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Effect of anisotropy on photo-mechanical oxidation of polyethylene

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Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

Abstract

Blown polyethylene (PE) film was exposed to UV irradiation while under tensile stress. Tests were conducted on unpigmented PE and on a series of five PEs containing TiO_2 pigments with different photo-activities. The yield strengths measured in tensile tests on unexposed films were typically 10% greater in the longitudinal (machine) direction than in the transverse direction. UV exposures were conducted with stress applied both parallel and transverse to the machine direction. The chemical degradation was followed using the FTIR carbonyl index. For all six materials, tensile stress accelerated carbonyl group development. Some samples cracked during UV exposure in tension and did so in a shorter time if the stress was applied in the machine direction than if it was transverse to it. The carbonyl index at the onset of cracking was lower for longitudinal samples than for transverse samples.

Unpigmented PE was slightly more sensitive to transverse strain and the anatase-pigmented PE slightly more sensitive to longitudinal strain. The carbonyl production rate for two of the rutile pigmented grades showed very little dependence on the straining direction whereas for a third the increase in rate was significantly greater when the deformation was applied in the machine direction than for transverse stretching. With the fourth rutile-pigmented grade, transverse stretching produced the greater effect. These differences cannot be correlated with the photoactivity of the different pigments. The highest ratios of longitudinal/transverse enhancement were found with the least photoactive rutile pigment and with anatase—the most photoactive of all those tested.

Keywords: Photo-mechanical oxidation; Polyethylene; TiO_2 pigmentation

1. Introduction

Polymers that have been subjected to thermo-mechanical processing almost always possess anisotropy. Most articles that have been produced by injection moulding, blow moulding or extrusion have quite different mechanical properties in the machine direction and in the transverse to flow direction. This is especially true for semi-crystalline polymers in which molecular flow during processing assists crystallization, giving rise to oriented crystals. The crystals are relatively massive and, when flow ceases, they are less easily randomised than oriented molecular segments in the amorphous state by relaxation processes. The crystals are, therefore, effective in ‘freezing in’ the anisotropy. The dependence of mechanical properties on orientation in anisotropic polymers has been studied exhaustively over the past 40–45 years. The main features are summarised in textbooks by Ward [1,2], whose contribution in the 1960s and 1970s to the research in this area was most influential.

Studies on anisotropy have extended beyond engineering properties, for example, into barrier properties, where it is important to know the effect of anisotropy produced by blow moulding a bottle for carbonated drinks on the permeability to carbon dioxide and oxygen. Popov, Rapoport and Zaikov have provided an extensive review on oxidation of oriented polymers, largely based upon research conducted by themselves and others in the former Soviet Union in the 1970s and 1980s [3]. They report that the rate of oxidation in drawn polyolefins is very strongly affected by the extension ratio.

The Russian School also studied the effect of an applied stress on the oxidation rate of their oriented polymers [3]. Most of their experiments were on thermal oxidation and it appears that all of their tests used tensile stress applied parallel to the orientation direction [3]. The effect of the tensile stress was to accelerate oxidation. Tensile stress was

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also found to alter the rate of photo-oxidation in polyethylene by Benachour and Rogers [4] and in polypropylene by Baumhardt-Neto and De Paoli [5,6] and by O'Donnell and White [7]. The application of tensile stress generally accelerates oxidation but Baumhardt-Neto and De Paoli claimed that in some circumstances the opposite might happen. Although it was observed that there is probably an effect of anisotropy on degradation rate, the exact relationship was not determined, and explanations remain speculative [4,8].

The studies described here used carbonyl index measurements to follow photo-oxidation and the effect on the photo-degradation rate of oriented polyethylene of applying a tensile stress was investigated. The effect of applying the stress parallel to the orientation direction was compared to that observed when the stress was applied in the transverse direction. We have not found any report of research into this in the literature.

2. Experimental

2.1. Materials

The materials used in this study were based on a low density polyethylene, LDPE Riblène MR10 (Polimeri Europa). For comparison, samples containing titanium dioxide pigment of various kinds were also tested. The TiO_2 pigments used included rutile and anatase forms. Anatase is a photocatalyst for many reactions and can be expected to be a pro-degradant for the matrix polymer, whereas rutile has less photoactivity [9,10]. Surface coatings of various kinds are applied to change the photoactivity of TiO_2 [11] and different commercially available and experimental rutiles were included in this study. The samples were provided by Huntsman Tioxide, (Billingham, Cleveland, UK and Calais, France) in the form of lay-flat blow moulded tube with wall thickness ~100 μm. The pigmented samples all had a pigment loading of 5 phr. In the Section 3, the unpigmented samples are coded U1, the anatase pigmented samples A2, and the rutile pigmented samples R3, R4, R5 and R6, respectively. The pigments used for samples A2, R3 and R4 have a light coating (1–2%), whereas those used for R5 and R6 have a medium coating (~5%). The film preparation conditions were adjusted to give approximately balanced orientation. For reasons of brevity, the tube axis direction (= 'machine direction') is used to indicate the orientation of samples.

2.2. Tensile testing

Tensile tests were conducted on specimens cut from each of the sample films prior to any UV exposure. Dog-bone testpieces with gauge length 20 mm and width 5 mm were cut both parallel and transverse to the machine direction. Four tests were conducted for each type of specimen. The crosshead speed was 60 mm min^{-1}.

2.3. Sample preparation for photomechanical exposures

A special testing frame was designed to conduct the photo-mechanical exposures. It consisted of a pair of flat rings that were placed on either side of the sample film (Fig. 1). Bolts that passed through both rings (and the sample film) were used to clamp the film between the rings. After clamping the rings onto the film, the surrounding film was cut away to leave a disc shaped sample mounted securely between the rings. Samples that were to be exposed in a stressed state were prepared by extending a piece of the lay-flat film 25 mm wide in a purpose-built stretching frame with initial grip jaw separation 24.7 mm and final grip jaw separation 44.7 mm, giving an extension of 80%. The film was held stretched in the frame while a portion of it was mounted in the ring-shaped holder, just as with the unstressed samples. When the ring with the mounted film was cut away as before, it was noted that there was no movement of the sample within the ring clamp, and it was assumed that no stress relaxation due to slippage in the grips had occurred. Some of the strained samples were prepared with the deformation applied parallel to the axis of the lay-flat tubes and others were prepared with the tensile axis in the transverse direction.

Many sets of ring clamps were made, permitting simultaneous testing of multiple samples, ensuring that conditions were identical for samples made from the several materials under investigation, and in both strain directions and in the unstressed state.

2.4. Stress relaxation

In order to assess the stress state of the samples prepared in the manner described above, the stress relaxation behaviour of the materials was examined in a separate series of experiments using a RDP-Howden Ltd tensile test

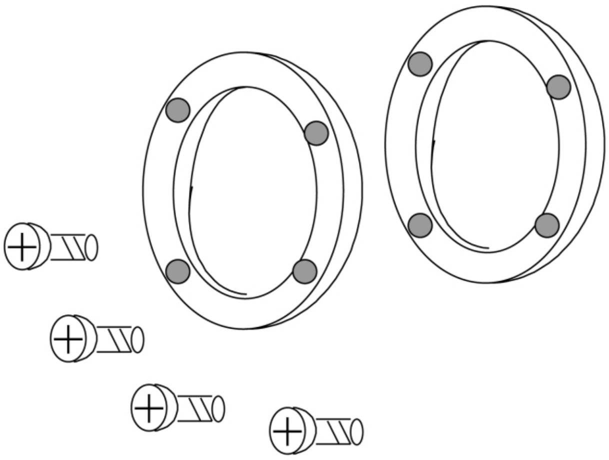

Fig. 1. Ring clamp used to maintain strain on samples during UV exposure.

machine. The sample dimensions matched those used in the hand-operated stretching frame as closely as possible and a 20 mm crosshead displacement was used. This was applied at 50 mm min^{-1} then kept fixed for 4 h during which the load was recorded periodically. The load fell approximately 30% within the first few minutes; it had fallen to between 50 and 60% of the initial value at the end of the first hour and, thereafter fell very slowly. The pigmented materials gave slightly higher initial load than the unpigmented material.

2.5. Ultraviolet exposure

The ring-mounted samples were transferred to a QUV machine (Q-Panel Company, Cleveland, Ohio, USA) in which the ultraviolet (UV) illumination was provided by UVA340 fluorescent tubes (Q-Panel Company). These tubes are widely used in photodegradation studies and give a spectral output similar to that in terrestrial sunlight in the UV wavelength range up to 360 nm [12]. The QUV machine was operated as a simple constant temperature enclosure set at 42 °C (no temperature or humidity cycling). In some cases the sample broke within the mounting ring during UV exposure, before the planned termination of the test. In each case the fracture was perpendicular to the tensile strain axis, independent of the preferred orientation of the sample.

2.6. Characterization

The exposed samples were removed from the QUV machine periodically and an infrared (IR) spectrum was obtained with the sample still mounted in the ring clamp, using a Bio-Rad FTS60A spectrometer with a liquid nitrogen cooled, narrow band MCT detector. The principal region of interest was 1700–1800 cm^{-1} in which carbonyl group stretching appears and absorbance measurements for this band were measured. In those cases, in which the sample broke within the mounting ring prematurely, the UV exposure and sequence of IR measurements was continued until the planned test duration had expired. A second use of the FTIR spectrum was for the monitoring of thickness when the films were deformed, using absorption bands produced by the polyethylene. Intensity measurements of bands centred at 1304 cm^{-1} (attributed to C–H wagging [13]) and another in the range 1350–1380 cm^{-1} (attributed to C–H bending [13]) were made for this purpose (see Section 2.7). The bands centred at 1304 cm^{-1} and in the range 1350–1380 cm^{-1} were also used to attempt to determine the dichroic ratio as a measure of molecular orientation in the samples [14,15]. The presence of the pigments had no obvious effect on the bands attributed to polyethylene. TiO_2 does not absorb in this wavelength region though it may scatter if the particles are in a certain size range.

2.7. Experiments to investigate effect of thickness on FTIR results

When the film is extended it reduces thickness. This means that the path of the interrogating infrared beam through the sample is decreased and the absorption will be necessarily reduced. It is relatively straightforward to take this into account as long as the distribution of the absorbing groups is homogeneous, as will be the case for the polyethylene absorbances used here.

2.7.1. IR absorbance in strained samples

Information was obtained on the absorbance of strained samples by using the hand-operated straining frame to hold samples at chosen extensions while conducting IR absorbance measurements. IR spectra were recorded for the unstrained length of $l_0 = 24.7$ mm and for deformations of 5–30 mm in 5 mm intervals for unpigmented polyethylene (U1), anatase pigmented PE (A2) and one of the rutile-pigmented PEs (R4). The deformation range includes the standard deformation (20 mm) used for the strained exposures (see Section 2.3). The absorbance bands centred at 1304 cm^{-1} and within the range 1350–1380 cm^{-1} were also measured for each applied strain using polarised IR in an attempt to obtain the dichroic ratio [14,15]. Spectra were recorded with the polarization axis, respectively, parallel and perpendicular to the strain axis and the ratio of the peaks obtained for the parallel and perpendicular alignment determined. It is emphasized that the reference (‘parallel’) axis is taken to be that of the applied strain in all cases; this means that for the ‘transverse’ samples, the ‘machine direction’ of the original film preparation is the ‘perpendicular’ direction.

2.7.2. Multi-layered samples

When dealing with photodegraded samples it is important to recognise that the carbonyl groups may not be homogeneously distributed through the sample thickness. It is well established that in polyethylene, polypropylene and many other polymers a steep degradation gradient develops at a surface exposed to UV [7,15–30]. In relatively thick samples (of the order of say 2–3 mm) made from relatively (UV) transparent materials, the molecular degradation can be very considerable within the first 100 μm of the exposed surface yet almost undetectable 0.5 mm from the surface. This is primarily the consequence of oxygen-diffusion-limited reaction [22,31–33]. Another contribution to the degradation gradient is due to the reduction in UV intensity as it penetrates deeper into the material. This is greater in pigmented materials, in which the UV intensity falls steeply with depth. In samples of the order of thickness dealt with in the work reported here, it is less clear to what extent the gradient in oxidation plays a part in the observations made with unstrained and (thinner) strained samples. In order to obtain some supplementary information on this, the following simple experiment was conducted. Triple-layered unstrained samples were mounted in the double-ring clamps and subjected to UV exposure. In the Section 3, the layer facing the UV source is labelled 'layer 1' and the one facing away from it is 'layer 3'. Layer 3 receives UV radiation onto its outward facing surface by reflection within the equipment and onto the forward facing surface by transmission through layers 1 and 2 (where 'layer 2' is the middle layer). The samples were removed periodically and IR measurements were made on the individual layers before remounting them in the same sequence and returning them to the UV exposure unit. The results enabled deductions to be made relating to the distribution of oxidation through the depth (see Section 3.4 and the Appendix A). Although this method provides a far less comprehensive analysis than the depth profiling procedure of Jouan and Gardette, based on microtoming and infrared microscopy [18,19], it is easy to perform and is less time consuming.

3. Results

3.1. Tensile testing

In each test on the unexposed materials the specimen displayed extensive drawing. In all cases there was a very well defined yield point, sometimes followed by a yield drop. Although the load-deformation characteristics for a particular type of specimen did not superimpose exactly, there was a significant type-to-type variation and the stress at yield has been taken to characterize anisotropy. The values obtained are recorded in Table 1. It is evident that the samples all displayed a higher yield stress when tested in the machine direction. The yield stress in the machine direction was typically 10% higher than that in the transverse direction.

3.2. Infrared spectra—general appearance

Typical FTIR spectra are shown in Fig. 2. The carbonyl group absorbance was absent from unexposed samples; it is quite different for the different materials tested and it increased with exposure. It is convenient to compare the relative oxidation of the different materials using the carbonyl group absorbance. FTIR spectra expanded in the lower wavenumber range are given later on, in Fig. 4.

Table 1
Yield stress in tensile tests (MPa)

	Longitudinal	Transverse
U1	10.6 ± 0.6	9.5 ± 1.4
A2	9.4 ± 1.2	8.8 ± 1.2
R3	9.3 ± 0.9	8.5 ± 1.5
R4	9.0 ± 1.2	8.4 ± 1.4
R5	10.0 ± 1.2	9.1 ± 1.4
R6	10.6 ± 0.3	9.1 ± 1.3

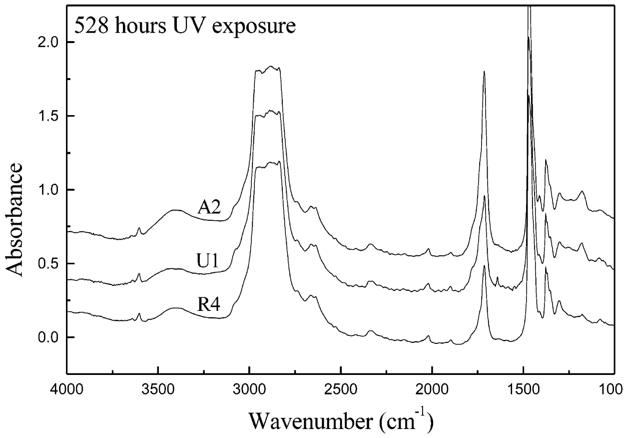

Fig. 2. FTIR spectra for U1, A2 and R4 after 528 h UV exposure, showing the carbonyl band in the range 1700–1760 cm^{-1} used for the assessment of the progress of oxidation. This band was absent prior to UV exposure.

3.3. Absorption in strained samples

For thin samples the intensity in a transmission IR absorption band will be proportional to the thickness (h) as long as the absorbing group is homogeneously distributed. For samples strained in uniaxial tension, the thickness decreases according to the equation $h = h_0(1 - \nu\varepsilon)$ where h_0 is the unstrained thickness, ν is Poisson's ratio and ε is the applied strain. If ε is taken to be the true strain ($= ln(l/l_0)$ where l is the extended length and l_0 is the unstrained length) this relationship is expected to hold for quite high strains and a plot of (h/h_0) versus $ln(l/l_0)$ should be linear, with gradient $(-\nu)$. Fig. 3 shows this plot for the IR band in the region 1350–1380 cm^{-1} for samples U1, A2 and R4. The plots are acceptably linear and the corresponding values for Poisson's ratios are 0.36 (U1); 0.29 (A2); and 0.29 (R4). Unfilled polymers have Poisson's ratios around 0.4 and filled polymers have smaller values that depend on the volume fraction of filler [34]. In the materials under investigation, the volume fraction of the filler was ~1%. The values obtained were, therefore, of the correct order and ranking but were slightly smaller than expected. This is probably because, for the strip samples used, the strain was

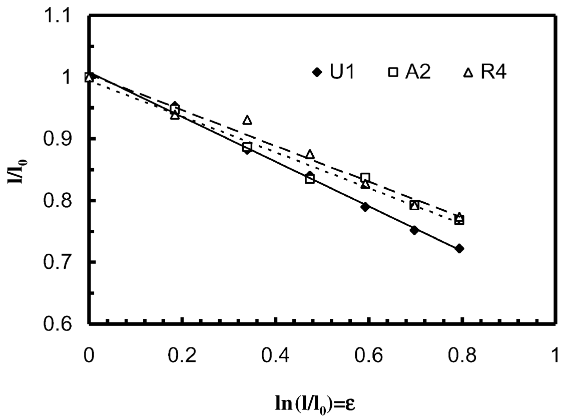

Fig. 3. Plots of $I/I_0(= h/h_0)$ versus ε for U1, A2 and R4.

not exactly uniaxial because of constraints in the grips. Somewhat higher values for Poisson's ratio were indicated when the same analysis was applied to the IR peak centred at 1304 cm^{-1} though this peak is less intense than the band at 1350–1380 cm^{-1} and the results were more scattered.

In accordance with the above analysis, corrections based on the intensity of the band at 1350–1380 cm^{-1} were made to account for the contribution to changes in IR absorbance due to the thickness variations caused by straining the samples mounted in the ring clamps, and corrected data obtained using this analysis are given in Section 3.5. The ratio of the intensity of the chosen band for the specimen in the stretched state and unstrained, respectively, was taken to be equal to the thickness ratio in these two conditions. It is assumed that the absorbing species is uniformly distributed and that stretching does not cause reorientation of the absorbing bonds in a way that would influence the absorption. The results (e.g. in Fig. 9) are given in terms of the absorbance that would be recorded in a stretched sample of the same thickness as the corresponding unstretched sample. More discussion of this analysis is given in Section 3.6. Benachour and Rogers [4] state that they made a correction for thickness based on their IR data and presumably they used a similar procedure.

The dichroic ratio was found to be very close to unity for films in the unstrained state. This is what would be expected if the fabrication process achieved 'balanced orientation' between the longitudinal molecular orientation caused by passage through the die and by the 'haul-off' action, and the hoop orientation produced by the inflation of the film. It is, however, in apparent contradiction to the tensile test results reported in Section 3.1, which indicated quite clearly that anisotropy was present. Characteristic changes in the IR spectra occurred when the films were strained (Fig. 4) and the dichroic ratio for 80% strain was measured to be between 1.2 and 1.3 for all specimens tested and for both transverse and longitudinal applied strain.

3.4. Multi-layered samples

The carbonyl group accumulation results for the experiments with multi-layered samples are shown in Fig. 5 for unpigmented polyethylene (U1) and for the anatase-pigmented material (A2) and one of the rutile-pigmented materials (R4). When comparing the exposed layers, A2 was found to oxidise more than U1 whereas R4 oxidised less. This confirms the expected pro-degradative property of anatase and the protective property attributed to some rutiles.

The main purpose of the experiments reported here was to investigate the oxidation at different depths, however. In unpigmented polyethylene, the slowest rate of carbonyl group formation was observed with the central layer, as would be expected if reaction was limited by oxygen starvation (Fig. 5(a)). The films were held tightly within the ring grips so although oxygen and other volatiles could move freely across the interface between successive layers, the source of oxygen was restricted. Although there appears to be a slight oxygen-starvation effect with the unpigmented polyethylene, it is likely to be very small in a single layer sample. (Recall that the triple layer experiment is based on samples 0.3 mm in total thickness, and that the centre is 0.15 mm from the surfaces exposed to the atmosphere in the conditioning test machine whereas in an experiment with a single layer, the centre of the sample is only 0.05 mm from the surfaces). Therefore, for unpigmented PE it is assumed that carbonyl group development continues without significant modification from oxygen starvation within the 0.1 mm single layered samples and that after application of the thickness correction based on the polyethylene band absorbance, the differences in the carbonyl group IR absorption for unstrained and strained exposure can be truly attributed to changes in the rate of oxidation caused by stress.

In the case of the anatase-pigmented material, the unexposed layer showed the slowest carbonyl group development, with the results for the central layer located between those for the exposed layer and those for the back-facing layer (Fig. 5(b)). This is what would be expected if the UV intensity were the controlling factor. This requires further analysis, and the reader is referred to the Appendix A.

In the rutile-pigmented material (Fig. 5(c)) the carbonyl group development was very much slower in the central layer and in the layer that faced away from the UV source than in the exposed layer. The oxidation of the central layer was only slightly greater than that in the back-facing layer and it seems that UV intensity is again the controlling factor here. The difference between the A2 and the R4 results is caused by the higher UV transmission of anatase pigmented films than rutile pigmented films [35,36]. Hird [36] reported careful measurements of UV attenuation by UV transparent films with either rutile or anatase pigmentation. Although his measurements were made at pigment volume concentrations 5–10 times greater than those used in the research reported in the current paper, the pattern of the results should be followed at least qualitatively. For anatase and rutile pigments of similar size, attenuation of UV wavelength 350 nm was only 45% of the attenuation by rutile. At 400 nm, attenuation by anatase was only 30% of that of rutile. For comparison, a change in rutile particle size from 0.17 to 0.20 μm caused a decrease in the attenuation coefficient to only 85% at 350 nm and a negligible change at 400 nm. As the pigments used in this study were within a similar size range, size differences are considered to have only a second order effect on the observed differences in UV transmission behaviour. Very little UV penetrated as far as the central layer in the R4 trial, giving a level of photo-oxidation only slightly greater than that in the back-facing layer. UV exposure of the third layer of the R4 stack was probably restricted to radiation scattered by the surfaces of the exposure enclosure, falling on the back face, with

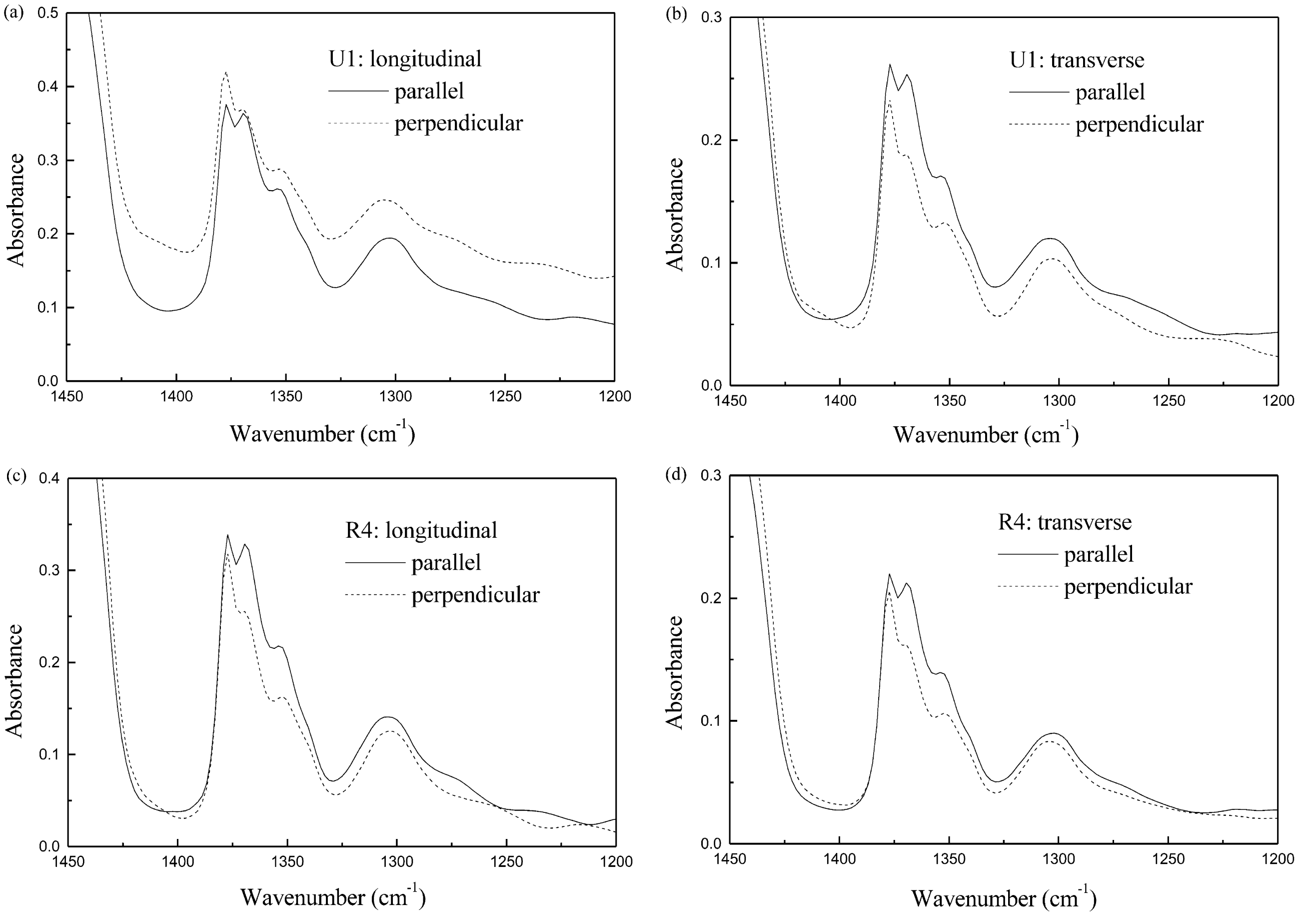

Fig. 4. FTIR spectra of strained samples taken using polarized IR, showing the range containing the polyethylene absorbances with peaks between 1300 and 1400 cm^{-1}. (a) U1 strained longitudinally; (b) U1 strained transversely; (c) R4 strained longitudinally; (d) R4 strained transversely. 'Parallel' and 'perpendicular' refer to the orientation of the polarization axis with reference to the applied strain axis. The applied strain was 80%.

practically none at all transmitted through the upper two layers.

From these results it is deduced that for R4, degradation can be expected to develop primarily near to the illuminated face of the first layer. Therefore, the total carbonyl group production through the first layer will be almost independent of the layer thickness. Transmission in the infrared is unaffected and the strength of the band at 1350–1380 cm^{-1} can be taken to be representative of the film thickness.

3.5. Single-layered samples

The majority of the experiments were conducted on single-layered samples. The experiments on multi-layered samples summarised in the previous section were conducted simply to investigate the effect of changing the thickness on the FTIR results, and to determine whether any correction for thickness is required when assessing strained samples that present a reduced thickness to the IR beam as the result of Poisson contraction.

Carbonyl group development in unstrained samples for exposures up to 22 days is given in Fig. 6. In each material the carbonyl group absorption increased progressively. Up to 400 h exposure, the curves are slightly concave upwards, possibly a consequence of auto-acceleration. The anatase-pigmented material showed the highest rate of oxidation. The rutile-pigmented materials show a range of oxidation rates. Two of them show rates that are greater than that of the unpigmented polyethylene U1; these rutiles are known to have a light coating and are designed for non-durable applications. The two rutiles that produced oxidation rates below U1 both have heavier coatings and are designed for applications in which UV photostability is a priority. The carbonyl absorption results for samples tensile strained in the longitudinal direction are given in Fig. 7. These results are uncorrected for thickness (see below). It is noted that the ranking of the materials is almost identical to that in Fig. 6. The anatase-pigmented material again shows the fastest reaction rate and the two rutile-pigmented materials that gave the highest rates in the unstrained state do so again and are in the same order. The two rutile-pigmented materials that oxidised slower than the unpigmented material are again placed below it, but in this series of measurements they are almost indistinguishable whereas in Fig. 6, R6 shows a significantly higher rate than R5. In the stressed series, the results for the unpigmented material are much

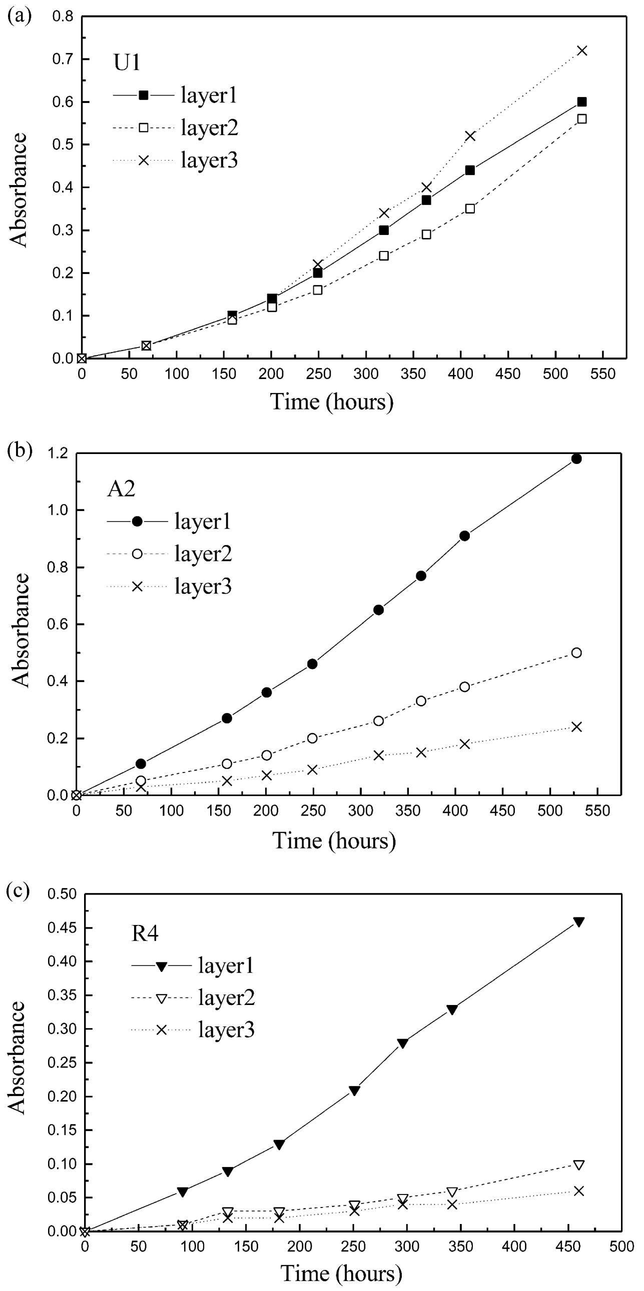

Fig. 5. Carbonyl group absorbance versus time of UV exposure for triple layered films (a) U1; (b) A2; and (c) R4.

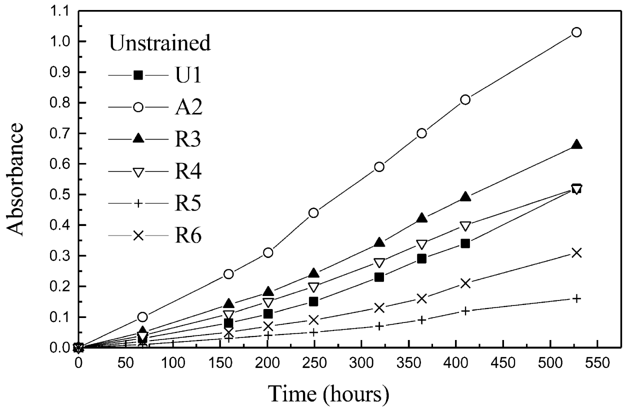

Fig. 6. Carbonyl group absorbance versus time of UV exposure for unstrained films.

closer to those for R5 and R6 than is the case in the unstrained state (compare Figs. 6 and 7).

Samples U1, A2, R3 and R4 all broke during the strained exposure, as marked on Fig. 7. It is of interest to note that the carbonyl group absorbance at break was approximately the same for all four samples (U1, A2, R3 and R4) and that this level of absorbance was not reached by the samples that did not break during the exposure (R5 and R6). Not too much should be read into this observation, especially as the measurements of absorbance are not corrected for thickness, and because it is believed that thickness corrections should be made for U1 and A2, but not for the rutile pigmented materials (see Section 3.6). Once the crack formed, the material retracted within the clamp and exposures beyond the break point were, therefore, conducted at much reduced strain, and assessment of carbonyl group production in this regime must take this into account.

The carbonyl absorption results for samples strained in tension in the transverse direction are given in Fig. 8. Again these results are not corrected for thickness. This time the ranking of the materials is identical to that in Fig. 6 and the spacing of the curves for the different materials displays a relationship similar to that in Fig. 6. Samples U1, A2, R3 and R4 again all broke during the exposure, as with the longitudinal samples, and the carbonyl absorption at this point was almost identical in all cases (see remarks in the previous paragraph regarding the thickness correction). Samples R5 and R6 did not reach this level of carbonyl group development by the time the tests were terminated, and did not break. The typical values of carbonyl absorbance level at which the transverse samples cracked were much higher than those at which the longitudinal samples cracked. The A2, R3 and R4 transverse samples all broke after a significantly longer time than it took for the

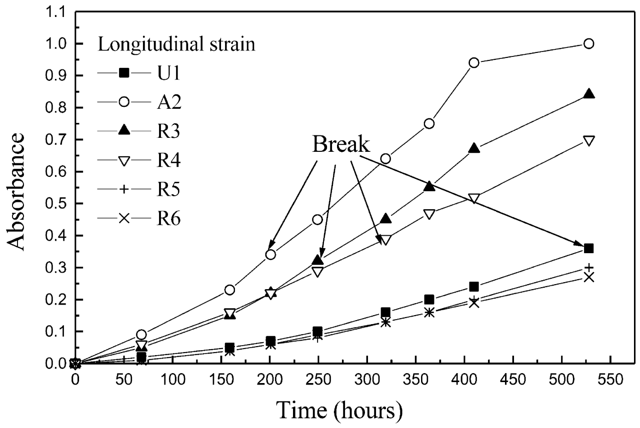

Fig. 7. Carbonyl group absorbance versus time of UV exposure for films strained longitudinally during exposure. The times when the samples broke are shown. The data are uncorrected for thickness changes.

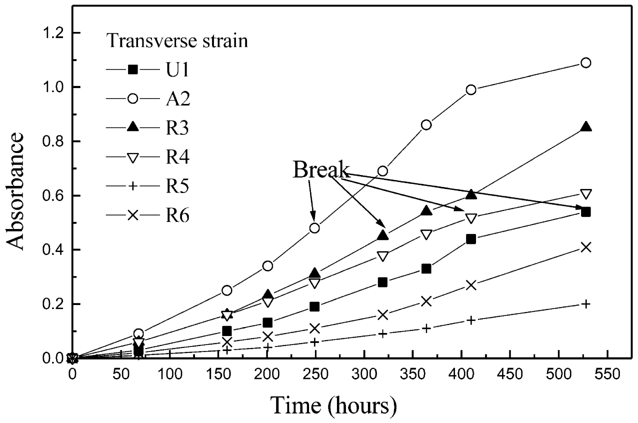

Fig. 8. Carbonyl group absorbance versus time of UV exposure for films strained transversely during exposure. The times when the samples broke are shown. The data are uncorrected for thickness changes.

corresponding longitudinal samples to break; the U1 samples broke after approximately the same exposure time.

On inspection of the carbonyl absorption versus time plots of samples that did not break (including those that were exposed unstrained) it is evident that they tend to be concave upwards, indicating auto-acceleration. In the case of strained samples that broke before the exposure period was complete, the plots tend to be concave upwards prior to the crack forming but, in some cases, the gradient falls after fracture. This is what would be expected to happen if stress assists the chemical transformation, since the formation of the crack partially or completely unloads the sample. It should be noted that the rate of oxidation after unloading is not expected to be the same as that in a sample irradiated in the unstressed state from the beginning. This is because the enhanced production of radicals and other reactive species during the stress-accelerated phase of the oxidation will leave the sample in a more sensitive state even when it is subsequently unloaded.

3.6. Correction for sample thickness

From casual inspection of the results presented in the previous section, it might be deduced that there is very little effect on the rate of carbonyl group production when stress is applied in the transverse direction, and that the major effect of stress in the longitudinal direction is to reduce the rate of oxidation in the unpigmented material, while having little effect on the pigmented materials. However, the results as presented above do not take any account of sample thickness and the effect of this must be considered before drawing any firm conclusions.

In Fig. 9 the results presented in Figs. 6–8 are replotted, together with thickness-corrected plots for the two sets of data for strained samples (for longitudinal and transverse deformation). The correction takes account of the thickness reduction in the strained samples, based on the intensity of the IR band at 1350–1380 cm^{-1} and implicitly assumes that the carbonyl groups are homogeneously distributed throughout the thickness of the film. When the thickness change caused by applying a tensile deformation is taken into account, the U1 samples strained in the longitudinal and the transverse directions during UV exposure both show an increase in carbonyl group generation rate compared to the unstrained film. The same is true for the anatase-pigmented polyethylene, A2. In the case of the rutile-pigmented polyethylene, R4, the analysis in the Appendix A indicates that the carbonyl groups are concentrated very close to the exposed surface and that the thickness correction should not be applied. Even if the thickness correction is not applied in this case (Fig. 9(d)), the strained samples still show significantly higher carbonyl group development than the unstrained sample exposed under the same conditions. The thickness correction is shown for completeness, despite the belief that it is not appropriate to use it. (If the thickness correction were valid, it would indicate even greater sensitivity of oxidation to stress than is represented by the original data). No IR measurements were made for triple layered samples of R3, R5 and R6 and it is assumed, without verification, that a thickness correction would be inappropriate, as with R4. The carbonyl absorption data for R3 and R5 are similar to those for R4, showing that strain enhanced the oxidation rate significantly, whether or not the thickness correction is needed. The interpretation for R6 is a little less straightforward, since the uncorrected carbonyl absorbance for longitudinal strain falls close to or just below that for the unstrained sample. When the thickness correction is applied, the strained sample appears to have oxidised more rapidly, though the validity of the thickness correction for this compound is not known. The uncorrected carbonyl absorbance for transverse strain is greater than that for the unstrained sample, showing unambiguously that strain applied in this direction enhanced oxidation.

In order to assess the enhancement of carbonyl group development caused by the application of stress, the carbonyl group absorbance at 200 h exposure for each of the strained samples was compared with that for the corresponding unstrained sample at the same time. The data taken for the strained U1 and A2 samples were corrected for thickness whereas the rutile-pigmented polyethylenes did not have the thickness correction applied, for reasons explained elsewhere. The ratios of the two

Table 2
Carbonyl group enhancement in 80% strained film after 200 h UV exposure (ratio of strained sample absorbance to unstrained sample absorbance)

	Longitudinal	Transverse
U1	1.4	1.6
A2	2.0	1.7
R3	1.3	1.3
R4	1.5	1.4
R5	1.6	1.0
R6	0.9	1.2

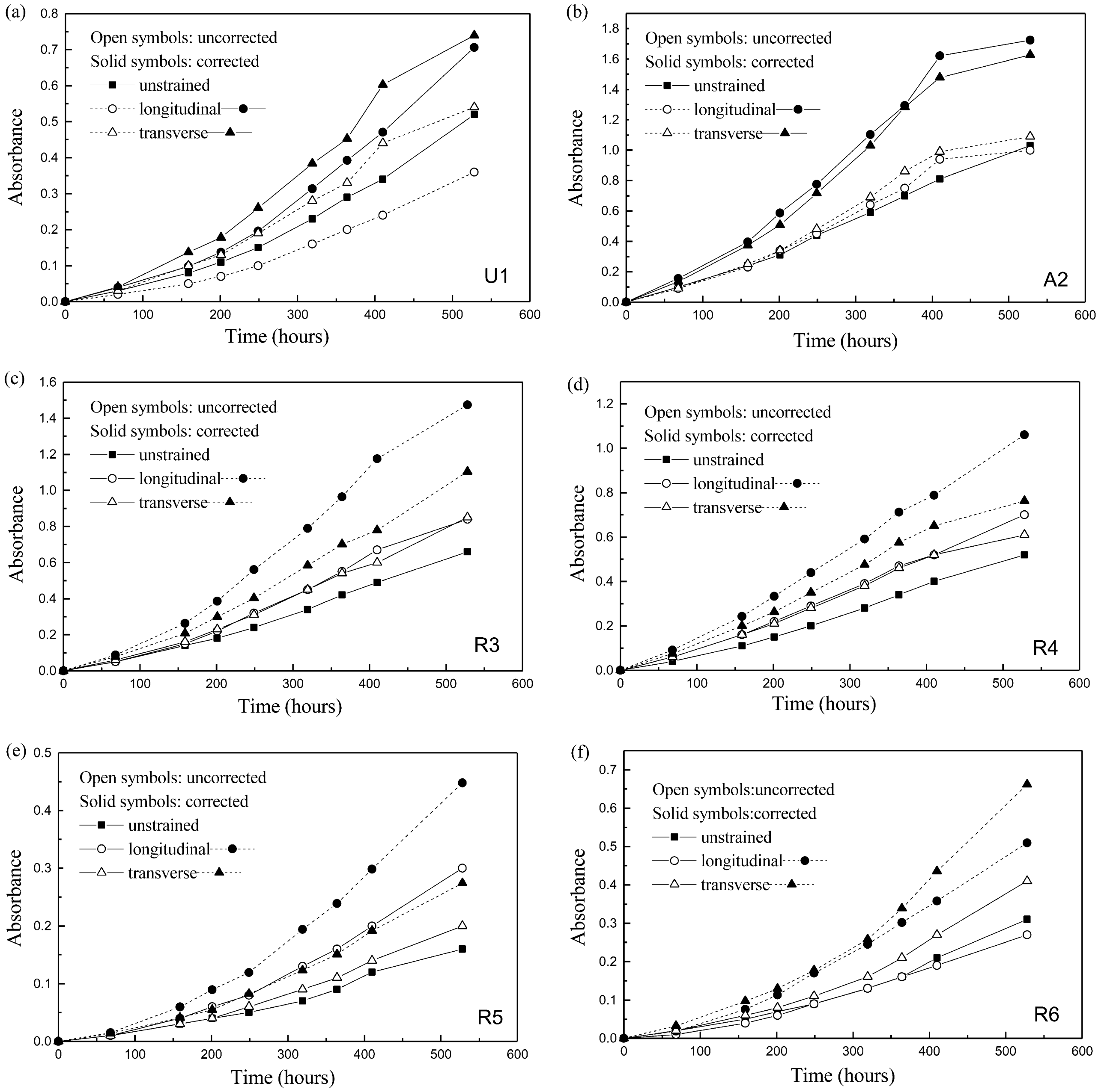

Fig. 9. Carbonyl group absorbance versus time of UV exposure, comparing data from samples exposed unstrained, longitudinally strained and transversely strained, and showing uncorrected and thickness-corrected measurements for the strained experiments: (a) U1; (b) A2; (c) R3; (d) R4; (e) R5; and (f) R6. Note that the correction is almost certainly invalid for R4 and probably invalid for the other three rutile-pigmented materials (R3, R5, R6). Thus the solid lines are the ones to be used to assess the effect of stress in all graphs, and the broken lines are shown for completeness.

absorbances are shown in Table 2. The time of 200 h was chosen because some of the samples broke at times longer than this. For pigmented polyethylenes A2 and R5 the ratio for samples exposed while strained in the longitudinal direction exceeded that for the corresponding material strained in the transverse direction. There was hardly any effect of test direction for R3 and R4. For R6 the ranking was reversed, with the transverse sample showing the greater rate. In unpigmented PE (U1) the transverse sample also appeared to degrade more rapidly than the longitudinal one.

It is evident from Fig. 9 that the thickness correction is greater for longitudinal testing than for the transverse samples. This indicates that the Poisson ratio is anisotropic; this is common in oriented polymers and is not entirely unexpected.

4. Discussion

Before considering the effects of anisotropy on photo-mechanical oxidation, it is noted that there remains some controversy over the effect of stress on polymer degradation. Chemiluminescence has been promoted as a sensitive probe for following polymer oxidation [37,38]. Although there is some dispute over the source of the luminescence, it is probably associated with the recombination of radicals produced by peroxide decomposition. Attempts by others to detect any significant stress-related changes in reaction rate using chemiluminescence have failed, but it is believed that this is because of the constraints of the method, requiring measurements to be conducted at temperatures that are much higher than typical service conditions [39,40]. For example, the temperature used to study the effect of stress on the oxidation of polypropylene by chemiluminescence was 95 °C [40]; at this temperature relaxation is extremely rapid and the observations must have been made at stresses far below those for which stress was shown to accelerate photodegradation in polypropylene at 30 °C (7–10 MPa) [7]. The chemiluminescence study of high density polyethylene was conducted at 110 °C [40] and, therefore, should not be expected to show strong correlation with the studies reported here, which were conducted at 42 °C. Furthermore, the selective aspect of the chemiluminescence signal, probably caused by the reaction between two peroxy radicals, may not be representative of the overall oxidation behaviour and, in particular, may not follow the effect of stress. The results presented here provide further evidence in support of the view that tensile stress accelerates photodegradation in polymers.

There are several ways in which stress may be expected to influence oxidation in polymers. Firstly, it may directly assist any thermally activated process in the manner proposed by Zhurkov [5,41–44]. It may influence the rate of recombination of radicals formed by photo-chemical scission reactions, effectively separating them before the molecules have a chance to repair themselves. This would explain why tensile stress was found to increase the rate of chain scission near to the surface of polypropylene bars but had very little influence on crosslinking rate, even though oxidation processes are involved in both scission and crosslinking [45]. Finally, stress may influence the diffusion rate of oxygen (or other reactants). Since tensile stress is usually dilatational, it would be expected to increase the diffusion rate of penetrants such as oxygen, though Baumhardt-Neto and De Paoli suggest that it might encourage molecules to align and pack closer, giving a reduced diffusion rate [6]. Furthermore, over an extended period of time it is possible that stress may cause an increase in crystallinity and this will be expected to influence the rate of degradation.

In the studies reported here, it is again evident that the application of tensile stress has increased the degradation rate, here represented by carbonyl group development. The unique feature of the work presented here is that data are obtained for tensile stresses applied both parallel to and transverse to the machine direction during fabrication of the material, in this case a blown lay-flat film, in which the tube axis is taken to be the machine (longitudinal) direction. The rate of carbonyl group development is increased by stress applied both parallel and transverse to this direction. With unpigmented polyethylene the effect of transverse strain was greater than that of longitudinal strain. The same was observed with rutile-pigmented polyethylene R6. With the polyethylene samples pigmented with the other rutiles and with the anatase-pigmented polyethylene, the rate of carbonyl production was greater for tensile stress applied in the longitudinal direction than for the transverse direction. Tensile tests showed that the films were clearly anisotropic though it is noted that measurements of dichroic ratio did not indicate any significant molecular orientation was present. The machine direction and hoop direction orientations are applied sequentially and it is perhaps not surprising that the sample is not isotropic in the plane of the film, even if the dichroic ratio is unity. Other measures of orientation, such as pole figure analysis, might be more revealing.

In attempting to interpret these results, it is important to recognise that the deformation condition for the UV exposures was strain-controlled. This means that the stress may not be the same in the parallel and transverse samples because of anisotropy in Young's modulus and also because the stress relaxation rates may be different in different directions. It is usually expected that the Young's modulus will be greater in the longitudinal direction than in the transverse direction, though this could not be confirmed by the tensile tests because they were not conducted under conditions that permitted sufficient measurement accuracy to enable discrimination. Furthermore, relaxation in the longitudinal direction is likely to be more restricted than in other directions. Thus, it is expected that the stress will be higher in the longitudinal samples and it is, therefore, interesting to note that for the unpigmented material, U1, the rate of carbonyl group increase was greater for the transverse samples than for the longitudinal ones.

The interpretation for the pigmented materials is more complex. If the pigment is not equiaxed, then it is expected to have a non-random orientation distribution, caused by flow during extrusion and blowing. This will in turn influence the polymer orientation distribution if the pigment particles nucleate directional growth in the polymer. In the study reported here, all the TiO_2 pigments were acicular, but not extremely so, with aspect ratio 1.5. The presence of the pigment will modify the flow of the polymer during fabrication, so leading to another potential source of modification of the polymer orientation distribution. The pigment provides pinning points that restrict molecular motion, altering the relaxation behaviour. The presence of the pigment may change the crystallinity (as the result of nucleation and/or changing the cooling rate) so changing molecular mobility.

The majority of the pigmented materials gave a greater rate of carbonyl group development for longitudinal strains, as would be the case if the effect depended on stress (which is expected to be higher for a fixed strain applied parallel to the machine direction). An exception was R6, however, for which the greater rate was observed for the transverse applied strain.

Another new observation was that strained samples that broke while under UV exposure did so at approximately the same level of carbonyl group development and that this level was different for longitudinal and transverse straining. Longitudinal samples broke at a much lower level of carbonyl group concentration than transverse samples. Bonds that are oriented during fabrication will be affected the most by stress applied in the longitudinal direction, and it is expected that they will be oxidised preferentially. This will lead to chain scission as well as to the production of carbonyl groups. The loss of the bonds with the greatest load bearing responsibility will cause localised redistribution of stress and bonds nearby will now become vulnerable to oxidative attack. This will lead to the development of microcracks and the consequent embrittlement of the material. This is essentially the hypothesis advanced by Zhurkov and developed by the Russian School [3,41,42,46]. When strain is applied in the transverse direction there will be fewer bonds in the parallel orientation and it would be expected that the rate of oxidation will, therefore, be lower than for longitudinal samples, and that the attack will be less localised, requiring a greater overall level of oxidation before a critical flaw develops.

The above discussion assumes that the preferred direction for load-bearing bonds coincides with the ‘machine direction’ rather than the tube hoop direction. Although it ignores the observation that the dichroic ratio was close to unity for all of the samples tested, it is evident that the dichroic ratio cannot be very sensitive to the source of the anisotropic behaviour. The tensile test results showed clearly that the samples were indeed anisotropic. The sense of the anisotropy indicated by the tensile tests is the same for all samples whereas the oxidation measurements indicate different behaviour for R6 and the other rutile-pigmented samples (R3, R4 and R5). Therefore, although anisotropy is seen to have a strong influence on the oxidation of samples when exposed to UV under tensile stress, there is no simple correlation between the enhancement of the rate of oxidation and the measures of anisotropy used to date.

5. Conclusions

The effect of stress on the rate of photo-oxidation in a series of blown film polyethylene samples in unpigmented form and containing different forms of TiO_2 pigment has been investigated, using carbonyl group development as the method of assessment. Tensile tests on unexposed samples revealed that they were anisotropic; all materials gave a higher yield stress when tested parallel to the machine direction than when tested transverse to it. Tensile stress has been shown to increase the rate of photodegradation. The carbonyl group measurements were made with the samples in the stretched state, which produced a reduction in thickness compared to the unstrained state. Therefore, to analyse the infrared absorption data it was necessary to perform a correction for thickness differences between samples.

In some cases, different rates of carbonyl group development were found for samples strained parallel and transverse to the machine direction. With unpigmented polyethylene, carbonyl group development was slightly faster when UV exposure was conducted with tensile stress applied in the transverse direction. Pigmented samples A2 and R5 gave the greatest carbonyl production rates when strained parallel to the machine direction whereas the rutile-pigmented polyethylene R6 displayed a greater rate for transverse stress. The oxidation of R3 and R4 under UV-stress conditions showed little effect of strain application direction. It is evident that the underlying anisotropy in some samples is sufficient to provoke a strong response in the oxidation behaviour under applied loading, even though it was not revealed by measurements of dichroic ratio. Samples loaded in the machine direction during UV exposure broke after a shorter time than samples of the same material loaded transversely. The carbonyl index was higher at the time of break in those samples strained transversely than those stressed longitudinally during exposure.

The influence of anisotropy on the photo-mechanical degradation of polyethylene revealed by this study was unexpected. It shows that even a long-established and intensively researched polymer such as polyethylene still has the capacity to surprise. We wonder whether at the beginning of his career, Ian Ward would have anticipated that he and other researchers would still find out new things about polyethylene in the 21st century?

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Appendix A. Analysis of the absorption characteristics of triple-layered samples

The purpose of the analysis that follows is to attempt to explain the absorbance measurements. When an electromagnetic beam passes through a material sample, the absorbance is not proportional to the film thickness, because of the attenuation of the beam as it passes through the sample.

During UV exposure, when the part of the UV beam that promotes the chemical reaction(s) that lead to the formation of the carbonyl groups passes through the polymer film in the thickness ($z-$) direction, the intensity falls according to $I = I_0\exp(-cz)$ (Beer's law). The fall in intensity is due both to interaction with the polymer and scattering by the pigment particles. The amount of carbonyl group formation in a slice of the polymer of thickness δz at depth z is proportional to $I(z)\delta z$ and for a single layer of thickness h_0 the infrared absorption measured for the carbonyl group band at $\sim 1712\ \mathrm{cm}^{-1}$ in a subsequent analysis for the whole layer is, therefore, proportional to:

$$A_{0,h_0} = \int_0^{h_0} I(z)\mathrm{d}z = I_0\{1 - \exp(-ch_0)\}/c \tag{A1}$$

(Here the effects of variations in carbonyl concentration due to exposure time and stress level are ignored since they are independent and separable).

In the same way the corresponding values for the second and third layers are:

$$\begin{aligned} A_{h_0,2h_0} &= I_0\{\exp(-ch_0) - \exp(-2h_0)\}/c \\ &= I_0\exp(-ch_0)\{1 - \exp(-ch_0)\}/c \end{aligned} \tag{A2}$$

$$\begin{aligned} A_{2h_0,3h_0} &= I_0\{\exp(-2ch_0) - \exp(-3h_0)\}/c \\ &= I_0\exp(-2ch_0)\{1 - \exp(-ch_0)\}/c \end{aligned} \tag{A3}$$

Therefore, for a particular exposure time and stress state we have:

$$\frac{A_{h_0,2h_0}}{A_{0,h_0}} = \frac{A_{2h_0,3h_0}}{A_{h_0,2h_0}} = \exp(-ch_0) \tag{A4}$$

or

$$\ln\frac{A_{h_0,2h_0}}{A_{0,h_0}} = \ln\frac{A_{2h_0,3h_0}}{A_{h_0,2h_0}} = -ch_0$$

Measurements at several locations (exposure times) on Fig. 5(b) confirmed the value of ch_0 for sample A2 is constant and gave $ch_0 \sim 0.875$. This confirms that the anatase-pigmented polyethylene is 'well behaved' and that reaction is controlled by UV intensity.

When this analysis was attempted for R4 it was found that the ratios in Eq. (A4) varied over quite a large range, especially when evaluated for different exposure times. This is probably because the intensity of UV reaching the bottom two layers of the triple layer stack was so small that the carbonyl group concentration produced in them was too small to measure accurately. It is implied that carbonyl group development will be almost exclusively confined to a very thin layer near the exposed surface, probably only a few microns thick. In this case, the thickness correction for the strained samples should not be applied when analyzing the carbonyl absorbance.

The analysis based on eq. (A4) is not appropriate for unpigmented polyethylene (U1) since oxygen diffusion limited conditions prevail, causing the middle layer to have lower carbonyl concentration than even the lowest layer. The differences in carbonyl group accumulation in the three layers in the U1 stack is not very great, however, indicating that the carbonyl group concentration does not vary very greatly. It is deduced from this that in a single U1 layer, the carbonyl group gradient through the depth of the film is not sufficiently steep to invalidate the thickness correction.

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