

Localization of oxidation in polypropylene

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The distribution of oxidative degradation in isotactic polypropylene has been monitored using ultra-violet microscopy. Reaction of carbonyl groups in the oxidized polymer with 2,4-dinitrophenylhydrazine allows the oxidation to be seen with illumination at 350 nm. There is much extraction of oxidized material during the staining process. It is shown that oxidation initially favours the atactic fraction of the polymer. With increasing oxidation prior to crystallization rejection of oxidized material to the spherulite boundaries leads to increasing weakness in these regions although there is no evidence that their subsequent oxidation rate is enhanced. Localized oxidation in diluent-phase polymer is shown to correlate strongly with the distribution of catalyst residues in the polymer. Similar localization can be observed in polymer formed on a high efficiency, gas phase, catalyst although catalyst residues are not directly visible in this polymer.

(Keywords: polyolefin; degradation; oxidation; ultra-violet microscopy; catalyst residues)

INTRODUCTION

Polyolefins, particularly those like polypropylene (PP) with tertiary hydrogen atoms, are very vulnerable to oxidative degradation under the influence of sunlight or modestly elevated temperatures, with the result that the material becomes discoloured and embrittled. The reaction sequence which is generally accepted to lead to the degradation of a polymer is the familiar peroxidation chain reaction¹, initiated by high temperatures and mechanical shear during processing, direct reaction of unsaturated impurities at processing temperatures or redox effects at photoactivated transition metal centres in catalyst residues or pigments, and leading to formation of hydroperoxides.

In addition to this chain reaction, the product hydroperoxides may decompose thermally, by light absorption or under the catalytic influence of metals, to initiate further oxidation, leading to autoacceleration. In liquid phase oxidation alkoxy radicals, produced by hydroperoxide decomposition, mainly abstract hydrogen, but in polymers they are more likely to undergo a β -scission reaction to break the polymer chain, producing a carbonyl group and a new alkyl radical and reducing the molecular weight of the polymer. It is now generally believed that the oxidation of a polymer in service is initiated by the traces of hydroperoxide produced in the processing operations and that embrittlement is caused by the chain scission.

The main technical problem with oxidative degradation is that mechanical breakdown occurs at very low levels of chemical reaction. Absorption of less than one oxygen molecule per 100 carbon atoms, leading to a reduction in molecular weight by a factor of about 2 can often lead to complete loss of toughness in a PP sample. Although this is undoubtedly due to the fact that PP is a semi-crystalline polymer whose oxidation is confined to the amorphous phase, the detailed reasons for embrittlement are not clear. Carlsson and Wiles² have suggested that photo-oxidation of PP takes place on the film surface,

leading to extensive recrystallization and the production of surface cracks which can propagate through thin film and fibre samples. Oswald and Turi³ proposed that embrittlement occurs because of preferential scission of 'tie-molecules', linking crystallites in the polymer and carrying a disproportionate amount of the applied stress.

Although it is reasonable to assume that oxidation is random in the molten liquid polymer it is by no means certain that this is still true of the amorphous solid. Aggregation of polar impurity groups in the hydrocarbon polymer or their rejection by the crystallization process might be expected to lead to local concentrations of the initiating centres and thus to local variations in oxidation rate. A number of observations suggest that degradation is indeed not wholly uniform but that some species or some parts of the sample are preferentially attacked. Thus discolouration is often seen as an expanding yellow spot on a sample, resembling the spread of rot in an apple and suggesting that oxidation products themselves locally enhance oxidation. Fracture of embrittled polypropylene samples often appears to follow the spherulite boundaries or spherulite radii rather than an arbitrary path^{4,5}; also embrittled polymers may be melted and remoulded with the regain of most of their toughness^{3,6}. This implies that spherulite boundaries and interfibrillar regions may be particularly vulnerable to oxidation.

In this paper we consider the effects which may lead to local degradation in PP. This includes whether there are species in PP which are particularly vulnerable to oxidation, whether these species are concentrated within particular regions of the sample and whether this leads to enhanced local oxidation and premature failure.

In order to reveal the distribution of oxidation we have used ultra-violet microscopy, a method which we have used in the past to study the behaviour of impurities in polymers⁷. In the present work we have used staining techniques to render the oxidized regions visible in sections of PP by reaction of the oxidized polymer with reagents which will form highly u.v. absorbing products bound to the oxidized regions.

EXPERIMENTAL

Materials

The isotactic polypropylene used for most of this work was supplied by ICI PLC as their powder grade HF18, containing no additives. The number average molecular weight was 60 000 and the weight average 465 000, giving a polydispersity of 7.7. This polymer is produced by a diluent process which removes most of the undesirable atactic polymer into the hydrocarbon polymerization medium. The Ziegler catalyst is removed by an alcohol wash with typical remaining levels of Ti, Al and Cl being 30, 45 and 45 ppm respectively. As we received the polymer it contained 2.5% residual atactic material extractable in boiling *n*-heptane. Some measurements were also carried out on experimental samples of gas phase polymerized PP. This is made on a high-efficiency catalyst and there is no washing to remove catalyst residues or atactic material.

Oxidation of HF18 has been studied in this laboratory with a wide variety of techniques. By following uptake of oxygen from air, the induction time, after which the oxidation rate becomes approximately constant, is found to be 4 h at 120°C or 12 h at 100°C (Figure 1). The polymer becomes noticeably embrittled after oxidation for times greater than one induction time. Because of the difficulty of sectioning embrittled material, most of our studies have been made by cutting sections with a microtome, which are then oxidized and stained.

Ultra-violet microscopy

The u.v. microscope which we use has been described in full detail elsewhere⁷. Basically it is a conventional optical microscope, modified by fitting quartz optics, a 150 W Xenon arc source, with appropriate filters and a TV camera system to allow viewing of the image. Samples are sectioned on a base sledge microtome with a glass knife and mounted in glycerol on quartz or glass slides. For the work at 350 nm described in this paper, glass slides were adequate and the light was filtered with the combination of a UG1 u.v. filter with a BG38 red suppression filter.

The staining reaction

Oxidation of PP in air at 120°C causes the build up of a weak, featureless u.v. absorption below 300 nm. To make this visible in the u.v. microscope thin (10 μ m) sections of polymer were immersed in an acid solution of dinitrophenylhydrazine (DNPH) in isopropanol for 24 h

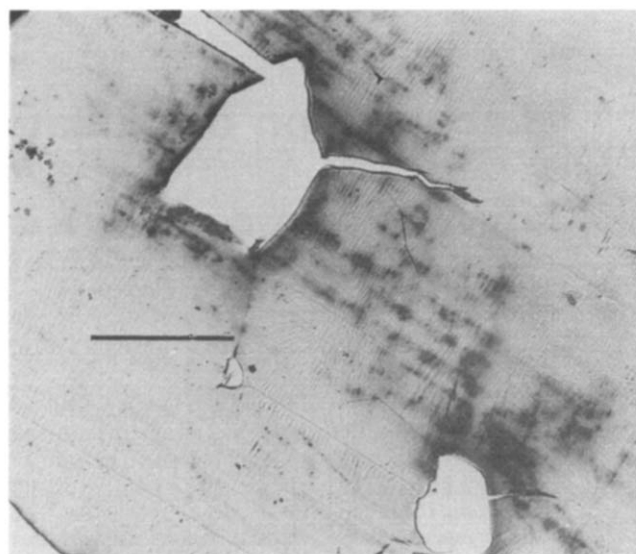


Figure 2 U.v. micrograph of a section of PP film, oxidized at 120°C in air for 2 h following crystallization at 125°C. Sample stained with DNPH and viewed at 350 nm. Bar is 50 μ m

at 60°C (1 g DNPH, 100 ml isopropanol and 5 ml conc. hydrochloric acid). The DNPH reacts with ketones and aldehydes in the film to produce highly absorbing hydrazones attached to the polymer backbone. Since DNPH itself is highly u.v. absorbing, excess reagent was extracted from the films by immersion for 24 h in isopropanol at 60°C. These conditions were established after experiments on large, 100 μ m thick, films showed that staining was complete in 48 h and no further reaction occurred when fresh reagent was added. A diffusion limited reaction in a 10 μ m film should be complete in 1/100th of the time necessary for a 100 μ m film.

The stained polymer has a strong u.v. absorption at 350 nm with an extinction coefficient 1000 \times that of the unstained polymer. As shown in Figure 2, oxidized regions could be clearly seen in u.v. light at around 350 nm.

Infra-red spectroscopy was used to follow the effect of the staining reaction on the oxidized species in polymer after oxidation for 6 h at 120°C. Treatment of the films with pure isopropanol at 60°C reduces the carbonyl absorption of the sample by more than 30%. The extract contains a 40 \times higher carbonyl concentration than the remaining insoluble polymer and was shown by differential scanning calorimetry (d.s.c.) to be a mixture of oxidized atactic and short isotactic material. The fraction of the total carbonyl extracted by isopropanol increases with oxidation time (Figure 3). No extraction occurs when unoxidized polymer is refluxed with isopropanol.

In an effort to avoid the complications introduced by this extraction, other less extractive solvents were tried for the DNPH treatment, including water and methanol, but were found unsuitable. Treatment of the films with acid isopropanol reduced the hydroperoxides by 70% while increasing the carbonyl slightly. Treatment with DNPH removed 66% of the carbonyl absorption at 1715 cm^{-1} remaining after an isopropanol extraction, and most of the hydroperoxide. A strong peak remained at 1735 cm^{-1} which could be removed by KOH and was attributed to esters and lactones.

Thus the DNPH stain is not ideal in that it extracts much of the oxidation and does not react with all

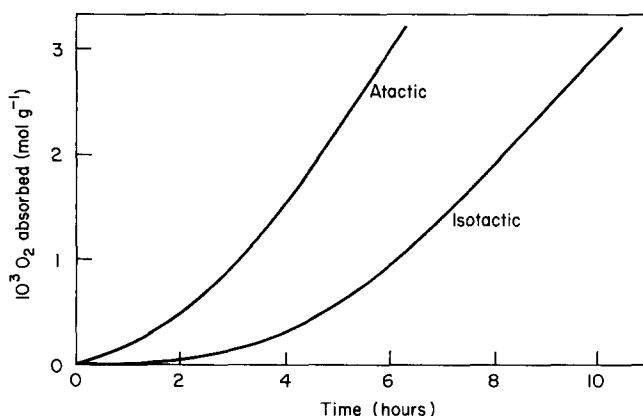


Figure 1 Oxygen uptake at 120°C of 100 μ m films of PP and of extracted atactic polymer

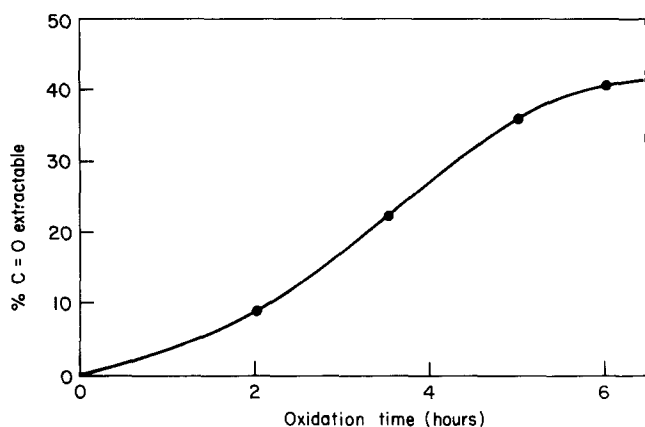


Figure 3 Decrease in carbonyl absorption of PP at 1715 cm^{-1} with isopropanol extraction as a function of the extent of oxidation

carbonyls, nonetheless it is a very suitable qualitative marker for local oxidation levels by making visible the local concentration of reactive carbonyl groups which are in the amorphous phase but firmly bound to the crystal structure.

RESULTS AND DISCUSSION

Relative oxidation rates of atactic and isotactic PP

All commercial samples of PP produced by conventional diluent phase processes contain small amounts of atactic polymer, generally of low molecular weight and having unsaturated end groups. In Figure 1, which shows the oxygen uptake curve for the standard sample of PP which we used, we also show the curve for the atactic material extracted from the bulk polymer with *n*-heptane reflux. The atactic fraction has about half the induction period of the whole polymer and oxidizes at about 3 times the rate. In staining experiments we find that large proportions of the carbonyl groups produced in the oxidation are extractable with heptane.

In a separate study⁸ we have used the DNPH reaction to monitor the carbonyl formation in the bulk polymer and in the heptane-soluble fraction as a function of oxidation time. We find that the amount of heptane-soluble material increases from 2.5% initially to 2.9% after 2 h and 12.8% after 4 h at 120°C ; it then increases rapidly and becomes crystalline. At the beginning of the reaction the heptane-soluble fraction (2.5%) has a carbonyl content equivalent to $7.25\ \mu\text{mol DNPH g}^{-1}$, with a corresponding value of 1.2 for the insoluble fraction. After 2 h the corresponding figures are 75.5 and 13.2 and at the end of the induction time (4 h) they have risen to 185 and $74\ \mu\text{mol DNPH g}^{-1}$. Thus after 2 h oxidation the concentration of carbonyl groups in the atactic fraction is 5.7 times higher than that in the isotactic polymer, even though the former represents only 2.9% of the total weight. D.s.c. analysis shows that the heptane-soluble fraction remains essentially amorphous up to about 3 h oxidation though its crystallinity rises rapidly thereafter.

From these observations we conclude that the 2–5% heptane-soluble fraction of PP oxidizes 2–4 times faster than the isotactic material, both in isolation and when present in the isotactic polymer. This is in agreement with the similar conclusion of Frank *et al.*⁹ Apparently this effect stems from the higher levels of unsaturation of the atactic polymer as Osawa *et al.*¹⁰ found that, on hydrogenation, atactic PP becomes as stable as the isotactic

polymer. In the later stages of oxidation the extractable fraction increases as more low molecular weight chains are formed. Polar solvents will tend to extract oxidized rather than low molecular weight material.

Localization of extractable material

We have reported elsewhere our studies of the rejection of impurities from growing polymer spherulites¹¹. When PP crystallizes from the melt, both atactic polymer and low molecular weight impurities are excluded from the crystals of the growing spherulite and tend to concentrate in the liquid ahead of the growth front. Rapidly diffusing species will tend to concentrate towards the spherulite boundaries while more slowly moving molecules become trapped in the interlamellar or interfibrillar regions. Since PP contains 2–5% of atactic material, this segregation will tend to give weak zones at spherulite boundaries and weak radial lines between the fibrils. With increasing oxidation, prior to crystallization, the amount of rejectable material rises rapidly and the boundary strength would be expected to decrease. Thus Figure 4 shows boundary cracking in a sample that has been oxidized for 12 h at 100°C then crystallized at 125°C and sectioned. Less oxidation prior to crystallization gives less cracking. At 135°C the slower crystallization rate allows much more segregation to occur and the boundary weakness becomes marked at lower oxidation levels. Samples cracked at random when they had been crystallized under vacuum, sectioned and then oxidized, showing that there is little tendency for the oxidation reaction itself to be limited to boundaries. In samples crystallized as thin films on a microscope slide we do see preferential radial and boundary cracking on subsequent oxidation which we believe is due to shrinkage stresses which arise on cooling. Thus we find that segregation of oxidized species does cause boundary weakening but we have no evidence for preferred crack paths in oxidation of solid samples.

Concentration of oxidation in spherulites

We have attempted to use the u.v. staining technique to confirm the localization of oxidation in degraded and crystallized polymer. Figure 5 shows a section of PP which has been oxidized for 12 h at 100°C before staining.

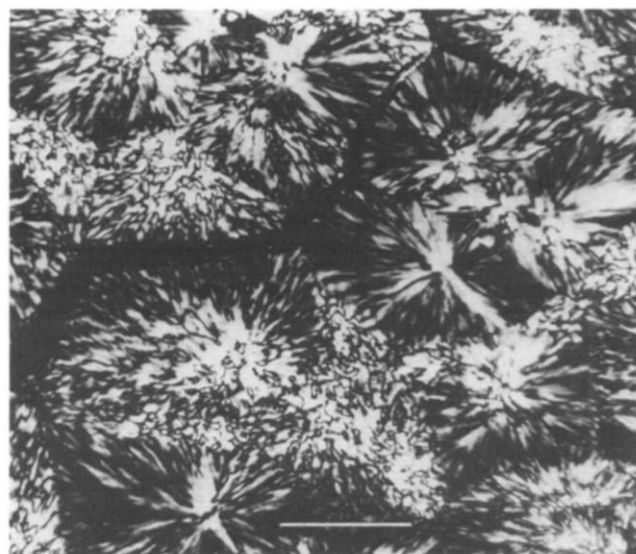


Figure 4 Section of PP film oxidized at 100°C for 12 h prior to bulk crystallization at 125°C . Viewed in crossed polars. Note the boundary cracking, produced by slight stressing of the section. Bar is $50\ \mu\text{m}$

It can be seen that much material has been extracted from the spherulite boundaries but there is no evidence of non-uniform staining of the remaining material. Samples crystallized at 135°C were similarly uniform. Thus with our staining technique we conclude that the only material which is rejected to the boundaries is that which is also extracted in the staining process. Non-uniform staining is seen in samples which are partly crystallized and quenched. (Figure 6) and in some cases we do see a wave of rejected material ahead of the growing spherulite which would be expected from our studies of rejection of other impurities¹¹. However, this effect may also be partly due to differences in extraction from the slowly crystallized and from the quenched regions. A similar effect is seen after photo-oxidation of partly crystallized sections (Figure 7).

Given that impurity species do tend to concentrate at spherulite boundaries we might expect that oxidation would be more rapid in these regions in slowly crystal-

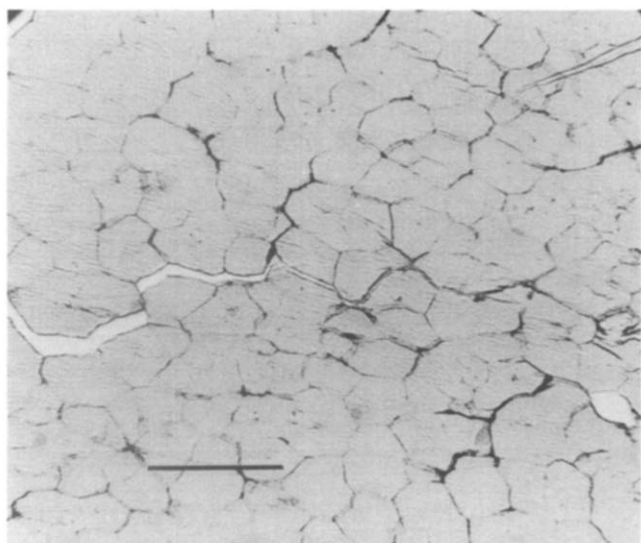


Figure 5 Section of PP film oxidized at 100°C for 12 h prior to bulk crystallization at 125°C. DNPH stained and viewed at 350 nm. Note the boundary cracking and extensive extraction of the boundary regions. Bar is 200 μm

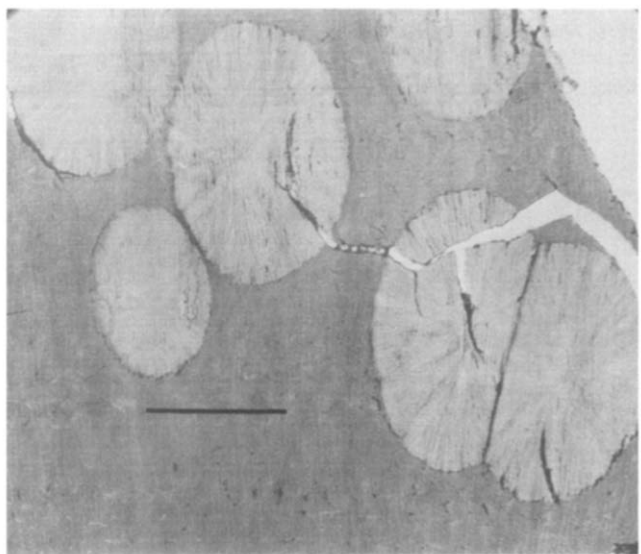


Figure 6 DNPH stained section of PP film oxidized for 16 h at 100°C prior to partial crystallization at 135°C. Viewed in u.v. Bar is 200 μm

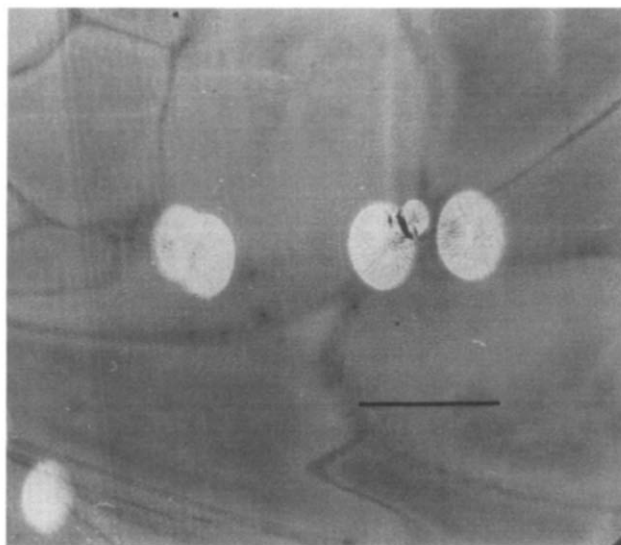


Figure 7 DNPH stained section of PP, crystallized partially at 135°C prior to photo-oxidation at room temperature. Viewed in u.v. Bar is 200 μm

lized, and thus more segregated, samples. Figure 2 shows a sample crystallized at 125°C and oxidized for 2 h at 120°C before staining. Non-uniform oxidation is evident but there is no sign of its preferring the boundaries. We have similarly looked for evidence of local oxidation in samples photo-oxidized after crystallization. Again no preferential oxidation associated with the spherulite morphology was seen. Thus although oxidized material is rejected to spherulite boundaries it does not apparently enhance the subsequent oxidation of the surrounding structure. We would not expect to detect enhanced oxidation unless it were to an extent of 20% or more.

Catalyst residues

In the absence of morphological effects on oxidation, an alternative source must be found for the uneven oxidation seen in many samples and typified in Figure 2. We discovered that lightly pressed films of PP showed a 'wood-grain' effect in section when oxidized and stained (Figure 8). Using very light compression we were able to produce films where the original polymer particles were still visible and which show that about 5% of them are oxidizing much faster than the rest as shown in Figure 9. Also visible in the sections are clusters of black dots, less than 1 μm in size. These are in patches that correspond to the individual grains of the original powder and are more evident in the more oxidized grains. Like the oxidation, they do not extend right to the particle boundaries. The differences between the different grains persist to high levels of oxidation (Figure 10). Very little staining was seen in such samples when unoxidized.

The dots are believed to be catalyst residues and can still be seen in molten particles of polymer (Figure 11). They show no sign of dissolving or coalescing on heating. We have not been able to obtain analyses of individual dots but energy dispersive X-ray analysis of ash from polypropylene shows Ti, Al and Cl present. The variability of individual polymer particles can also be shown by DNPH staining of oxidized powder, which produces a mixture of light and dark particles, resembling a mixture of salt and pepper. Support for the catalytic role of the residues has recently been obtained by extracting the ash

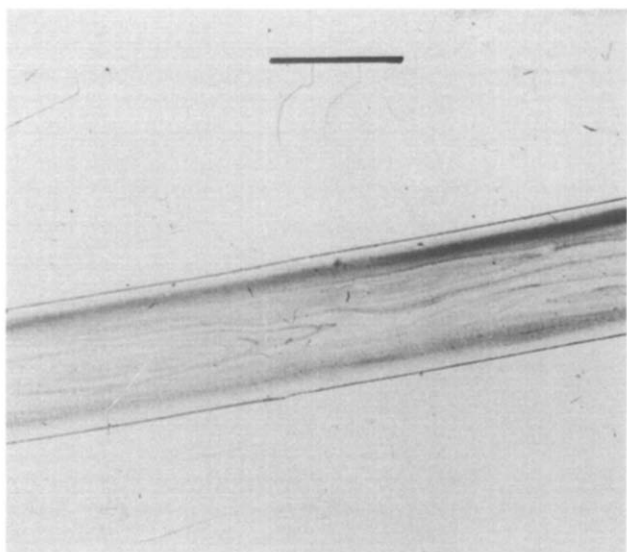


Figure 8 Section of compression moulded PP film oxidized at 100°C in air prior to DNPH staining. Viewed in u.v. Bar is 100 μm

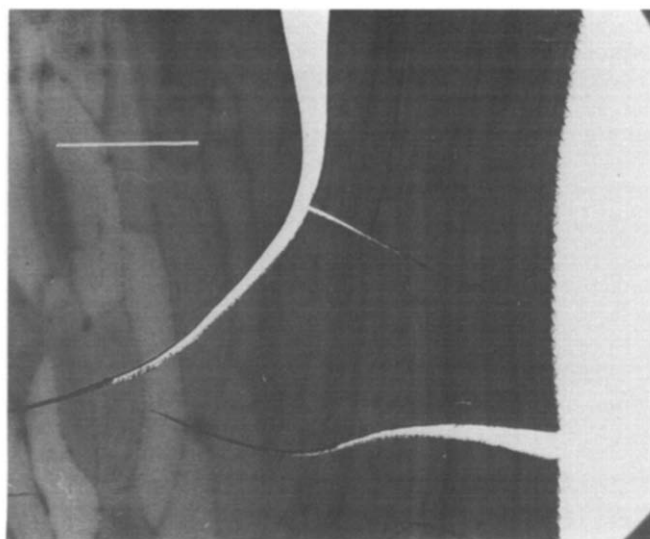
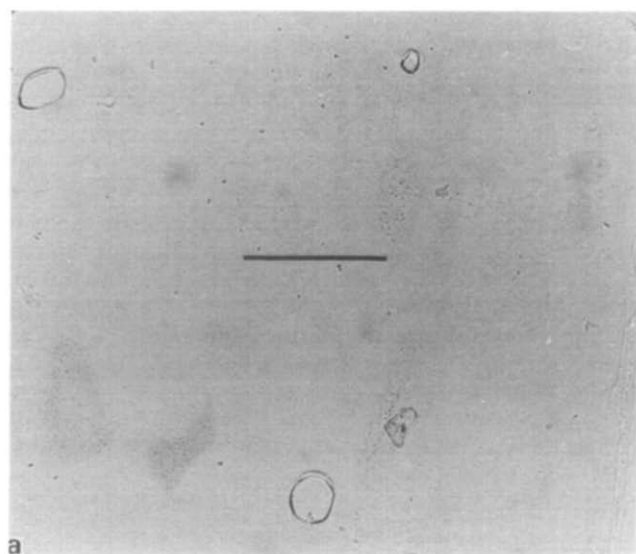


Figure 10 Section cut from plaque of PP prepared as for *Figure 9* but oxidized for 5 h at 120°C. Viewed in u.v. Bar is 200 μm



a

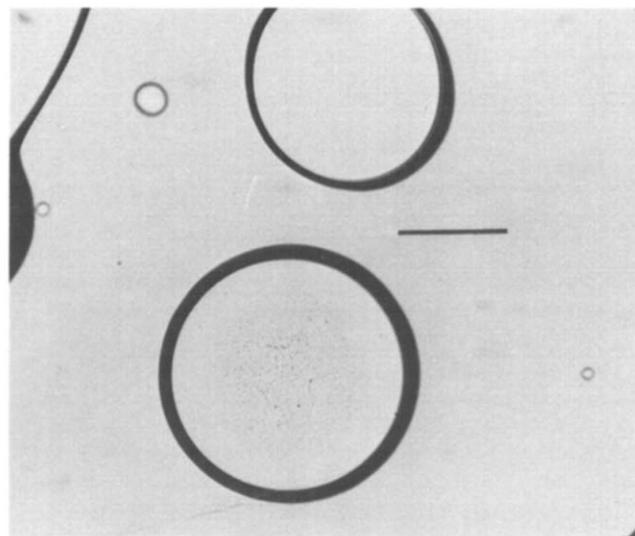
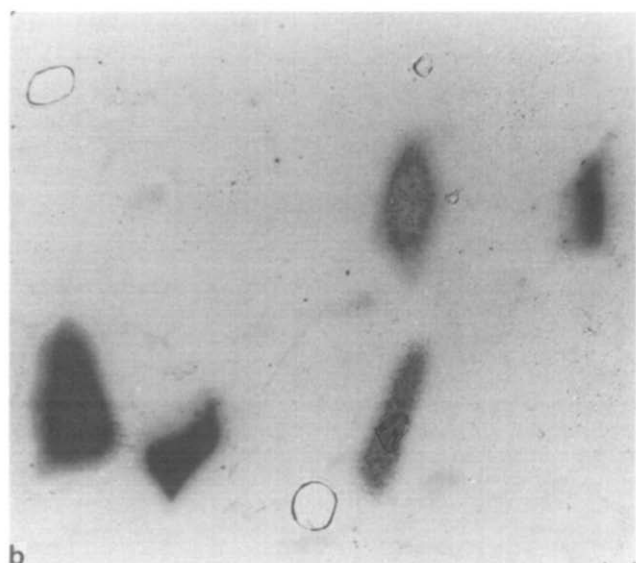


Figure 11 Particles of diluent PP viewed in visible light at 170°C. Note the high concentration of particles in the left-hand globule and their absence from the other. Bar is 100 μm



b

Figure 9 Section microtomed from a PP plaque produced by gentle compression moulding from powder. Oxidized for 2 h in air at 100°C and DNPH stained. Upper picture viewed in visible light, lower in u.v. Bar is 200 μm

from a batch of PP and introducing it into a new film; oxidation and staining show extensive local oxidation around the ash particles¹².

Gas phase polymerized polypropylene

In the gas phase polymerization process a high efficiency catalyst is used which is not then extracted from the polymer. In these materials different grains were again found to oxidize at different rates (*Figure 12*) but individual grains also often showed unexpected 'picture frame' oxidation as shown in *Figure 13*. The micron-sized dots of catalyst residue, easily seen in diluent PP, were not seen in the gas phase polymer.

CONCLUSIONS

Our concern in this paper has been to establish whether there are effects which can account for the apparent significant localization of degradation in PP. Our first interest is in whether spherulite boundary oxidation could be enhanced by concentration of atactic polymer or other

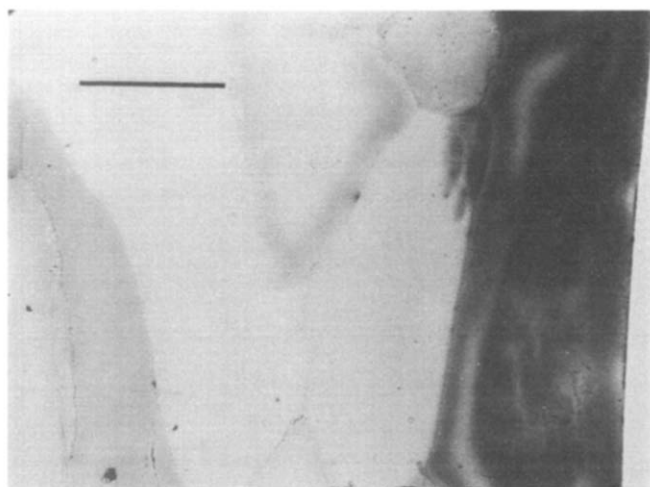


Figure 12 Section from a plaque moulded from gas phase PP powder under low pressure. Oxidized at 120°C for 6 h then stained and viewed in u.v. Bar is 200 μm

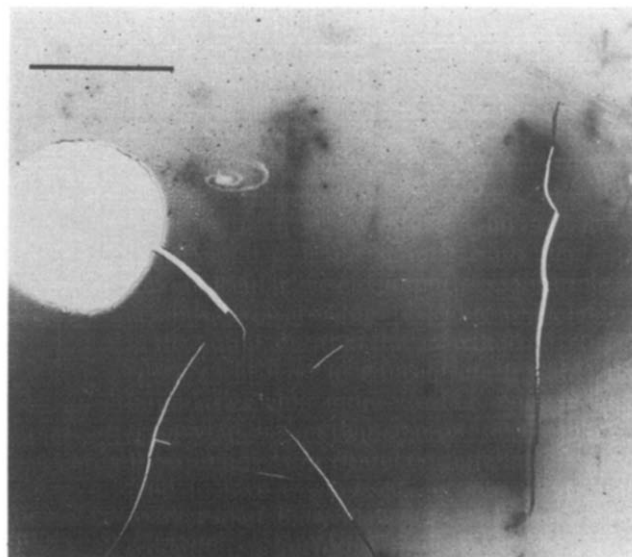


Figure 14 Section cut from an extruded pellet of gas phase PP, oxidized at 120°C for 6 h then stained. Viewed in u.v. Bar is 200 μm

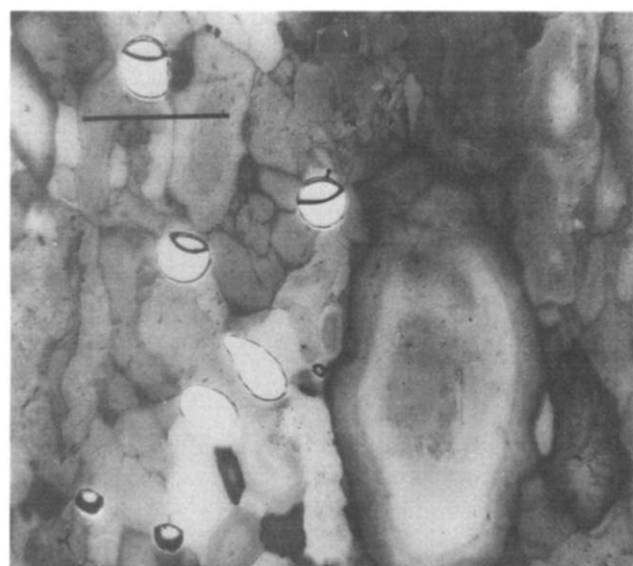


Figure 13 Section from a plaque moulded from gas phase PP powder under low pressure. Oxidized at 120°C for 6 h then stained and viewed in u.v. Bar is 200 μm

initiating centres at the boundaries during crystallization. Atactic material does oxidize more rapidly than isotactic but with an average concentration of only 2–5% the concentrations at the boundaries are unlikely to be sufficient to produce dramatic increases in boundary oxidation. This is especially true of commercial products where the high cooling rates are unlikely to allow much redistribution of atactic polymer. Thus we do not expect an important effect due to rejection of atactic material alone.

In addition to atactic material there will also be segregation of partly oxidized chains, either because the carbonyl groups may be excluded from the crystals or, more likely, because these chains will be short. This effect can undoubtedly be made to weaken the boundaries and lead to cracking as described above but we find no evidence in our results that it also leads to enhanced oxidation.

There is positive evidence for enhanced oxidation of some of the initial polymer particles in both the diluent and gas phase polymerized materials and we believe that

this is associated with local concentrations of catalyst residues. These effects can be carried over into particles extruded under commercial conditions as is shown in Figure 14 for a pellet of PP extruded on a screw extruder in a factory line for producing polymer pellets from the powder. Such effects may give rise to local weakening even in samples subjected to the mixing effects of a screw extruder. Thus it is clear that residue particles can act as centres for oxidation but it is not clear how their effect spreads from the initiating centres into the rest of the polymer. In principle the spread of degradation could be due to the fact that the chain reaction chemistry causes hydroperoxidation to migrate through the structure of the polymer, either inter- or intramolecularly. Alternatively, the release of short chain fragments or small molecules, containing peroxides or other activating groups, may cause the reaction to migrate by a more physical mechanism.

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