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Crystallization and melting behaviour of photodegraded polypropylene — I. Chemi-crystallization

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An investigation has been conducted into the effects of photodegradation on the crystallinity and melting behaviour of isotactic polypropylene (PP). PP samples having different structural characteristics were prepared and exposed to ultraviolet radiation (u.v.) in the laboratory for periods of up to 48 weeks. The changes in crystallinity during exposure were followed by X-ray diffraction and differential scanning calorimetry (d.s.c.), whereas the chemical degradation of the specimens sampled was evaluated by gel permeation chromatography (g.p.c.) and Fourier transform infrared spectroscopy (f.t.i.r.). An increase in fractional crystallinity during u.v. exposure was noted for all types of samples studied, and the gain in crystallinity was usually between 6% and 7% and was virtually independent of the initial structure of the polymer. Measurements conducted at different depths within the test bars indicated that the fractional crystallinity increased during u.v. exposure due to crystal growth using molecule segments released by the scission of molecules (probably taut molecules). This process, called chemi-crystallization, is restricted by the chemical defects introduced into the molecules by the photodegradation. Possible mechanisms for the chemi-crystallization process are discussed. The melting thermograms of most types of samples exhibited single peaks with melting range increasing with exposure time. The broadening of the melting thermograms occurred during the period between the commencement and the completion of the chemi-crystallization. Secondary crystallization proceeded much more slowly in the interior of the test bars because of the limited oxygen supply, but the final crystallinity was the same as the plateau value, which was attained more rapidly when the material in the interior was exposed by machining away the surface prior to u.v. exposure. © 1997 Elsevier Science Ltd.

(Keywords: polypropylene; photodegradation; chemi-crystallization)

INTRODUCTION

When exposed to a source of chemical degradation, the morphology of semi-crystalline polymers may be modified[1–3], and in some cases disruption of the crystalline order occurs as detected by reduction in the fractional crystallinity[4,5]. In other cases, however, the crystallinity has been reported to increase during exposure[6–8]. It is generally accepted that the latter occurs because chemical degradation causes molecular chain scission, with the consequent release of segments of entangled and tie chain molecules in the amorphous region that were unable to crystallize during the original solidification process. These freed segments can then rearrange into a crystalline phase, provided they have enough mobility. This process is known as chemi-crystallization[7,9], and it should be differentiated from secondary crystallization produced by simple annealing where the increase in crystallinity occurs as the result of mobility increased by thermal activation with no change in the molecular sizes[10].

Chemi-crystallization caused by a variety of degradation processes has been detected in many polymers[11–15], and there are some examples that involve the photodegradation of polypropylene[16–20]. The most important practical consequence of chemi-crystallization is the spontaneous formation of surface cracks caused by contraction of the surface layers[1,16]. The presence of surface cracks is indeed one of the main reasons for the embrittlement of ductile semi-crystalline polymers, causing serious deterioration in the mechanical properties of the products after short-term exposures[21].

Although the occurrence of chemi-crystallization has been recognized for many decades[6], no detailed investigation has been published to date. In many reports in the literature the effect of degradation on the fractional crystallinity is analysed, but little emphasis is placed upon it. In some cases the change in crystallinity is estimated by density methods, which can be misleading because oxidative reactions change the chemical nature of the polymer molecules causing an increase in density, regardless of any change in fractional crystallinity[22]. Experimental investigations into the mechanisms of chemi-crystallization are rather scarce, and the factors that control the process are still unknown. The influence of the initial polymer morphology has not been determined in detail either.

This paper describes an investigation into the chemi-crystallization of isotactic polypropylene (PP) caused by photo-oxidation in samples with different initial structures produced by compression moulding and by injection moulding using different conditions, and also by using a

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nucleating agent. The changes in crystallinity caused by photo-oxidation were followed for exposure times of up to 48 weeks, and the extent of chemical degradation was assessed accordingly. The melting behaviour of the as-exposed samples was also investigated. The crystallization and melting behaviour of photodegraded PP crystallized from the melt is presented in the accompanying paper[23].

EXPERIMENTAL

Material and sample preparation

Injection and compression moulded bars were prepared with a general purpose commercial grade of isotactic polypropylene (GXE 35) manufactured by ICI. The injection moulded samples in the shape of tensile bars 3.1 mm thick were produced using a Butler–Smith 100/60 injection moulding machine. The injection pressure was 107 MPa, the barrel temperature was 200°C (all zones) and the nozzle temperature was 200°C. Batches were produced using three different mould temperatures (20, 40 and 60°C), and they were labelled, respectively, 20 PP, 40 PP and 60 PP. The flow of the melted material into the mould was through a tab gate (thickness 0.5 mm) located at one end of the cavity. The gate left a witness mark that allowed identification of the back/front of the moulding. This identification was important in the measurement of crystallinity since the structure of the material near the bar front was different to that near the back face. A minimum of 30 samples were rejected at the beginning of the production run to ensure equilibrium conditions had been established in the moulding machine.

Polypropylene containing nucleating agent was prepared by tumble mixing granules of GXE 35 with 0.5 wt% talc prior to injection moulding. Although it is known that injection moulding alone does not provide an intensive mixing of the components, the use of an additional mixing technique (like extrusion or internal mixing) was avoided because it would change the concentration of chromophores within the matrix through thermal degradation[24] and hence alter the kinetics of photodegradation.

Compression moulded plaques (~2.7 mm thick) were produced with a picture frame mould sandwiched between degreased aluminium sheets. After 10 min at 200°C the heat controls were switched off and the whole press allowed to cool to room temperature, which took about 5 h. After the cooling was completed, a mark was made to identify the side in contact with the top platen of the press and the plaques were machined into strips 12.7 mm wide. The strips close to the mould boundaries were rejected in case the thermal conditions were different from those in the middle of the plaque. Due to the contact with the aluminium sheet, these specimens showed a transcrystalline layer (120–150 μm thick) near the moulded surface[25,26].

In some injection moulded bars (40 PP samples) surface layers 0.2 and 0.6 mm thick were removed from both sides of the tensile bars to expose material with different morphological features. This procedure has been described elsewhere[19]. At a depth of 0.2 mm there is a high content of β(hexagonal) phase spherulites, whereas at a depth of 0.6 mm there are equiaxed spherulites with no preferred orientation[25].

After moulding, all samples were kept at room temperature for at least 3 weeks before u.v. exposure to minimize post-moulding ageing effects such as secondary crystallization.

Exposure procedure

The ultraviolet exposure was conducted at 30 ± 1°C in a constant temperature room following other studies in this laboratory[19,27]. The source of u.v. radiation was fluorescent tubes UVA-340 supplied by Q-Panel Company. The tubes (1.2 m long) were used in pairs, producing a uniform output over the central metre. The intensity reaching the sample was measured weekly using a Bentham spectroradiometer and set to 2.2 $\mathrm{W m^{-2}}$ in the wavelength range 290–320 nm. The injection moulded bars were exposed with the face opposite to the tab gate facing the u.v. source. The compression moulded samples were exposed with the surface in contact with the lower platten of the press facing the u.v. lamps. The penetration of u.v. radiation through the several types of specimens showed similar characteristics, with comparable values of absorption coefficients and reflectivities[25].

Extent of chemical degradation

The extent of chemical degradation was measured by Fourier transform infrared spectroscopy (f.t.i.r.) and gel permeation chromatography (g.p.c.). Unless otherwise stated, samples used for the analyses were collected by gathering the material milled away to a depth of 0.2 mm from the exposed surface of the test bar.

Infrared spectra were obtained in transmission with a Nicolet 20 PC-IR Fourier transform spectrometer. The equipment was set to operate in the range 400–4000 $\mathrm{cm^{-1}}$ with a resolution of 4 $\mathrm{cm^{-1}}$, obtaining a spectrum that represented the average of 32 scans. A carbonyl index was computed as the relative areas under the carbonyl peak (1700–1800 $\mathrm{cm^{-1}}$) and a reference peak, not affected by photo-oxidation (centred at 2720 $\mathrm{cm^{-1}}$).

The g.p.c. measurements were made at Rapra Technology Ltd, using a 300 mm length column filled with gel supplied by Polymer Laboratories (PLO gel 2 × mixed gel-B) with particle size 10 μm. Solutions with 1,2 dichlorobenzene were run at 140°C with a flow rate of 1 ml/min and an injection volume of 0.2 ml. Discussion on the procedure adopted by Rapra to measure the molecular weight of degraded polymers was presented elsewhere[28].

Differential scanning calorimetry (d.s.c.)

A Mettler FP90 controller connected to a FP85 Heat Flux d.s.c. cell was used with specimens (weighing 5–6 mg) removed from the exposed surface by milling away a depth of 0.2 mm. The equipment was calibrated for temperature and calorimetric sensitivities of the cell with indium. Thermograms were recorded under nitrogen flow (50 ml/min) using a heating rate of 13°C/min, from 40 to 210°C.

X-ray diffraction

X-ray analysis was carried out using a Phillips PW1050 diffractometer using CuK_α Ni-filtered radiation (wavelength 0.154 nm) in the diffraction angle range $2\theta = 7$–$31°$. The fractional crystallinity (f_c) was calculated from the diffractometer traces using the method described by Weidinger and Hermans[29]. According to the authors, this method gives consistent results that are in agreement with those obtained by the more rigorous but time-consuming method of Ruland[30]. The error bars on the f_c data are the standard deviations for three measurements. A detailed description of the structure and morphology of the starting materials used in this investigation is given elsewhere[25,26].

RESULTS

Extent of chemical degradation

The main effects of photodegradation on the molecular structure of polypropylene are the reduction in molecular size and the incorporation of chemical groups like carbonyls and hydroperoxides. The various types of polypropylene samples, prepared by varying the processing technique and conditions, showed only minor variations in the extent of degradation at the chosen times as measured by g.p.c. and f.t.i.r. These results have been described in detail elsewhere[25,26]. A typical example of the dependence of molecular weight and carbonyl index on the exposure time is shown in *Figure 1* for the case of 40 PP samples.

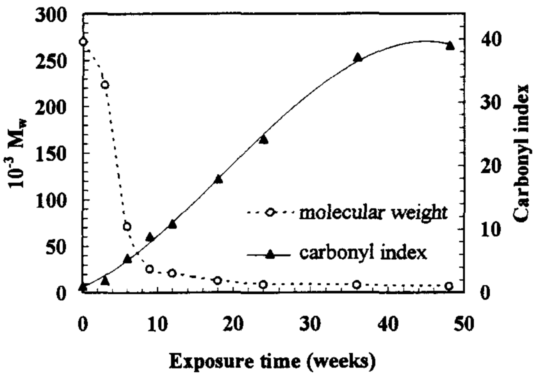

Figure 1 Effect of exposure time on the molecular weight and carbonyl index of an injection moulded PP sample (40 PP). The error bars, if plotted, would be slightly larger than the data symbols

Changes in crystallinity during u.v. exposure

Figure 2 shows that the ultraviolet radiation did not cause any substantial change in the position and shape of the peaks in the diffractograms of PP. The only significant change was the height of the amorphous background, which reduced with exposure, reflecting the increase in crystallinity. This indicates that photodegradation did not cause crystal transformations and that any new crystals formed during u.v. exposure grew with the same crystal lattice as the pre-existing ones. Measurements of change in crystallinity during exposure were made by both X-ray diffraction and d.s.c. As shown in *Figure 3*, the results obtained with these two techniques were very consistent. We present here mainly the X-ray crystallinities, which showed less scatter.

The occurrence of chemi-crystallization is very clear in *Figure 3*. with the crystallinity starting to increase after 3 weeks, and reaching a steady value after 18–24 weeks of exposure. This general trend was observed with all other types of samples investigated here (*Figures 4–6*). A common characteristic was that the change in crystallinity was rather similar for most types of samples, regardless of the initial value of f_c.

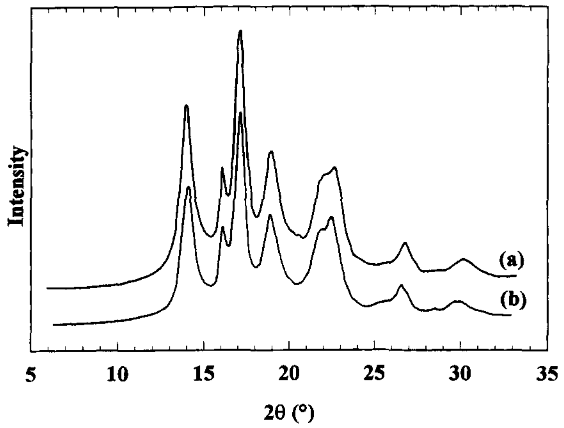

Figure 2 X-ray diffractograms of injection moulded PP (40 PP): (a) unexposed; (b) after 24 weeks of exposure

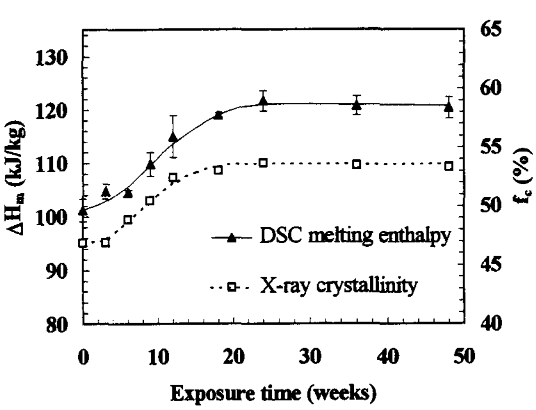

Figure 3 Comparison between the changes in DSC melting enthalpy (ΔH_m) and X-ray crystallinity (f_c) with u.v. exposure at the exposed surface of an injection moulded bar

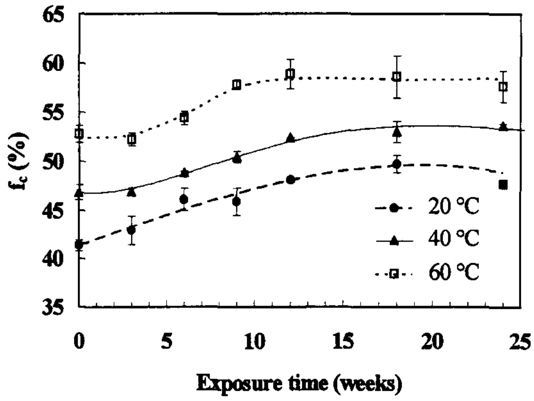

Figure 4 Effect of mould temperature on the crystallinity of exposed injection moulded PP

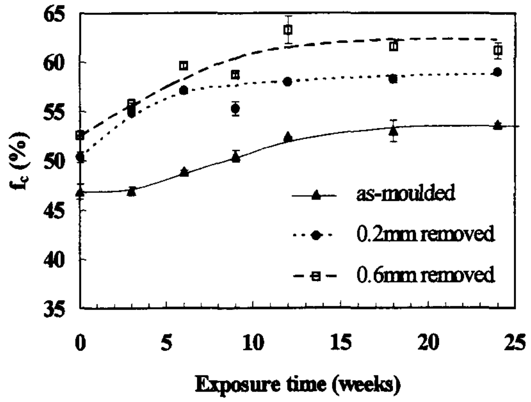

Figure 5 Degree of crystallinity as a function of exposure time at different depths within an injection moulded bar (layers removed before exposure)

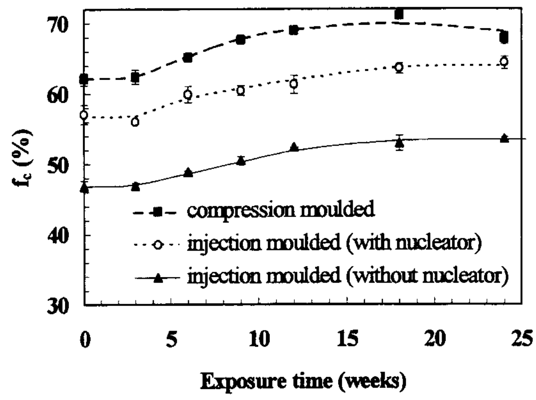

Figure 6 Effect of exposure time on the X-ray crystallinity of compression moulded PP and injection moulded PP with added nucleator. Results for 40 PP injection moulded bars are shown for comparison (e.g. from 3)

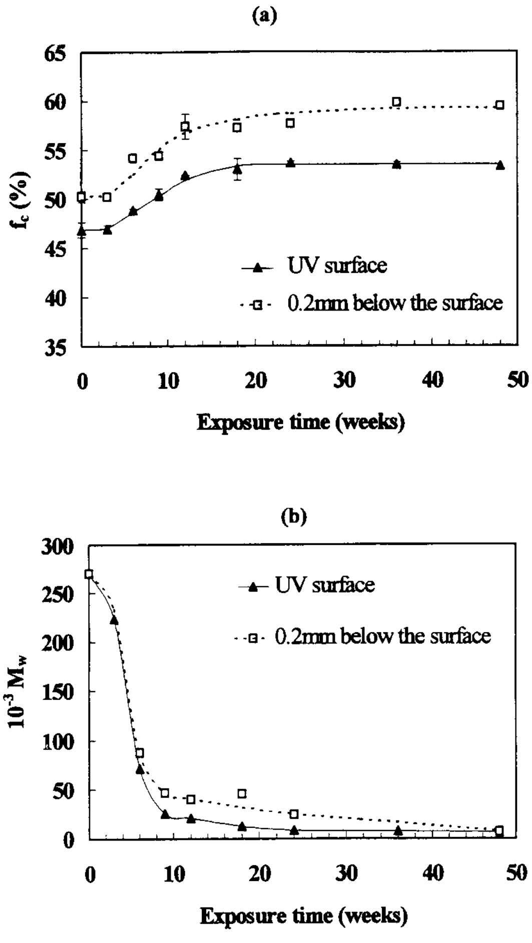

Figure 7 (a) Comparison between the change in crystallinity with exposure time at the surface and 0.2 mm below the surface; (b) change in M_w with exposure time at the same locations

The effect of exposure time on the crystallinity at other depths within the bars is given in *Figures 7 and 8*. In the interior of thick samples like those used here the oxidation takes place slower than at the surface due to oxygen starvation[27] and, consequently, changes in crystallinity are expected to be inhibited or delayed. The correlation between the drop in molecular weight and the increase in f_c is especially clear for a depth 0.6 mm below the surface (*Figure 8*). In that case the crystallinity remained virtually constant up to 24 weeks and then rose sharply, coinciding with the drastic reduction in M_w.

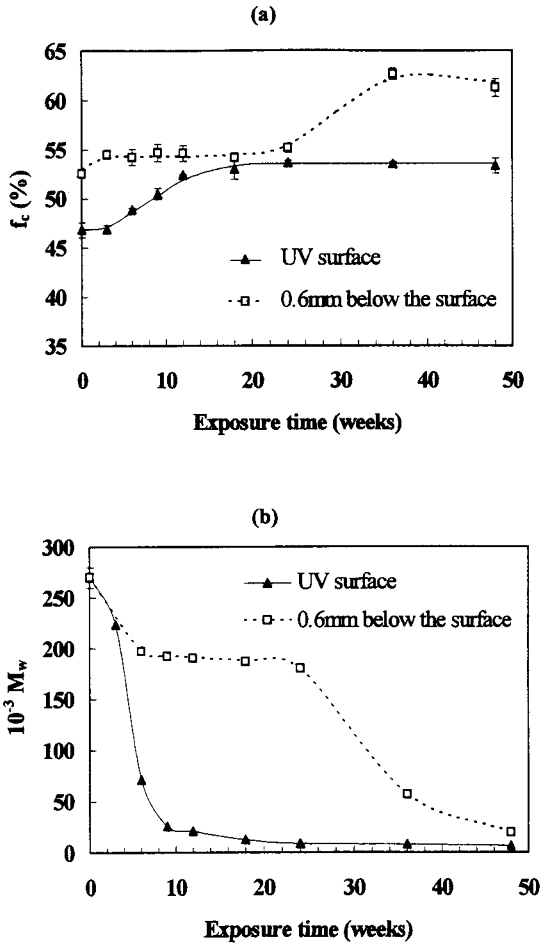

Figure 8 (a) Comparison between the change in crystallinity with exposure time at the surface and 0.6 mm below the surface; (b) change in M_w with exposure time at the same locations

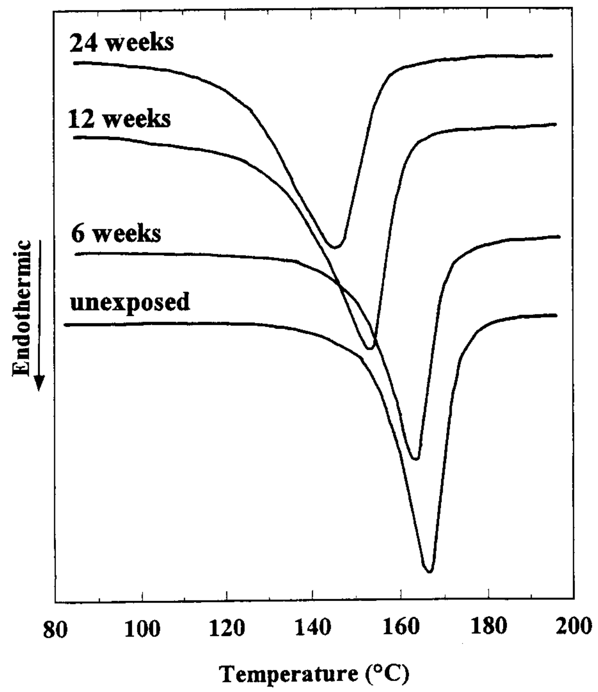

Figure 9 Heating thermograms of samples removed from the exposed surface of 40 PP

Melting behaviour

The melting thermograms of the as-exposed materials generally showed single peaks only, with the maximum in thermal absorption shifted to progressively lower temperatures as the exposure time increased (*Figure 9*). The decrease in melting temperature with exposure is due to oxidative reactions on the crystal surface that increase the surface free energy of the crystals[5,31]. The melting range was calculated as the width at the half-height of the melting peaks, and typical results are shown in *Figure 10*. Similar trends were obtained with the other types of samples under investigation.

Single melting peaks were obtained at all positions within the injection moulded bars and for all degradation times, with the exception of samples removed from a depth 0.2–0.4 mm and exposed for times longer that 18 weeks, which displayed double peaks (or peak and shoulder) upon heating (*Figure 11*). The intensity of the subsidiary peak increased with exposure time, but its position showed little variation, with the maximum in the range 137–139°C, regardless of the exposure time. Possible reasons for the occurrence of single and double peaks during d.s.c. meltings will be discussed further later on.

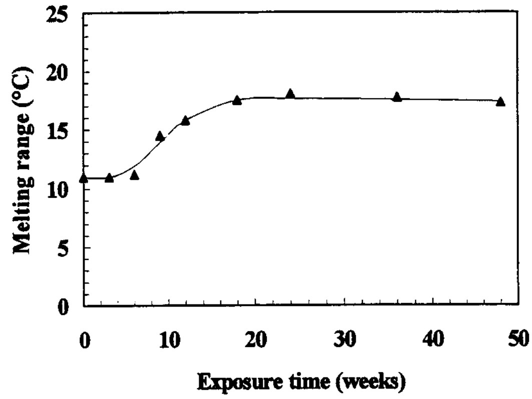

Figure 10 Melting range (width at the half-height of the melting peaks) as a function of the exposure time. Data obtained from the exposed surface of 40 PP

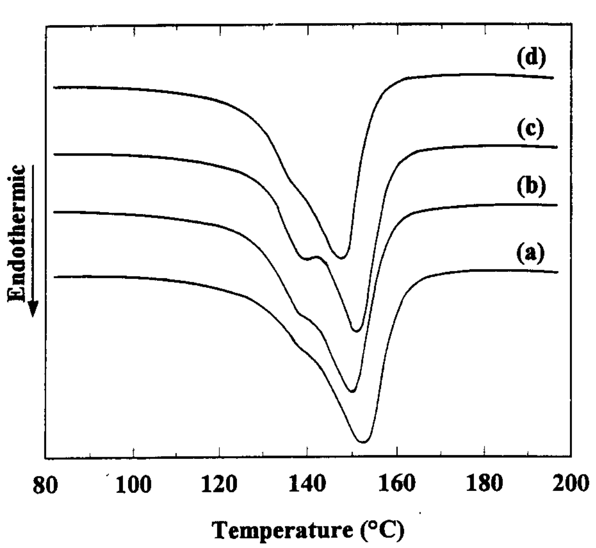

Figure 11 Melting thermograms obtained during the first heating run of selected samples: (a) 0.2-0.4 mm layer from the exposed side 24 weeks; (b) 0.2-0.4 mm layer from the exposed side, 36 weeks; (c) 0.2-0.4 mm layer from the unexposed side, 36 weeks; (d) exposed surface of a sample with a 0.2 mm layer removed before exposure, 24 weeks

DISCUSSION

Mechanism of chemi-crystallization

The main issues here are the causes of the increase in crystallinity, the limitations on the process of chemi-crystallization, and the mechanism(s) of chemi-crystallization.

Due to the macromolecular nature, a high concentration of entanglements is expected to be present in the melt from the virgin polymer, and this restricts the crystallization during processing. At room temperature the molecule segments in the amorphous region have significant mobility (the glass transition temperature of PP is below −20°C), but further crystallization is highly restricted by these entanglements. Tie chain segments will also be prevented from rearranging into crystals. If a semi-crystalline PP sample is exposed to u.v. radiation, oxidation reactions occur, resulting in chain scissions. These reactions occur preferentially in the amorphous fraction because of the higher permeability to oxygen[24], and also due to the rejection of chromophore impurities by the growing crystals[16,32]. The strained or entangled sections of the molecules can then be released, and further crystallization occurs by the rearrangement of these freed molecule segments.

It is reasonable to conclude that chemi-crystallization is connected with the reduction in molecular size and that it involves segments released by scission from entanglements or tethering to crystals (in the case of tie molecules). Evidence for this is given above by the correlation between the increase in f_c and the decrease in molecular weight. Significant changes in crystallinity coincided with a drastic reduction in molecular weight, which, for samples taken from the surface, occurred after 3 weeks of exposure. Although the measurement intervals were too long to confirm it positively, there is a suggestion that there is an incubation time of about 3 weeks before significant chemi-crystallization occurs near to the surface. Measurements made on material taken from 0.6 mm below the exposed surface where the photodegradation is significantly slower (*Figure 8*) indicated that the induction time for increase in f_c was ~24 weeks and again coincided with a large reduction in molecular size.

With the progress in photo-oxidation the number of chain scission events increased and so did the degree of crystallinity. However, the crystallinity reached a plateau value (normally after 18–24 weeks at the exposed surface) after which no further increase in f_c was detected but further reductions in molecular size were still observed. It is suggested that the other aspect of chemical degradation, namely the generation of impurity groups like hydroperoxides and carbonyls, limits the secondary crystallization by reducing the molecular regularity. It is well known that the crystallinity of polypropylene is substantially reduced if the regularity decreases, as occurs, for instance, when a co-monomer is present[33] or with reduced tacticity[34]. During photodegradation the reduction in molecular weight and the formation of impurities compete in the process of changing the crystallinity. At short-term exposures the chain scission effect dominates over irregularities and the crystallinity increases. At the exposed surface, for exposure times more than 18 weeks, the large number of chemical defects in the chain prevents further crystallization. At this stage the molecule segments, with bulky and randomly distributed chemical groups, can no longer fit into the crystal lattice and the chemi-crystallization process ceases even though the molecules may be completely disentangled.

If the explanation above is correct, then the gain in crystallinity caused by photodegradation should be approximately the same for all types of samples studied, regardless of their initial values of f_c, assuming that their mechanisms of oxidation are the same. This in fact was what was observed (*Figures 3–6*), with the gain in crystallinity about 6–7% for most samples, including those with low and high initial crystallinities. In the least crystalline type of sample (20 PP) a large fraction of the material (~52%) was still uncrystallized after prolonged exposures but, despite extensive reduction in molecular weight (to lower than 5000), the crystallinity remained virtually constant as exposure continued beyond 18 weeks. More evidence in favour of this interpretation is given in *Figures 12 and 13* where the crystallinities at depths of 0.2 mm and 0.6 mm were compared in samples with the surface layers removed before and after exposure, respectively. The maximum (ultimate) values of f_c at a particular depth were nearly the same irrespective of whether or not the bar was machined prior to u.v. irradiation, despite the large difference in the rate of degradation between the surface material and that in the interior.

Turning now to the mechanism of chemi-crystallization, the above observations cannot determine exactly how it takes place but can provide useful pointers. Three possible explanations for the changes in f_c will be considered:

(1) the freed molecule segments are incorporated into pre-existing crystals[7,35];
(2) the freed molecule segments form new crystals in the bulk of the amorphous region[12]; and
(3) the increase in crystallinity results not from rearrangement of material from the amorphous fraction but from the partial elimination of this region by volatilization of oxidation products, as has been suggested by Kulshreshtha[36].

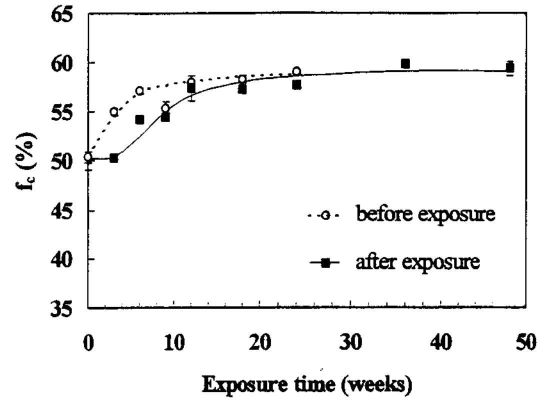

Figure 12 Evolution of crystallinity in a layer 0.2 mm below the surface: comparison of behaviour when the surface was removed before exposure and after exposure, respectively

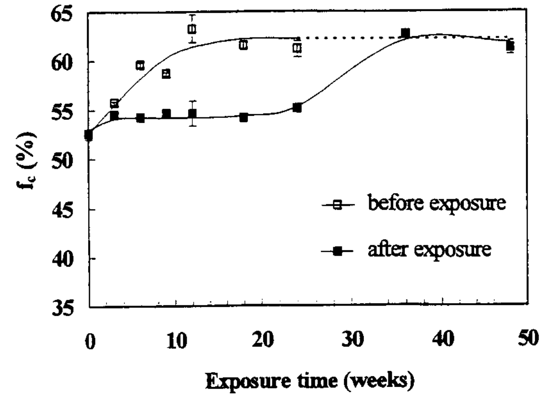

Figure 13 Evolution of crystallinity in a layer 0.6 mm below the surface: comparison of behaviour when the surface was removed before exposure and after exposure, respectively

The third explanation can be ruled out because it is inconsistent with the observation of a plateau value of f_c. If loss of the amorphous fraction were the explanation for the increase in f_c, it should progress with degradation and should not be limited to such low values. If this mechanism operated, it is difficult to explain why, after degradation, f_c should be limited differently according to the original crystallinity.

Consider now the possible mechanisms of crystallization of the molecule segments freed by scission. It is first necessary to consider the arrangement of the molecules prior to photodegradation. The crystalline phase contains lamellae that are arranged in parallel stacks: this is true whether in the skin of the moulding, where significant orientation is present, or in the core, where a spherulitic morphology forms. For a sample that is 50% crystalline this means that the amorphous regions between the lamellae are at most of the same thickness as the lamellae. Thus, any new crystals nucleated within the amorphous phase can grow to a thickness no larger than that of the pre-existing lamellae and are likely to be much thinner than this. Nucleation of such crystals would require several molecule segments to be released in close proximity: this would account for the incubation time (before significant increase in crystallinity is observed).

The alternative mechanism of chemi-crystallization is through the growth of pre-existing crystals by addition of segments freed by scission. This is expected to be favoured because of the known readiness of polypropylene for self-nucleation[37]. The growth could occur either on {hk0} growth planes or on the (001) fold surfaces. Except in the case of molecules already located near to the growth faces, segments released by scission would have to migrate through the amorphous phase to reach the {hk0} faces. This would generally be possible only if they were totally free, implying that two scission reactions are required on the same molecule to release a segment that can contribute to secondary crystallization in this way. This again could explain the presence of an incubation time—growth would not begin immediately because time would be required for a significant number of molecules to suffer two scissions and for the necessary diffusion of segments to the growth front. The new growth formed in this way would be distinguished from the pre-existing crystal because (a) it would be formed from shorter segments and would be less likely to have long cilia stretching into the amorphous phase and (b) it would be formed from segments that become progressively more defective with increasing exposure time.

Alternatively, crystal overgrowths on the (001) fold surfaces may be contemplated. Molecules emerging from the crystal at the fold surface will already be close to the appropriate orientation and adjacent molecules will already have the appropriate spacing. Thus, if such segments are freed from entanglements in the amorphous phase they will be in a favourable state to initiate self-epitaxy, forming an overgrowth crystal on top of the fold plane of the pre-existing crystal. Although the overgrowth crystals would be expected to share some molecules with the pre-existing parent crystal, their melting behaviour would be expected to be essentially independent and would be controlled mainly by the increasing defect content as growth proceeds using progressively more defective molecule segments as the exposure increases. This type of crystallization may be an interface controlled process in which the rate of (secondary) nucleation is much higher than the rate of growth. In this way it resembles regime III polymer crystallization[38], though the growth habit is different.

Of considerable relevance to the present discussion is the existence of an interphase next to the crystal lamellae with a structure intermediate between complete crystalline order and the random state that characterizes the truly amorphous phase. Mandelkern[39] reviewed this topic and presented data that indicated that the fraction of interphase in the non-crystal material depends on the chemical structure and the molecular weight but not on the crystallization conditions. For PP the interphase content was shown to be 12–30%. In reviewing the results presented above we are drawn to the hypothesis that photodegradation-promoted crystal growth occurs mainly within the interphase and that it is the result mainly of scission occurring within or very close to the interphase. This is consistent with the measured changes in crystallinity, usually 6–7%, which are less than the interphase content. Moreover, the change in crystallinity with photo-oxidation in 20% and 40% talc-filled PP was similar to that in the unfilled polymer[20]. Since the molecular mobility required for crystallization in polymer containing fillers is highly restricted[40], this observation suggests that the ordering during exposure involves short range movements of the molecules, favouring the interpretation given above.

The X-ray diffraction data from the exposed materials were consistent with these ideas. The diffraction peaks did not broaden significantly, as would be expected if there had been a large increase in the distribution of crystal sizes[41]. Although overgrowth crystals on the fold surfaces must be thinner than the pre-existing lamellae (much thinner if they are confined to the interphase), their lateral dimensions need not be particularly restricted and this is what determines the broadening of the {hk0} reflections. Furthermore, the relative intensity of the peaks showed no change with exposure either. This was true for samples with widely different initial structures (injection moulded—with and without a nucleating agent—and compression moulded PP with a transcrystalline layer at the surface) and suggests that the crystals generated during u.v. exposure grew with the same orientation distribution as the pre-existing ones. This is more likely to occur if overgrowth predominates rather than the formation of new crystals.

Melting behaviour

From the above discussion, it is likely that the increase in the melting range caused by photo-oxidation (*Figure 12*) is due to crystals created during exposure that are less perfect than the pre-existing ones because they were formed from defective molecules and in less favourable conditions (i.e. low mobility). This deduction is also based on the observation that the shape of the curve for the melting range *versus* exposure time for the first melting is remarkably similar to the corresponding f_c *versus* time relationship (*Figures 3, and 10*), with an induction time and a steady value achieved after 18–24 weeks of exposure. Thus, the variation in the melting range is likely to be connected to the commencement and the completion of the chemi-crystallization process. These observations do not discriminate clearly between {hk0} or (001) overgrowth.

In many d.s.c. studies of polymer degradation reported in the literature double peaks were obtained during the heating scan of as-exposed samples[11,31,42–47]. This has been attributed variously to the melting of small crystals formed during the exposure[44,45], reorganization during heating[46] or crystal transformation[47]. Other possible explanations include decomposition of oxidation products or free radical reactions during heating[31].

The occurrence of a single (often broad) peak in the melting thermograms obtained from samples taken from near the surface, such as those shown in *Figure 9*, can be explained with reference to the crystallization scheme described above. The new crystals formed from polymer released by degradation can be expected to have lower melting temperatures than the pre-existing crystals because of the defect content. The defect content increases progressively with exposure time, however, and the molecules that were deposited last (and therefore not obstructed from melting) will have the lowest melting temperature. Thus, melting should be a continuous process and it is not expected that a bimodal population of crystals with different melting temperatures (one characteristic of the pre-existing crystals and the other from the overgrowth crystals) will develop at any stage of the exposure. Melting is therefore expected to commence at a lower temperature when the exposure time is increased, but the endotherm should then continue through to the melting temperature of the pre-existing crystals as the overgrowth crystals progressively melt, the latest to be deposited disappearing first.

Double melting endotherms were observed in samples taken from a depth 0.2–0.4 mm from the surface and exposed for an extensive period. A subsidiary peak appeared on the low temperature side of the main endotherm (*Figure 11*). This is believed to be related to the presence of a significant β-phase content at this location. Apart from the presence of high β-phase content in this region[19,25], the reasons for making this connection are several:

1. the intensity of the subsidiary d.s.c. peak was highest for a specimen removed from the side of the bar that contained the gate, which was shown in other studies to have a higher β-phase content[25], even though this was the side facing away from the u.v. source (*Figure 11*);
2. in a set of exposures conducted with the gate side facing the u.v. source the samples removed from the exposed surface displayed the more intense double endotherms; and
3. the double endotherm at this particular depth is not related to a diffusion-limited oxygen starvation effect, since samples which had a 0.2 mm layer removed prior to u.v. exposure also displayed double peaks on the first melting when irradiated for more than 18 weeks. Samples with 0.6 mm removed before exposure (a depth at which the β-phase is effectively absent) displayed only single peaks at all exposures.

To understand why the β-phase is connected to the double melting behaviour in *Figure 11*, it is important to explain first how this phase behaves on heating, and why single peaks are observed in unexposed samples removed from this layer in injection moulded bars.

The β-phase of PP is well known to be thermodynamically unstable and some researchers reported that this phase can melt and recrystallize during the d.s.c. experiment into the more stable monoclinic form[48–50] or into a more perfect β-modification[51,52]. This results in the appearance of a double melting peak in d.s.c. thermograms. In the studies cited[48–52] the PP used contained mainly β-phase, produced by a variety of methods. In the current work, however, only single melting curves were observed for unexposed specimens removed from the layer with highest β-phase content (depth 0.2–0.4 mm) even when scanned at various heating rates (3–20°C/min). The β-phase content is too low and the double peak was not detected, possibly because the endotherm corresponding to the melting of the β-phase was superimposed on top of the exotherm corresponding to the formation of α-phase, since the process of melting of β-phase and its recrystallization into α-phase is a simultaneous transformation[49,53]. This effect was also considered to explain the single peaks observed during a smectic–monoclinic transformation in PP[54].

Since the rate of crystallization of photodegraded polypropylene is highly reduced due to the presence of chemical irregularities within the molecules[23], it is reasonable to expect that in highly degraded specimens the $\beta - \alpha$ transformation is reduced or suppressed. If this occurs, then the melting of the two phases present would take place in two discrete temperature ranges that are shown as double peaks in the d.s.c. thermogram. With increasing exposure time, the ability of the β-phase to transform into the α-phase becomes progressively lower and, therefore, the intensity of the lower temperature peak (corresponding to the melting of β-phase) increases, in as much as the recrystallization exotherm superimposed is reduced accordingly. If this explanation is correct, it is surprising that a depression of the melting peak of β-crystals with degradation was not observed as was the case with the monoclinic phase (*Figure 9*).

CONCLUSIONS

The process of chemi-crystallization during ultraviolet degradation has been detected with various types of polypropylene samples prepared using different conditions. A strong correlation was found between the increase in the degree of crystallinity during exposure and the decrease in the polymer molecular size. The gain in crystallinity is limited by the presence of chemical irregularities like carbonyl and hydroperoxides that form progressively on photo-oxidation with no dependence on the initial fractional crystallinity. Secondary crystallization proceeded much more slowly in the interior of the mouldings because of the lower chain scission rate but the ultimate crystallinity was not affected. From the information gathered in this work a mechanism of chemi-crystallization is proposed, based on the deposition of molecular segments released in the interphase region onto the pre-existing crystals following the same crystal orientation distribution. With increasing photo-oxidation, the perfection of these newly formed crystals decreases and eventually the chemi-crystallization is ceased.

The melting behaviour of photodegraded PP was consistent with the mechanism proposed for chemi-crystallization, with a progressive increase in the melting range which began when the secondary crystallization process commenced and ceased when the secondary crystallization was completed. With most samples, single melting peaks were observed, but with some highly degraded specimens containing a higher amount of β-phase, double peaks were obtained. This can be explained if the highly defective molecule segments attached to the β-crystals (or even defective molecules within the β-crystals) inhibit the transformation into the α-phase so that the observation of the melting of the β-phase is not obscured by the exotherm corresponding to recrystallization into the α-phase.

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