CH_2$	$\delta(CH_2)$	890
$C{=}C$	$\nu(C{=}C)$	1640–1660
 $-C(=O)-CH{=}CH-$	$\nu(C{=}C)$	1680–1690
 $R-C(=O)-R$	$\nu(C{=}O)$	1715–1720
 $R-C(=O)-OH$	$\nu(C{=}O)$	1710–1715
 $R-C(=O)-H$	$\nu(C{=}O)$	1730–1745
 $R-C(=O)-OR$	$\nu(C{=}O)$	1735–1745
 $R-C(=O)-OOR$	$\nu(C{=}O)$	1763
 $R-C(=O)-OOH$	$\nu(C{=}O)$	1785

In the present work, the peak maximum occurred at 1742 cm^{-1}, suggesting that ester groups are the major carbonyl-containing species present. The extinction coefficient of model compounds containing ester groups was duly measured and the value obtained did not differ substantially from those accepted by Rugg *et al.*[19]: viz. $1.2 \times 10^{-19}\,\mathrm{cm}^{-1} \times (\mathrm{groups/cm}^3)^{-1}$. Further vinyl and carbonyl groups proved convenient for this study because bands from both increased significantly in intensity upon drawing.

Turning to the effect of thickness, if a suitable standard band had been present in the spectra, it would have been possible to eliminate this problem and hence to follow the increase in concentrations of these functional groups. Unfortunately, such standard peaks are not available because the drawing process in polyethylene affects the chain orientation and hence the intensities of all bands. Frequency shifts also occur[22], which make the subtraction of the spectrum of the undrawn sample from that of the drawn sample meaningless.

The increase in the new end-group concentration was therefore assessed by measuring the increase of the appropriate peak absorbances in the drawn sample over those found in the original sample. The decrease of thickness resulting from the strain was taken into account and, by using the Beer–Lambert law, the following equation was derived and utilized:

$$C = [A_0(\mathrm{d})/e(\mathrm{d}) - A_0(\mathrm{u})/e(\mathrm{u})]/\varepsilon$$

where C is the increase in concentration of the functional group being studied, $A_0(\mathrm{d})$ and $A_0(\mathrm{u})$ are the appropriate absorbance values measured for the drawn and undrawn samples, ε is the relevant extinction coefficient for the peak in question, and $e(\mathrm{d})$ and $e(\mathrm{u})$ are the thicknesses of the drawn and undrawn samples. Assuming that each broken bond gives two new groups, each of which is detected, the maximum number of broken bonds should be equal to half the total number of all the new groups formed as the result of deformation. Hence,

$$\text{number of broken bonds per unit volume} = \textstyle\sum C/2$$

RESULTS

The influence of four variables upon the concentrations of carbonyl and vinyl groups formed during plastic deformation was assessed. Thus, the effects of (1) the atmosphere surrounding the sample during deformation, (2) the time elapsed between deformation and spectroscopic examination, (3) the sample temperature during deformation, and (4) the sample thickness were measured, by carrying out a series of connected and in other cases interrelated experiments as follows.

(1) Samples about 350 μm thick were selected and degassed under a vacuum of 0.05 bar for 3 days. They were then placed in an atmosphere of nitrogen or oxygen, as relevant, for 2–3 days before being drawn. The results, presented in *Figure 1*, show that vinyl group formation is favoured in nitrogen, in fact quite markedly so. In both cases, the concentration of the two types of functional group increases with increasing draw ratio. In three cases out of four, the rate of formation of the functional group increases quite considerably at high draw ratios, indicating, as was anticipated, that chain scission is more prevalent under these conditions. Only in the case of the carbonyl groups formed by drawing in a nitrogen atmosphere is the increase of concentration with draw ratio small. This is predictable if one surmises that carbonyl group formation involves the limited amount of residual oxygen present in the sample.

(2) The relationship between end-group concentration and the time lapse between deformation and spectroscopic examination has been investigated. There is no significant time dependence for vinyl group concentration, whereas the carbonyl group concentration shows a slight increase with time. The peak centred at 1742 cm^{-1} reaches a maximum intensity after 48–72 h. *Figure 2* shows the time dependence of this peak for two randomly selected draw ratios.

(3) The effect of temperature was examined over the range 7–60°C; the lower limit is set by the increasing brittleness of the polymer as it is cooled, fracture occurring before yield is reached. The results, presented in *Figure 3*, show that the concentration of vinyl and carbonyl groups, for a given draw ratio, decreases with increasing temperature.

(4) Measurements were completed on samples over a range of thicknesses and are presented in *Figure 4*. There is an inverse relationship between sample thickness and functional group concentration for a given draw ratio but the slope of the plot for the carbonyl absorption intensity is approximately three times that for the vinyl group when samples are drawn in oxygen.

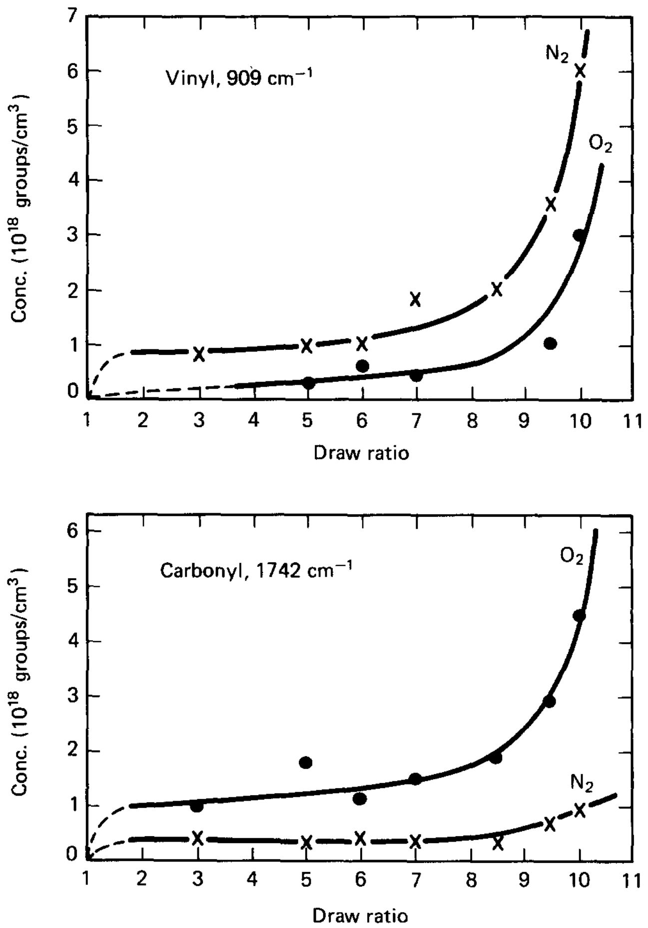


Figure 1 New end-group concentrations as a function of draw ratio and atmosphere for samples 350 μm thick at 20°C

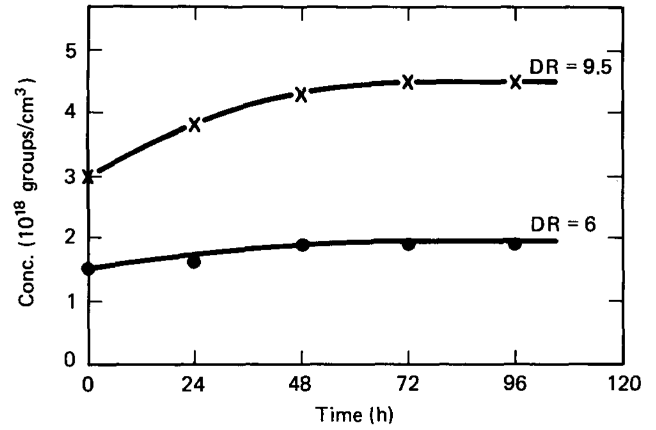


Figure 2 Carbonyl group concentration as a function of time elapsed after deformation for samples 350 μm thick at 20°C in O_2

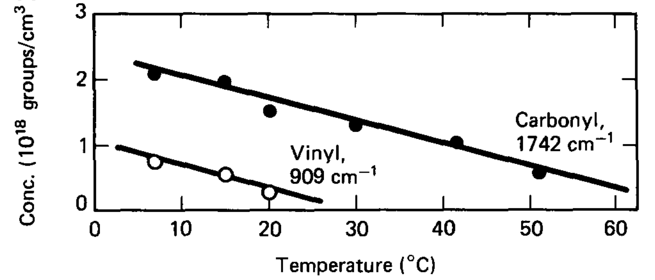


Figure 3 New end-group concentrations as a function of temperature for a draw ratio of 1.10 for samples 350 μm thick in O_2

Values obtained for the carbonyl and vinyl group concentrations from the range of experiments noted above are given in *Table 3*, from which it is clear that the incidence of bond rupture in the early stages of plastic deformation is rare.

Before discussing these results in more detail, it is pertinent to consider the precision and accuracy of the spectroscopic measurements from which they were obtained.

The information presented in *Figures 1* to *4* is essentially comparative in nature and the precision of the spectroscopic measurements is of prime importance. The estimation of peak intensities with a precision 1–2% is routine with modern spectrometers. Allowing for the effect of the thickness correction noted above, the overall intensity precision probably lies below 10%. An appreciably greater uncertainty attaches to the $\Delta L/L_0$ values, and it is this latter fact which is dominant in determining the scatter of the points in *Figures 1* to *4*. Fortunately, this modest scatter does not hinder their interpretation.

The accuracy of the determination of functional group concentration is dependent on the reliability of the molar extinction coefficients for these functional groups. The value used for the vinyl out-of-plane deformation mode band at 909 cm^{-1} is probably accurate to within 20%, because this peak, used to estimate the concentration of vinyl chain-terminating groups in some types of polyethylene, has been studied[23] extensively and is thought to be reliable.

Greater uncertainty attaches to the ε value for the carbonyl peak at 1742 cm^{-1}, for two reasons. A range of values has been noted for low-molecular-weight esters[24], and it is unlikely that the observed peak is the consequence of ester groups only. Nevertheless, even on the pessimistic basis that ε, and therefore the measured carbonyl concentrations, are in error by a factor of 2, it will be demonstrated below that this is of no practical consequence for the interpretation of our results *vis-à-vis* the type of plastic deformation process that leads to the formation of vinyl and carbonyl groups.

DISCUSSION

The results of this study are such that, during and following the plastic deformation of high-density polyethylene, the following points can be made.

(a) The concentration of carbonyl groups produced by a given draw condition is appreciably greater when the specimen is drawn in oxygen rather than nitrogen. The formation of such groups in nitrogen must be a

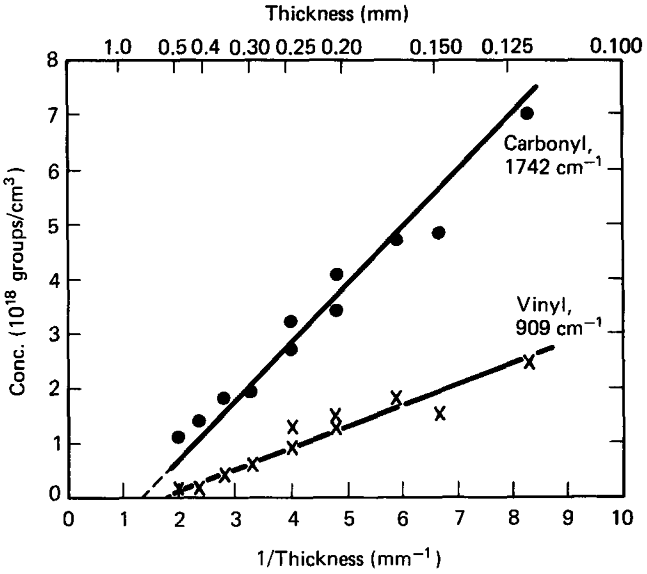


Figure 4 New end-group concentrations as a function of original thickness for a draw ratio of 0.76 in O_2 at 20°C

Table 3 Summary of results for samples prepared using a range of plastic deformation conditions

Drawing conditions[a]		Concentration (10^{18} groups/cm^3) Carbonyl	Vinyl	Total
20°C, O_2, 350 μm	$\Delta L/L_0=0.9$	1.3	0.3	1.6
	$\Delta L/L_0=1.5$	2.0	0.8	2.8
	$\Delta L/L_0=2.2$	4.6	3.0	7.6
20°C, N_2, 350 μm	$\Delta L/L_0=0.9$	0.45	1.0	1.45
	$\Delta L/L_0=1.5$	0.45	2.5	2.95
	$\Delta L/L_0=2.2$	1.0	6.0	7.0
20°C, O_2, 350 μm, $\Delta L/L_0=0.93$	0.5 h	1.4	0.5	1.9
	96 h	1.8	0.5	2.3
20°C, O_2, 350 μm $\Delta L/L_0=1.78$	0.5 h	3.0	1.0	4.0
	96 h	4.5	1.0	5.5
O_2, 350 μm $\Delta L/L_0=1.10$	7°C	2.0	0.75	2.75
	60°C	0.4	0	0.4
20°C, O_2 $\Delta L/L_0=0.76$	120 μm	7.0	2.4	9.4
	500 μm	1.1	0.2	1.3

[a] See points (1)–(4) in text for further information and clarification

consequence of the presence of some residual oxygen, not removed by the degassing routine.

(b) The end-group concentration is directly related to the extent of the deformation to which the sample is subjected.

(c) There is a dependence of the carbonyl group concentration on the time lapse between drawing and spectroscopic examination. This may be the result of two factors, the permeability of the sample to oxygen and the relatively high stability of secondary radicals or intermediate species before eventual reaction with oxygen.

(d) An increase in the drawing temperature facilitates the drawing process by providing the polymer with the thermal energy required to aid the removal of chains from the core without rupture occurring.

(e) The concentration of new end groups is inversely proportional to the sample thickness. This is in agreement with the work of Vettegren and Tschmel[11] who found that surface effects were important in loaded samples.

(f) The total number of broken bonds/cm^3 lies between 5×10^{17} and 4×10^{18} in oxygen or nitrogen at ambient temperatures. These values represent only 10^{-3} to $10^{-2}\%$ of the total number of backbone carbon atoms/cm^3 and, as noted above, a systematic error by a factor of 2 is of no practical consequence. Assuming that chain rupture is most likely to occur in the interlamellar regions, the number of broken bonds is still remarkably small.

These results therefore confirm the experimental evidence given by Peterlin[1,2] that very few chains rupture during the process of plastic deformation. However, it also serves to emphasize the incongruity of his theory of plastic deformation, viz. that there must be a massive reorganization of the material from a chain-folded lamellar–spherulitic structure into an oriented fibrillar one and that this only involves the rupture of a very small number of chains. Further, if one accepts that 20–30% of these chains bridge the intercore zones in the lamellar stacks, this conclusion is insupportable. However, it is not difficult to reconcile the present observations with the model of Juska and Harrison[4]. Their model proposes that deformation occurs by a local stress-activated transition to the melt phase, i.e. drawing involves melting, followed by extension of the molecules in the melt phase and recrystallization at the draw temperature. Support for this general hypothesis has already come from work in this laboratory, which has shown that temperatures in the vicinity of the polymer melting point can be generated in small zones during drawing[25].

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