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Humidity Dependence of Carbon Dioxide generation during photodegradation of biaxially oriented polypropylene in oxygen

Running Title: Humidity dependence of polypropylene photodegradation

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Abstract

UV generation of CO₂ gas from a range of biaxially oriented polypropylene (BOPP) films exposed in oxygen gas has been measured by *in situ* infrared spectrometry and compared with the development of absorption at 1713 cm⁻¹ due to carbonyl formation in the same films. As in studies of other polyalkene films, the CO₂ measurements, which take only 3 hours, correlate well with carbonyl development measurements that require hundreds of hours.

Upon UV irradiation of BOPP in dry oxygen an induction time of ~ 60 minutes preceded a linear increase of photogenerated CO₂. In wet oxygen, no noticeable induction time preceded the linear increase of CO₂. The rate of CO₂ increase was greater when the oxygen was humidified. This pattern was observed for four different types of film and for films of different thickness. The increase in the rate of CO₂ photogeneration with increased humidity was greater for thicker films. The correlation between the amount of CO₂ generated and the strength of the carbonyl absorption developed under standard conditions was better for BOPP oxidation in dry than in humidified oxygen. The inclusion of recycled polymer caused an increase in the rate of photodegradation.

Although measurements on each sub-set of films demonstrated a clear increase in the photogeneration of CO₂ at high humidity, the mechanism by which the CO₂ generation from BOPP is enhanced remains unclear and further work is necessary to resolve this puzzle.

Introduction

Polymeric products are exposed both to oxygen and to solar ultraviolet radiation (UV) when used outdoors, and the resulting photo-degradation can significantly shorten their useful life. The degradation may result from direct photolysis or from photo-oxidation, but both mechanisms require absorption of UV and for solar wavelengths at terrestrial sites this means wavelengths above ~290 nm. Polypropylene (PP) and polyethylene (PE) both photodegrade more rapidly in air than in an inert environment indicating that photo-oxidation dominates, rather than photolysis. Although neither pure PP nor pure PE absorb at wavelengths longer than 290 nm, radical-based oxidative processes may be initiated by the absorption of sunlight by (i) internal in-chain impurities such as carbonyls formed during processing or storage, (ii) external impurities such as residues of the polymerization catalyst or metal traces from processing equipment [1], or (iii) charge transfer complexes formed between the polymer and oxygen [2, 3]. In general, the relative importance of these processes is not clear.

The study described in this paper used Fourier transform infrared (FTIR) spectrometric measurement of photogenerated carbon dioxide [4] to monitor the photo-oxidation of biaxially oriented polypropylene (BOPP). Measurement of CO₂ generated by photodegradation has been used previously to elucidate the reaction mechanisms occurring during UV exposure of polyethylene [5], polypropylene [6] and polyphasic ethylene-propylene (PE-PP) polymers [7], but these studies, using gas chromatography, normally required exposures of tens or hundreds of hours [2,8]. A significant improvement which allows the photo-generated CO₂ to be measured after times as short as 10 minutes has been achieved using a novel approach that is based on simultaneous UV irradiation of a polymer sample and IR interrogation of the surrounding atmosphere [4,9,10]. For PE good correlation was demonstrated between the FTIR measure of CO₂ generation and the development of carbonyl absorption when a series of samples of the same polymer, pigmented with different grades of TiO₂, were exposed in QUV equipment to UVA-340 radiation for many hundreds of hours [4]. Similar correlations based on FTIR measurement of photogenerated CO₂ have been demonstrated for poly(vinyl chloride) (PVC) plastisols [11].

An important feature of the *in situ* measurement of CO₂ is that the experimental method allows the polymer photodegradation to be monitored in a variety of atmospheres. The study presented in this paper used this advantage to focus on the effect of humidity on the oxidation of BOPP. Previous studies of the degradation of acrylic paint films [12] PE [4] PVC [13] and poly(ethyleneterephthalate) (PET) [14] have shown that the rate of carbon dioxide generation increases with increasing humidity. Most of these studies were of polymers pigmented with TiO₂ and it was postulated that the increased rate of CO₂ formation was a consequence of enhanced photocatalysis by the TiO₂ as a consequence of enhanced formation of hydroxyl radicals at high humidity. However, it has been shown that high humidity can also increase the rate of CO₂ photo-generation from unpigmented polyethylene [4]. The present investigation extends a previous study of CO₂ photogeneration from a single unpigmented polypropylene (UPP) film [9]. It does not focus on differences between regular and biaxially-oriented PP. Instead it investigates the humidity dependence of the CO₂ formation rate for both unpigmented and pigmented BOPP of different thicknesses and compares CO₂ measurements with carbonyl development for films of different photoactivity.

Experimental

Film samples and their characterization

Measurements were made on different sets of biaxially oriented polypropylene film. Three separate sets of clear film, designated 'B' 'C' and 'R' were examined. All were supplied by Innovia Films (Wigton, UK) and were manufactured by a film blowing process – the bubble process – for which the general principles have been described by Mills [15]. As is normal for commercial material, the polypropylene, has an (undisclosed) stabilisation package but is not sold as a thermally or UV stabilised grade. No HALS were included in the formulation. The films were extruded at ~ 260 °C and then drawn in the machine direction by a speed differential between a first and second nip. Simultaneously, the film was drawn in the orthogonal, transverse, direction by blowing a bubble with air. The temperature during the draw process was ~160 °C. B films corresponded to one layer of the polymer, formed by splitting the bubble after the second nip. C-films were made by applying pressure at the second nip and laminating the two sides of the bubble together. Both sets of films were used to study the effect of film thickness, which can be controlled by the process conditions. R-films were manufactured

with an increasing content of recycled polymer, originating from the film production process. The stronger UV absorptions at 225 nm suggest that these films had increased carbonyl content. (Some R films were modified by a standard corona discharge treatment, but, except for film R1, which had no recycled material, there is no evidence of significant changes in the spectra caused by this.) Films pigmented with rutile TiO₂ were made by the same bubble process and designated WB and WC. UV absorption by the TiO₂ was expected to limit the UV penetration to the irradiated surface of the pigmented films and therefore limit the depth within which reaction occurred.

The thickness of films was measured using a micrometer screw gauge. The code BXY describes a sample of film-type B, XY microns thick. Although a C film (e.g. C58) may correspond to approximately double the thickness of a B film (e.g. B28), the two films were from different production batches. The UV absorption spectra were measured from 190 to 400 nm using a Shimadzu UV-1240 spectrometer.

Measurement of CO₂ photogeneration

Sample discs of polymer film were placed in a specially constructed cell [9, 10] which was then flushed for ~30 minutes with cylinder oxygen. Oxygen direct from the cylinder was designated 'dry oxygen'; attempts to dry it further by passing it through silica gel increased the water content. Alternatively, the cylinder gas was humidified by passing it through two water bubblers in series; this humidified oxygen was designated 'wet oxygen'. The cell taps were then closed and the cell was then placed in the sample compartment of a Bio-Rad FS60 FTIR spectrometer equipped with a liquid nitrogen cooled narrow band detector. In this location, the BOPP disc could be irradiated by the output from a xenon lamp via a light pipe and a CaF₂ optical window. The xenon lamp illumination was filtered by a 10 cm water filter to remove IR, and minimise heating of the sample, and by an AM0 filter to remove UV with wavelengths below ~290 nm. CO₂ in the cell was monitored by measuring, at 2360 cm⁻¹, the P branch of its asymmetric stretching vibration [4, 12]. Irradiation of an empty cell gave very low CO₂ absorbances, ~4 x 10⁻⁴ in 3 hours; no corrections have been made for this background. Before measuring polymer oxidation, the CO₂ level was monitored for an hour prior to switching on the UV lamp, to check for instrumental stability.

Results

UV absorption measurements

The UV spectra of both the B and C films (Fig.1a) and of R films containing deliberately added recycled material show absorptions close to 200, 225 and 275nm. The absorptions near 225 and 275 nm are much more evident in the spectra of films which have added recycled material (R3, R4, R5 & R6) or have been corona discharge treated (R2, R4 & R6)). The UV absorption at wavelengths greater than 290 nm was negligible in all of these spectra of unpigmented films. The UV-visible spectra of the two TiO₂-pigmented films, designated 'W', were also recorded. W-films had absorbances greater than 2.5 in the visible region of the spectrum which increased to above 3 for wavelengths below 405 nm (the absorption edge of rutile).

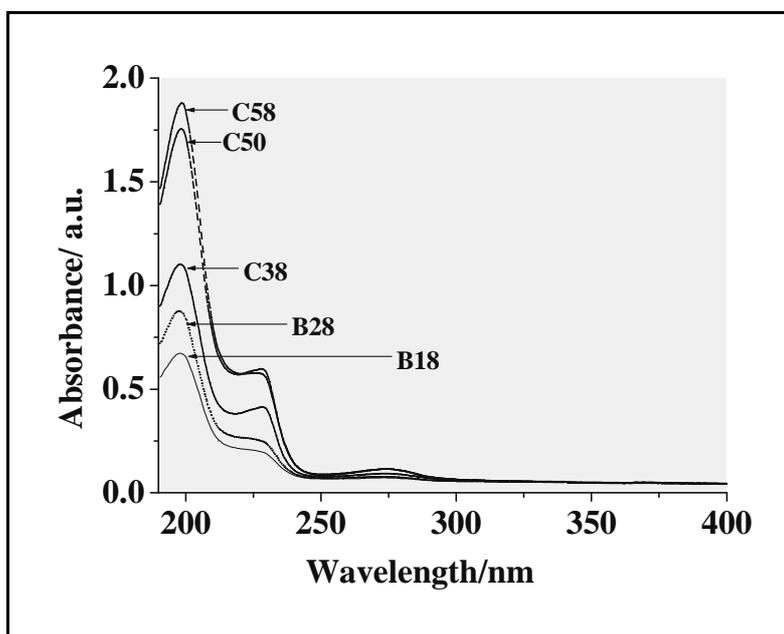


Figure 1a Transmission spectra for sets B and C of un-pigmented BOPP films of varying thickness (microns).

Fig. 1b shows that the absorbances of the peaks near 200 and 225 nm of film-types B and C increase linearly with film thickness (quantitative intensity measurement of the 275 nm band was impractical). For each wavelength, a common line can be drawn through the

two sets (B and C) of data points and this suggests that there is no major difference between the absorption characteristics of the two sample sets. In addition, the near-linearity within each set suggests that the absorbing groups are distributed throughout the thickness of the film instead of being concentrated in a surface layer.

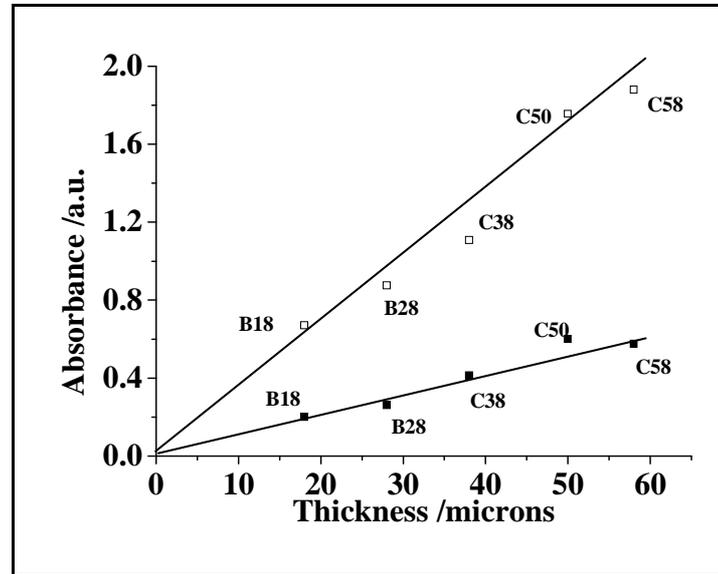


Figure 1b Absorbance at 225 nm (■), and 200 nm (□) of un-pigmented BOPP films from sets B and C as a function of thickness (microns).

Measurements of the photogeneration of carbon dioxide

Fig 2 shows the results of CO₂ photogeneration, measured in both dry and wet oxygen, for three type C films of different thickness. In both atmospheres, the amount of carbon dioxide increased with increasing film thickness and for C58, C50 and C38 the ratios of the rates of CO₂ formation (1.7:1.3:1 in wet oxygen) were similar to the ratios of film thicknesses (1.5:1.3:1).

An induction time for CO₂ generation from unpigmented polypropylene, UPP, has been reported and discussed previously [9]. For BOPP films, also, there was a significant induction time in dry oxygen; very little CO₂ was generated during the first 60 minutes UV irradiation (from 60 to 120 minutes in Fig.3). However, in wet oxygen, CO₂ was generated immediately UV irradiation began (at 60 minutes in Fig. 2). Increasing the humidity also increased the amount of photogenerated CO₂. For C38, C50 and C58 films, the ratios of the CO₂ growth rates in wet and dry oxygen (excluding the points from any induction step) were ca. 2.2, 2.6 and 2.7 .

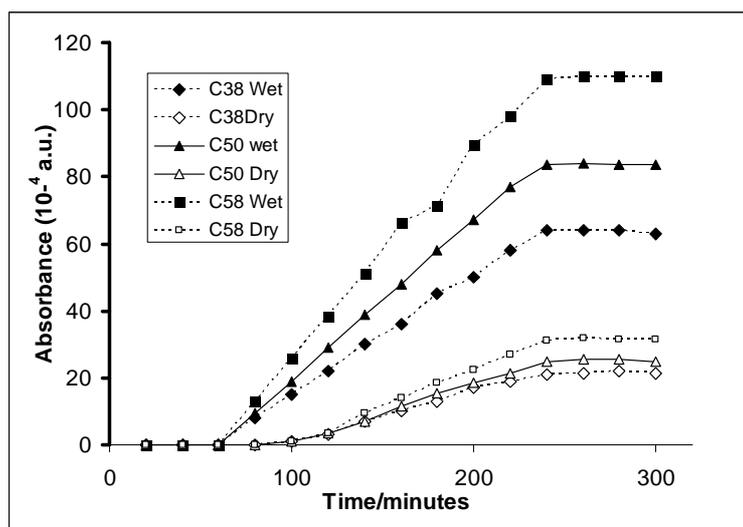


Figure 2 Photogeneration of CO_2 from C-films in wet and dry oxygen. Irradiation began at 60 minutes and ended at 240 minutes

Similar measurements, in both wet and dry oxygen, were made on the two (single-layered) B-films. CO_2 formation was greater from B-films than from (double-layered) C-films. The amount of CO_2 was again greater in wet oxygen than in dry conditions and in each atmosphere the amount of CO_2 approximately scaled with film thickness, as shown in Fig. 3. After allowing for the induction time with dry oxygen, the rate of CO_2 generation in wet oxygen was approximately double that in dry oxygen.

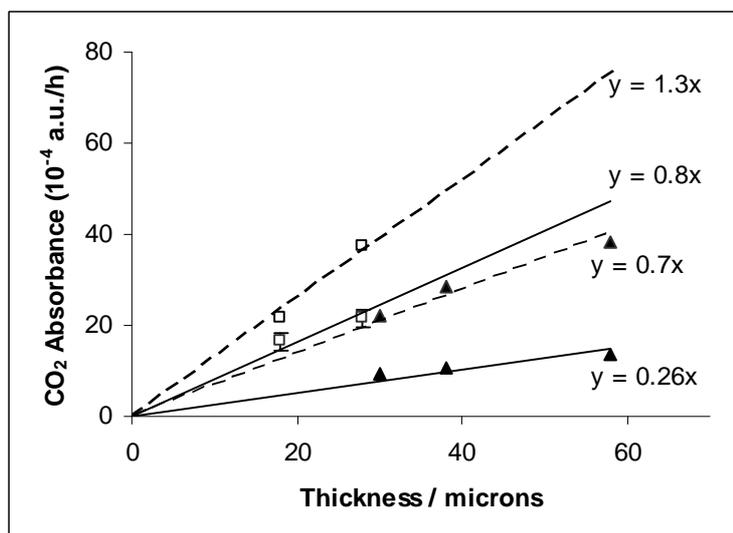


Fig. 3. The dependence of the CO_2 formation rate (corrected for induction time) on film thickness for two B-films (\square) and three C-films (\blacktriangle) when irradiated in dry oxygen (full lines) and in wet oxygen (broken lines).

The linear relationship between the amount of CO₂ evolution and film thickness for all sets of measurements implies that the CO₂ is generated throughout the films and that this is not particularly limited either by attenuation of photoactive UV or by oxygen diffusion into these clear polymer films. Furthermore, the observations indicate that evolution of CO₂ to the gas phase is not seriously limited by carbon dioxide diffusion through the sample. This is consistent with our earlier results for PE films [4]. When the results in Fig 4 were extended by examining the properties of samples composed of two individual films laid one above the other, CO₂ evolution increased by ~1.5 for the 2 x 28 μm B-film but for the 2 x 58 μm C-film under wet oxygen conditions CO₂ generation appeared to approach a limiting rate (Table 1). The overall conclusion is that oxidation of BOPP samples up to ~60 μm is not limited by UV attenuation or diffusion effects.

Table 1 The rates of increase of CO₂ absorbance (10⁻⁴ absorbance units per hour) in wet and in dry oxygen measured after the induction period, if any.

Sample	Wet O₂ condition (10⁻⁴ a.u. hour⁻¹)	Dry O₂ condition (10⁻⁴ a.u. hour⁻¹)	(CO₂)_{wet} rate: (CO₂)_{dry} rate.
B18	21	16	1.3±0.1
B 28	37	22	1.7±0.1
2 x B28	57 = 37 x 1.54	33 = 22 x 1.5	1.7±0.1
WB 28	31	16	1.9±0.1
C 38	22	10	2.2±0.1
2 x C38 films	40 = 22 x 1.8	13 = 10 x 1.3	3.0±0.1
C 50	29	11	2.6±0.1
C 58	37	14	2.7±0.1
2 x C58	43 = 37 x 1.2		
WC 58	35	18	1.9±0.1

The results in Table 1 also show that the rates of CO₂ generation for two TiO₂ pigmented films (WB28 and WC58) fell in the same range as those from the corresponding unpigmented films (B28 and C58) and that the enhancement in humidified oxygen, (a factor of 1.9), fell within the range for unpigmented films. There was an induction time in dry, but not in wet, oxygen.

Measurements on films deliberately manufactured with increasing content of recycled polymer, (R-films), are shown in Fig. 4. An increase in the proportion of recycled material increased the amount of CO₂ generated during three hours irradiation by $\sim 1 \times 10^{-4}$ absorbance units for each 1% of recycled polymer. In dry oxygen there was, again, an induction period and a lower rate of CO₂ formation. Films R2, R4 and R6, labelled DT in Table 2, received a standard corona discharge treatment during manufacture. This might be expected to lead to a large increase in the surface –COOH groups [16] which would hydrogen bond relatively strongly to water and be more likely to decarboxylate to CO₂. However, a small decrease, rather than an increase, in CO₂ generation was observed in dry conditions, and under wet conditions any increase was less than 5%.

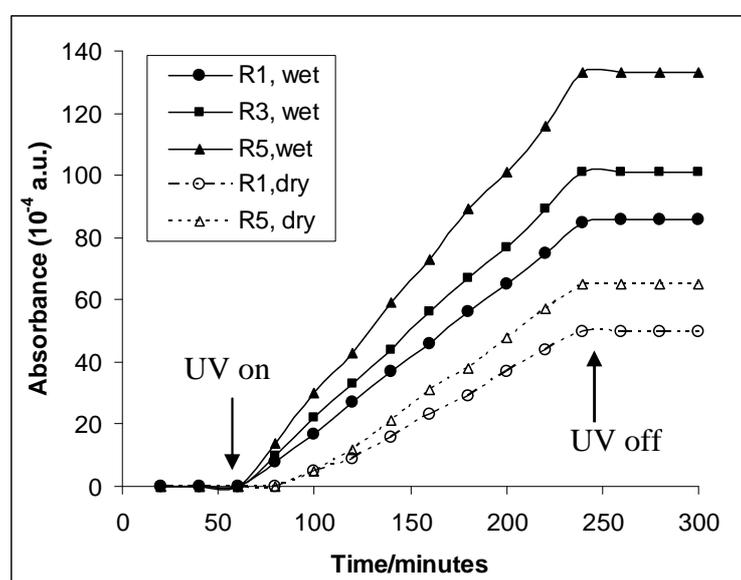


Fig. 4 The effect of increasing content of recycled polymer on the photogeneration of CO₂ in wet oxygen and dry oxygen.

Table 2 The effect of deliberate addition of recycled polymer, and of discharge treatment of the film surface, on the amount of CO₂ generated in 3 hours.

Sample	3 hour CO ₂ evolution in wet O ₂ (10 ⁻⁴ a.u.)	Increase caused by Corona Discharge	3 hour CO ₂ evolution in dry O ₂ (10 ⁻⁴ a.u.)	Increase caused by Corona Discharge	Ratio of (CO ₂) _{wet} : (CO ₂) _{dry}
R1 – 0%,	86		50		1.9 ± 0.2
R2 – 0%, DT	89	3	43	-7	
R3 – 15%,	102		No results	No results	No results
R4 – 15%, DT	108	6			
R5 – 33%,	133		65		2.3 ± 0.2
R6 – 33%, DT	136	3	54	-11	

Development of Carbonyl Groups

The development of carbonyl groups in the polymer films exposed to UVA-340 fluorescent tubes was monitored by conventional FTIR spectrometry. Typical spectra in the 1700 cm^{-1} region of the IR spectrum for unpigmented and pigmented films show the development of the principal absorption centred near 1713 cm^{-1} with shoulders near 1732 and 1770 cm^{-1} (Fig. 5a and 5b). Carlsson et al. [17] and others [7, 18,19] have assigned these bands to carboxylic acids, esters and peresters or γ -lactones, respectively. Although the contribution of the overlapping absorptions at 1732 and 1770 cm^{-1} cannot be ignored it is convenient to use the absorption at 1713 cm^{-1} as a measure of the comparative development of carbonyl bands in different samples and this is done for the unpigmented film sets B and C in Fig 6a and for the R-films in Fig 6b.

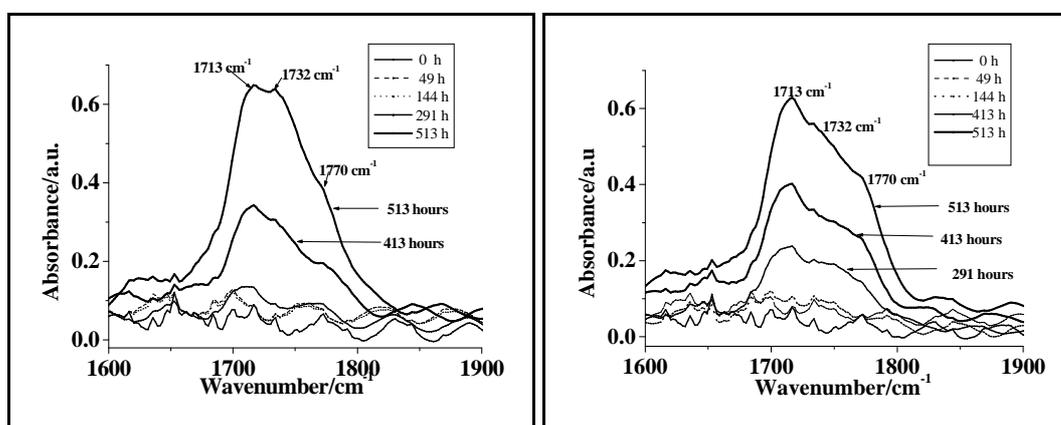


Figure 5 The development of carbonyl bands in the spectral range $1600\text{-}1900\text{ cm}^{-1}$ during the exposure of (a) C58 and (b) W58 BOPP film to QUV irradiation.

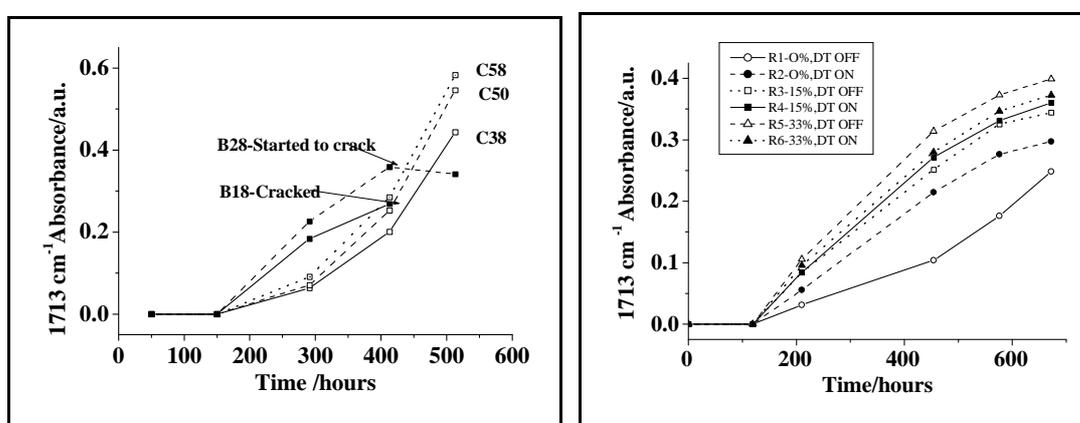


Figure 6 The absorbance of the 1713 cm^{-1} band with increasing QUV exposure time for (a) unpigmented BOPP B-films and C-films (b) R-films with recycled polymer.

Inspection of the results in Figure 6a shows that initially the 1713 cm^{-1} absorption developed more quickly in the B-films than in the C films, as had the CO_2 photogeneration. For the B-films the trajectory of the 1713 cm^{-1} carbonyl absorbances passed through a maximum after roughly 400 hours exposure, probably because 1732 cm^{-1} absorption overtakes the 1713 cm^{-1} absorption at this exposure. Cracking was observed in these samples at about the same time as the maximum occurred. A similar correlation between the appearance of cracking and the reversal in gradient of the 1713 cm^{-1} absorbance was also observed with a different polypropylene [20]. By contrast no cracking of the C-films occurred even after 700 hours QUV exposure. In summary, even though the initial carbonyl absorbance of the two sets of films (B and C) was similar, the B films gave more CO_2 , showed earlier and more extensive development of carbonyl absorption and cracked before the C-films.

Discussion

CO_2 induction time.

Studies reported in a previous paper [9] demonstrated that there was an induction time for CO_2 formation from unpigmented polypropylene (UPP) in wet oxygen. Since pre-exposure of unpigmented polypropylene (UPP) to UVA both caused a measurable absorption of C=O groups (at 1713 cm^{-1}) and reduced the induction time for CO_2 formation [9], it was suggested that the carbonyl groups were precursors of the CO_2 . The present study of BOPP has shown a clear induction time in dry oxygen for B, C, R and W films but has not shown any induction time in wet oxygen.

The UV absorptions near 225 and 275 nm in BOPP are probably due to C=O groups [21] introduced before or during the film blowing process, though the possibility that they are due to small amounts of residual antioxidants (e.g. Irganox 1010 which absorbs near 284 cm^{-1}) cannot be excluded. A comparison of the absorption intensities near 225 cm^{-1} suggests that, although the as-received commercial BOPP films did not contain enough carbonyl groups to be detectable in the i.r. (because the 1713 cm^{-1} absorption coefficient is ~300 times weaker than that at 225 cm^{-1} [21,22]), they may contain more carbonyl groups than the laboratory prepared, UPP films [9]. This may explain why the induction period for CO_2 formation from BOPP in wet oxygen is much less than that for UPP in wet oxygen.

An alternative explanation for the different behaviours would be that some processing stabilizer remained in UPP samples after film formation and inhibited CO₂ formation for 15 -30 minutes, but that this did not occur in BOPP. Although plausible, this explanation is not preferred, because significant induction times were observed for CO₂ generation from both BOPP and UPP in dry oxygen. A definitive answer would require measurements to be made on polymers that are known to be completely free of stabilizers and a more clearly defined mechanism for the role of water.

The influence of humidity on rates of CO₂ generation.

Increased humidity eliminated the induction time for CO₂ formation (Figs. 2 & 4) and enhanced the rate of CO₂ formation (Tables 1 & 2) for all four subsets of BOPP. For the similar, unpigmented films from sets B and C the extent of the humidity-enhancement appears to increase with film thickness as shown in Fig. 7 .

The enhancement for the TiO₂ pigmented films was of the same order as for the unpigmented films, but there was no evidence that the enhancement increased with film thickness. The strong attenuation of UV (absorbance > 3 for WB28) implies that more than 90% of the UV is absorbed by the front 10 µm of these films and that, consequently, photo-oxidation occurs mainly in a surface layer, not throughout the film thickness. Therefore, for TiO₂-pigmented films thicker than 10 µm humidity enhancement is expected to be independent of film thickness, as seen in Fig. 7 .

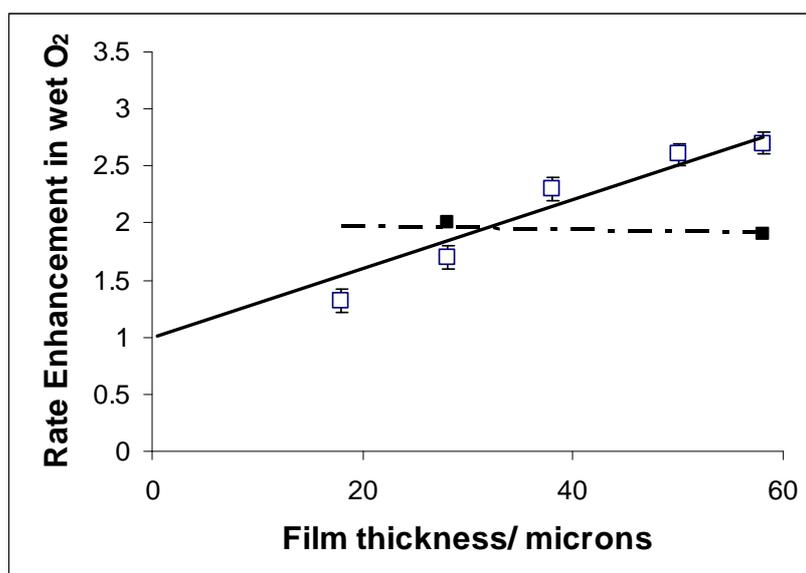
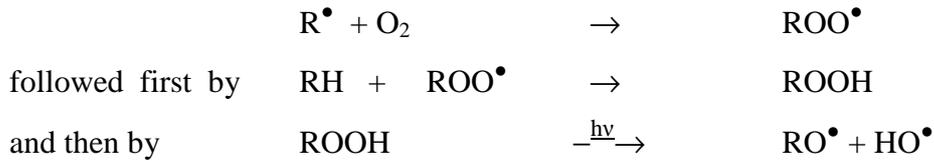


Figure 7 8. The dependence on single-film thickness of the enhanced degree of CO₂ formation caused by high humidity. Results are taken from Table 1 for clear films (□) and pigmented films (■).

A second consequence of the strong UV absorption of pigmented films is that apparently similar rates of CO₂ formation from pigmented films ($35 \times 10^{-4} \text{ h}^{-1}$ for WC58) and unpigmented films ($37 \times 10^{-4} \text{ h}^{-1}$ for C58) relate to different depths. Since the amount of CO₂ generated in unpigmented films approximately trebled when the thickness was increased from ca 20 μm to 60 μm , it follows that only about $12 \times 10^{-4} \text{ a.u. h}^{-1}$ originated from the front 20 μm of the thicker film. This is much less than the 35×10^{-4} estimated to originate from $\sim 10 \mu\text{m}$ at the irradiated surface of the pigmented film. This increased rate of local reaction is a consequence of the often demonstrated photocatalytic activity of the TiO₂ [4, 23, 24] which is generally considered to be a consequence of the generation of highly reactive hydroxyl radicals [25-27] at the surface of the TiO₂ by absorption of all wavelengths below $\sim 400 \text{ nm}$ [28]. It is well established that this photocatalysis can lead to oxidation of both aromatic and aliphatic compounds to CO₂ and H₂O [24].

Many practical studies of polymer weathering suggest that increased humidity increases photodegradation. This may be associated with the dissolution or washing away of reaction products. Alternatively the presence of liquid water at the surface of polyalkene samples can affect the extraction of hindered amine light stabilizers (HALS) so that the HALS efficacy is a balance between their migration ability within the film and their extractability from it [7, 29]. In the present experiments, changes in the photogeneration of CO₂ cannot be attributed to such effects because the CO₂ does not remain, nor is liquid water present, on the film surface and no HALS were included in the film formulation. Further, if the enhancement due to water were caused by leaching of stabilizers from the film surface, enhancement would be expected to decrease with the increasing film thickness especially because the solubility of water in BOPP is, by analogy with PE, expected to be very small. (Nmr studies suggest a weight fraction of only 1×10^{-6} of water in 200 μm LDPE [30].) However, the results in Figure 7 6 suggest that the enhancement is greater in 60 μm than 20 μm films.

It is generally proposed [1, 8] that, during the initial stages of polyalkene oxidation, hydroxyl radicals are generated by the reaction sequence:-



Rivaton *et al.* have shown that, during the photo-oxidation of blends of poly(butylene terephthalate) (PBT) with PP, hydroperoxides formed in the PBT sequences generate hydroxyl radicals that induce oxidation of the PP component [31], and Delprat *et al.* have proposed the involvement of hydroxyl radicals in the formation of CO₂ during the photooxidation of polyphasic ethylene-propylene polymers [7]. Because the increase in the rate of CO₂ formation from TiO₂ pigmented films is of the same order as that of unpigmented films, and because of the importance of hydroxyl radicals in photocatalysis by TiO₂, it is speculated that in unpigmented films, as in pigmented polymers, the demonstrated increase in CO₂ formation at high humidity may involve hydroxyl radicals. MacManus *et al.* found that during the initial stages of the treatment of PP with UVC (shorter wavelengths than used in the studies presented here) more oxygen uptake by the polymer surface occurred in the presence of water vapour and this was attributed to the formation of hydroxyl radicals by the reaction of singlet oxygen atoms, O(¹D), with water [32]. However as the filtered radiation from the xenon lamp used in the present studies, contained no wavelengths below 290 nm the mechanisms of the enhancement remain to be clarified.

The correlation between photogenerated CO₂ and the development of photochemically formed carbonyl groups.

A clear correlation of CO₂ photogeneration with the development of carbonyl absorption for a series of *pigmented* PEs exposed to UVA radiation has been demonstrated previously [4]. A similar correlation between CO₂ evolution, after 3 hours irradiation in wet oxygen, and the development of the 1713 cm⁻¹ carbonyl absorption, after nearly 700 hours exposure in QUV equipment, is shown in Fig.8 ~~9~~ for *unpigmented* BOPP films. These films, R1 to R6, had the same nominal thickness of 23 μm but differed in their content of recycled material and discharge treatment. As shown in Figs. 4 ~~5~~ and ~~7b~~, their photoactivity increased with the content of recycled polymer. It has been noted in other

studies of polypropylene that recycled polymer can act as a pro-degradant [33-35], and the results in Fig. 4 5 further support the conclusion that the use of recycled polypropylene in products that may be exposed to UV in service must be exercised with extreme caution.

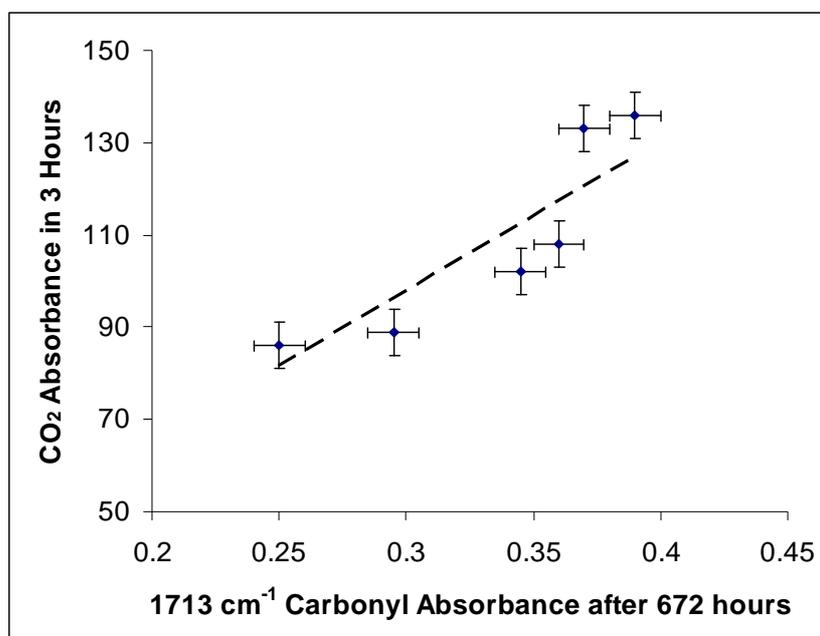


Figure 8 9. *CO₂ evolution in the FTIR cell after 3 hours irradiation under wet O₂ and 1713 cm⁻¹ carbonyl group absorbance after 672 hours QUV exposure for samples R1 to R6 containing increasing amounts of recycled material.*

Because the amount of CO₂ generated increases with oxygen humidity, and particularly because the extent of this increase depends on the thickness of the polymer film, as shown in Fig. 7 8, it is appropriate to consider whether changes in humidity may affect the quality of the correlation of CO₂ generation with carbonyl development. Therefore, results for films of different thickness from sets B and C which have different photoactivities have been compared. The CO₂ generation, measured in both dry and wet oxygen, is compared with the carbonyl development under UVA-340 exposure laboratory air in Figure 9 10. This shows that the correlation is slightly less good in wet oxygen ($R^2 = 0.81$) than in dry oxygen ($R^2 = 0.89$). Different film thicknesses may contribute to the poorer correlation. There may also be a contribution because the induction time in the development of carbonyl absorbance was paralleled by an induction time for CO₂ generation in dry oxygen, but not in wet oxygen. If so, it would follow that the correlation

of CO₂ and carbonyl would be less sensitive to humidity for PE than for PP, because induction times for carbonyl development are much less evident for PE than for PP (e.g. compare the results of Fig 6 7 with those of Fig .6b of ref. 4).

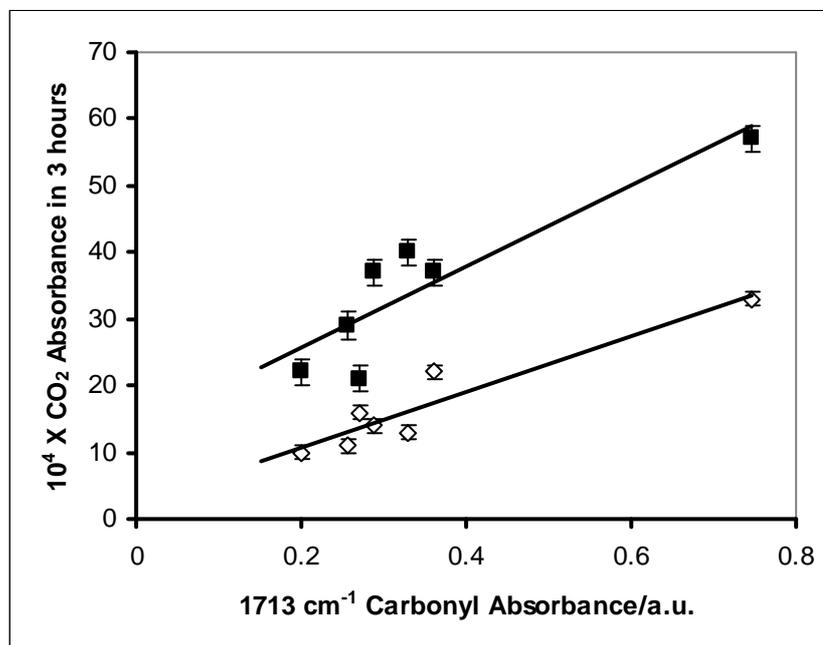


Fig. 10 Correlation of CO₂ absorbance after 3 hours irradiation in (a) wet O₂ (■) and (b) dry O₂ (◇), with carbonyl absorbance after 413 hours QUV exposure for B-films and C-films.

Conclusions

In situ FTIR measurements of CO₂ photogeneration from a range of biaxially oriented polypropylene (BOPP) films confirm earlier conclusions based on results for unpigmented polyethylene and polypropylene that the CO₂ is generated throughout the thickness of unpigmented polyalkene films.

Irradiation of BOPP films in humidified oxygen eliminated the induction period found in dry oxygen and increased the rate of CO₂ formation. The increased CO₂ photogeneration found at high humidity suggests that practical weathering tests carried out under wet conditions may be sensitive not only to effects such as leaching of stabilisers from the film but also to water-related mechanistic changes. It is speculated that the mechanistic changes may relate to hydroxyl radical formation.

Good correlations were found between carbonyl development after nearly 700 hours QUV exposure and carbon dioxide generation after 3 hours irradiation. The correlation was slightly better for CO₂ measurements in dry oxygen.

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