Crystallization and chemi-crystallization of recycled photo-degraded polypropylene

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Abstract

Injection moulded bars have been made from virgin polypropylene and from blends containing recycled photo-degraded polypropylene, then subjected to further ultraviolet (UV) exposure. Crystallinity measurements have been made at different depths from the exposed surface using X-ray diffraction and differential scanning calorimetry. Strong evidence for chemi-crystallization is provided for the photo-degraded samples. The crystallinity results are interpreted in terms of molecular scission and photo-initiated molecular defects. Scission leads to greater crystallizability and accounts for the observed chemi-crystallization. Molecular defects inhibit crystallization and eventually limit chemi-crystallization, as observed with a blend containing 75% virgin material and 25% recycled photo-degraded polymer after further UV exposure.
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1. Introduction

The crystallization of polymers depends on many factors including the shape and stereoregularity of the repeat unit, the presence of branches and crosslinks, and the molecular chain length in the linear segments. With polypropylene (PP), the repeat unit is small and can easily be assembled into crystal form. When polypropylene is subjected to photo-oxidation several changes occur that influence the crystallinity and the crystallizability of the material. This paper is concerned with oxidation that occurs at or near to ambient temperature, when the polymer is in solid form, well below the crystallization temperature. The changes occur predominantly in the non-crystalline phase because oxygen can diffuse through such regions relatively freely but is almost excluded from the crystalline regions. The principal changes are (i) chain scission; (ii) crosslinking;

and (iii) the formation of molecular defects such as carbonyl groups. Chain scission releases chain segments that were previously entangled and allows them to crystallize. If enough material of this kind becomes available to crystallize, new crystals could form but it is more likely that these segments will attach to the growth faces of pre-existing crystals nearby. This will increase crystallinity and is a form of secondary crystallization often known as 'chemi-crystallization' [1–3]. Crosslinks inhibit further crystallization of the chain segments that are connected by them. Molecular defects such as carbonyl groups that form do not fit into the crystal lattice and the parts of the molecular segments containing them will not be able to take part in secondary crystallization.

Chemi-crystallization is caused by a variety of molecular degradation processes and has been detected in many polymers [4–8] and there are several examples that involve photo-degradation of polypropylene [9–13]. If, as expected, oxidation within the crystal phase is relatively rare, the net effect of photo-oxidation will be an increase in crystallinity and the formation of material in the amorphous phase that

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becomes increasingly unable to crystallize even if scission events or elevated temperature mobilize the chain segments. Thus it is expected that, after a certain exposure, the rate of chemi-crystallization will decay to zero.

Chemi-crystallization is an important phenomenon because the density of the crystals is higher than that of the amorphous material and shrinkage occurs. Under UV irradiation, the scission (and hence secondary crystallization and, in turn, shrinkage) tends to vary very sharply with distance from the exposed surface [14,15] and this leads to the development of tensile residual stresses near the surface [16,17]. The residual stresses can lead to cracking of the material that has already been embrittled by the molecular degradation, through the loss of entanglements and the consequent loss of mechanical integrity provided by the molecular network, and through the reduced flexibility that results from increased crystallinity and crosslinking that may be present additionally [14,15]. Serious deterioration of engineering properties may therefore occur. If the cracks are not very deep and do not lead to total failure, the appearance may become unacceptable because of fine surface cracks that spoil the glossy appearance, etc. Residual stresses lead to distortion if they are not balanced across the moulding section.

When photo-oxidized material is melted and cooled down again, the crystallinity of the newly solidified material will depend not only on the polymer and the cooling conditions but also on the molecular changes that occurred during photo-oxidation. The shorter chains produced by scission events will crystallize more readily whereas crosslinks and molecular defects will not be able to crystallize and will be rejected from the newly formed crystals. Thus there are opposing effects, one that promotes greater crystallizability and the other inhibiting crystallization. Therefore recycled polymer that has been subjected to photo-oxidation in its first life, prior to recycling, may have greater or smaller crystallinity when reprocessed, according to whether the short chain effect or the molecular defect effect dominates. Because of the sensitivity of polymer properties to crystallinity, it is of considerable importance to investigate this effect and this is the subject of the work presented here.

2. Experimental

2.1. General strategy

This work was part of a study of the effects of including photo-degraded polymer in recyclate [18]. Samples were injection moulded from virgin material in large batches. Some mouldings were used for property measurement to characterize the virgin materials. Others were exposed to ultraviolet irradiation (UV) in the laboratory and used as a source of photo-degraded material. The recycled material was mixed with virgin granules of the same polymer type;

tumble mixed, and reprocessed into tensile test bars by injection moulding as before. The mouldings containing recycled materials were exposed to UV in the laboratory and their properties measured periodically.

2.2. Materials and sample preparation

The material used in the studies reported here was a polypropylene copolymer (PPCO) provided by BP (grade 400-GA03). It contained no photo-stabilizer but probably contained some thermal stabilizer. A parallel study was conducted on three representative polyethylenes (one each of high density polyethylene, low density polyethylene and linear low density polyethylene) and will be reported on separately.

Injection moulded tensile test bars measuring approximately $145\,\text{mm} \times 10\,\text{mm} \times 3\,\text{mm}$ were made from the virgin polymer (PPCO-V). The photo-degraded recyclate was obtained from bars that were exposed to UV for 3 weeks on both sides then regranulated. Blends with virgin polymer were made of two compositions, containing, respectively, 10 and 25% recycled photo-degraded material (PPCO-V+ 10P, PPCO-V+25P).

2.3. UV exposure

UV exposures for both the production of photo-degraded recyclate and for the photo-degradability trials were conducted in a constant temperature room at $30 \pm 1\,^{\circ}\text{C}$. Fluorescent tubes type UVA-340 (Q-Panel Company) were used as the UV source. The output of the tubes matches the solar radiation spectrum closely in the UV range [19]. The tubes were used in pairs and gave intensity in the range $2.0 \pm 0.3\,\text{W m}^{-2}$ in the wavelength range 290–320 nm (the total radiation below 320 nm). This corresponds to the upper level of terrestrial intensities in a hot climate [20] but exposures were conducted uninterrupted, 24 h per day.

2.4. Characterization

Fractional crystallization measurements were made by differential scanning calorimetry (DSC) and by X-ray diffraction (XRD). Samples for DSC were prepared by removing material from the exposed surface of the bars to a chosen depth using high speed milling with a single point cutter ('fly-cutting' action). Repeated passes were made, removing 0.1 mm each time. Material was removed only part way along the length of the bar; at one end of the bar, terraces were formed, each 0.1 mm deep. The surfaces exposed in this manner were used for the XRD measurements. Each terrace measured approximately 10 mm along the bar axis direction, and cuts were finally made to separate each individual terrace for mounting in the diffractometer.

DSC measurements were made under flowing nitrogen with a Mettler FP90 controller connected to a FP85 Heat Flux cell. A heating rate of 13 °C/min was used within the

range 40–210 °C. Once the termination temperature (210 °C) was reached the instrument was set to cool at the same rate (210–40 °C) and the recrystallization thermogram recorded. Finally, the sample was reheated to produce the second heating thermogram (13 °C/min within the range 40–210 °C). The first heating thermogram characterizes the material in the form that existed at the end of UV exposure and contains memory of the original processing as well as of changes promoted by the photo-oxidation (characterized as DSC1). The second heating (DSC2) provides information about the degraded molecules, free from the original processing signature and modifications related to chemi-crystallization [21]. XRD was conducted using a Philips X'Pert Pro diffractometer and used to estimate the crystallinity of the samples using standard procedures based on the integrated intensities of the peaks [22,23]. For PP the crystallinity measurements used the formula given by Weidinger and Hermans [22–24]. It is noted that the DSC measurements were made using samples of well-defined depth (i.e. the nth layer comprised material between $(0.1n)$ mm and $(0.1(n+1))$ mm from the exposed surface) whereas the XRD measurements sampled material within an unknown depth, $0.1n$ to $(0.1+A)$ mm where A is the X-ray penetration depth. The sampling position, as displayed on the graphs, is given as $(0.1(n+0.5))$ mm for DSC data and $(0.1n)$ mm for the XRD data.

3. Results

3.1. General observations

Typical DSC runs made using samples obtained at different depths from PPCO-V after 6 weeks UV exposure are shown in Fig. 1. The thermogram from an unexposed sample is given as reference. The crystal melting peak in the thermogram for the sample taken from the exposed surface (0–0.1 mm) is seen to be displaced significantly towards lower temperatures. Crystal melting peaks for samples taken from locations deeper into the bar were displaced less (Fig. 1). The X-ray diffractometer traces did not show such visually obvious sample to sample differences: a typical example is given in Fig. 2.

For all samples and at all conditions (unexposed or exposed to UV for 3 weeks or 6 weeks) the lowest crystallinity values were recorded at the surface (where the cooling rate during the moulding operation is greatest) and the crystallinity climbed progressively with distance from the surface of the moulded bar. With one exception, this was shown by all materials (virgin PP and blends of recyclate with virgin polymer) and for all three measurement methods.

3.2. PPCO-V

Crystallinity results for as-molded virgin polymer PPCO-V are given in Fig. 3(a). This was the material that showed the only exception to the rule that the DSC2 crystallinity exceeded the DSC1 result for all of the materials (virgin and blends) at any condition (unexposed and exposed to UV). The exception was the result obtained for the first DSC heating run at 0.15 mm depth, and is regarded as anomalous. Although the DSC2 crystallinity values exceeded the DSC1 values, PPCO-V, they did so by a quite small amount whereas the XRD values were much higher (Fig. 3(a)).

After 3 weeks UV exposure, the crystallinity values at all positions and by all measurement techniques were greater than those obtained for the unexposed bars (Fig. 3(b), c.f. Fig. 3(a)). The DSC values increased by more than the XRD values, and the DSC2 values are quite close to the XRD values. After 6 weeks UV exposure (Fig. 3(c)) the crystallinity values climbed still further, and now some of the DSC2 values exceeded those measured by XRD.

3.3. PPCO-V+10P

The as-moulded bar made from the blend containing 10% photo-degraded recyclate had the lowest crystallinity values at the surface (Fig. 4(a)). With this material, the XRD
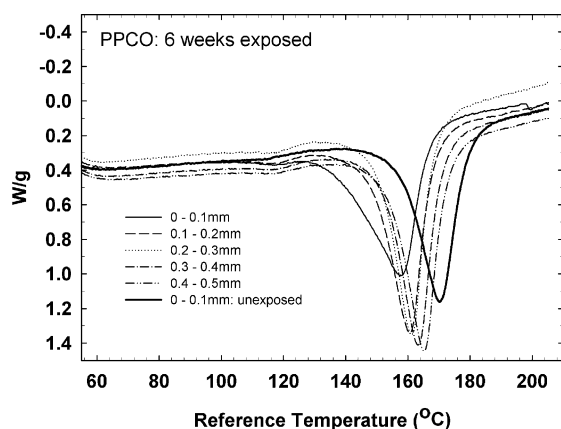

Fig. 1. DSC thermograms for PPCO samples exposed to UV for 6 weeks. Data for samples taken from 5 different depths are shown. Data from an unexposed sample are shown for comparison (bold line).
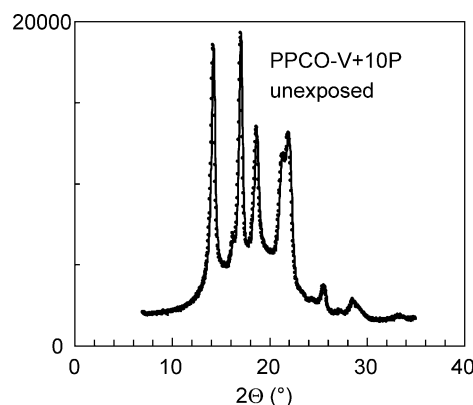

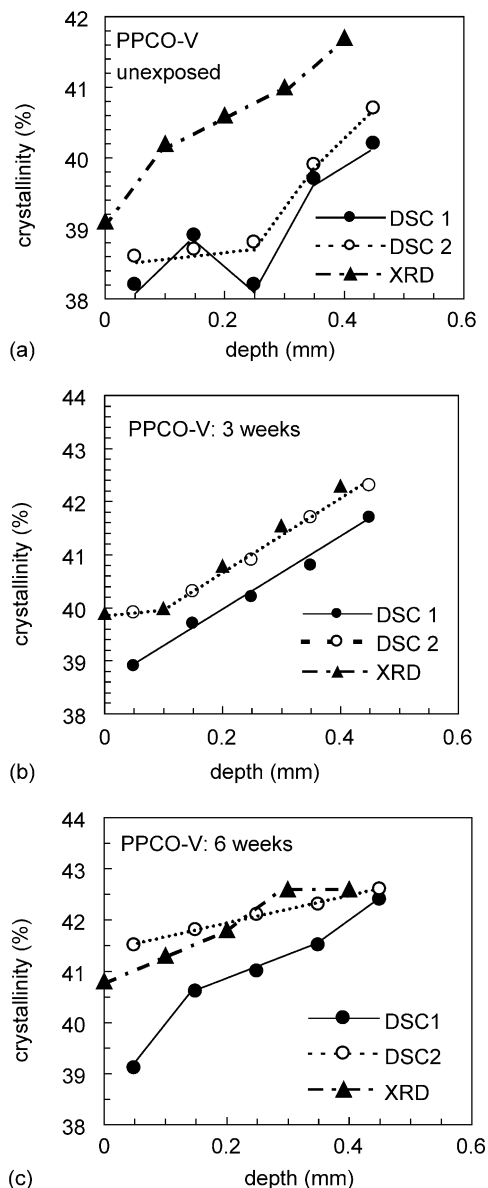Fig. 2. XRD for unexposed PPCO-V+10P (moulded surface).

Fig. 3. Crystallinity measurements obtained using DSC first heating (DSC1) and second heating (DSC2) runs and by XRD for PPCO-V at different depths from the exposed surface (a) unexposed; (b) 3 weeks exposure; (c) 6 weeks exposure.
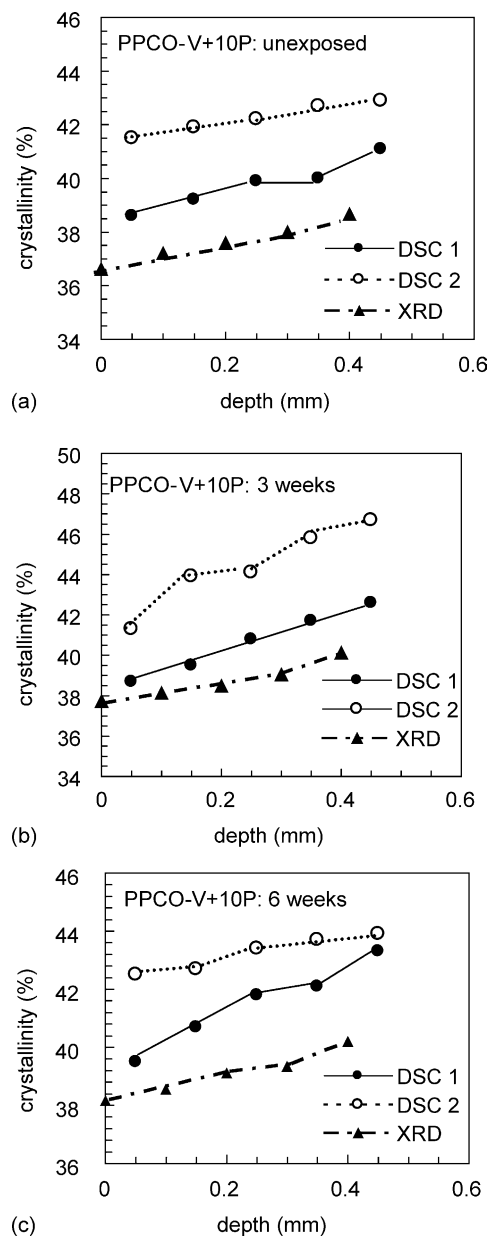

Fig. 4. Crystallinity measurements obtained using DSC first heating (DSC1) and second heating (DSC2) runs and by XRD for PPCO-V + 10P at different depths from the exposed surface (a) unexposed; (b) 3 weeks exposure; (c) 6 weeks exposure.

crystallinity values were lower than the DSC values. After UV exposure the XRD crystallinity values remained the lowest and the DSC2 values the highest at all depths (Fig. 4(b) and (c)). The change in crystallinity produced by UV exposure was much less than that obtained with PPCO-V.

3.4. PPCO-V + 25P

The lowest crystallinity values were recorded with the PPCO-V + 25P blend (Fig. 5). As with PPCO-V + 10P, the highest values were obtained from the analysis of the DSC2 run. The XRD measurements were lowest for the unexposed

blend, and the DSC1 the lowest after 6 weeks UV exposure. After 3 weeks UV exposure, the XRD and DSC1 values were fairly similar. UV exposure caused the crystallinity to increase but the change obtained in the second three weeks (from 3 to 6 weeks exposure) was much less than that obtained in the first 3 weeks. Indeed, the DSC2 measurements after 6 weeks exposure were lower than those after 3 weeks exposure (compare Fig. 5(b) and (c)). This indicates that the material is less crystallizable after 6 weeks exposure than after 3 weeks exposure, presumably because the molecular defect content has grown sufficiently to dominate over the small molecule effect.
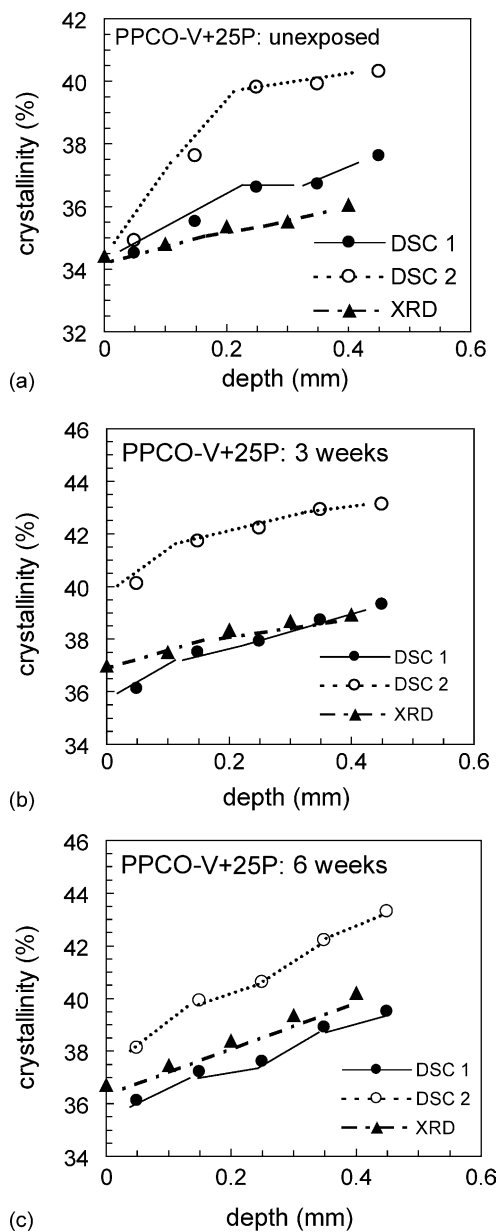
Fig. 5. Crystallinity measurements obtained using DSC first heating (DSC1) and second heating (DSC2) runs and by XRD for PPCO-V+25P at different depths from the exposed surface (a) unexposed; (b) 3 weeks exposure; (c) 6 weeks exposure.

4. Discussion

4.1. Comparison of crystallinity measurement procedures

The XRD and DSC crystallinity measurements were in very good agreement. Exact agreement is not expected because: (i) the DSC measurements were made on samples from layers 0.1 mm thick whereas the XRD measurements sampled a much smaller depth (dictated by X-ray penetration) and are not strictly comparable when strong variation with depth exists; (ii) there is likely to be secondary crystallization during the heating phase of the

DSC run, an effect that does not occur with the XRD measurements, that are conducted at room temperature. Quite apart from the points raised above, absolute values of crystallinity cannot be obtained because of the inadequacies of the two-phase (crystal-amorphous) model. The results of single measurements are reported in Figs. 3–5. From the internal consistency of the results, and occasional repeat measurements, and from the agreement with the XRD measurements it is estimated that the data are accurate to ± 0.2%. The error bars are therefore of the order of twice the size of the data decals used in Figs. 3–5 and are not plotted to avoid cluttering the graphs.

It is noted that the only material for which the XRD crystallinity measurements were higher than those obtained from the DSC data were those obtained with the as-moulded virgin polymer. This material will have less small-molecule content than the other materials, which will have small molecules present in significant concentrations due to the photo-degraded recyclate content or to UV exposure or both. As a consequence PPCO-V will be less able to exhibit secondary crystallization during the DSC heating (whether first or second heating runs) than the other materials.

4.2. Depth profiling

For all of the materials studied, the crystallinity was smallest at the surface and increased progressively on moving inwards towards the centre. This is attributed to the difference in cooling rates at different depths during the injection moulding process. Curiously, some depth dependence was still evident in the second heating data (Figs. 3–5) even though the processing signature should have been erased by the first heating. This implies that some partitioning of molecular species must have occurred during moulding, with less crystallizable molecules segregating to the surface. Alternatively, if thermal degradation occurred during processing, it would be expected to vary with depth because of the large temperature gradient that exists within the mould, and may be the source of different crystallization behaviour at different depths.

4.3. Secondary crystallization

The crystallinity is plotted versus exposure time in Fig. 6 for samples extracted from two depths: (a) the surface layer (0–0.1 mm) and (b) the layer between 0.3–0.4 mm. Both XRD and DSC1 results are displayed; DSC2 contains no information about the secondary crystallization because its effect is erased during the first heating run in the DSC. Data are given for virgin polymer and for both blends containing recyclate. In most cases, the crystallinity increased with increasing exposure. There was one exception: the crystallinity of the material at the surface of bars made from the blend containing 25% photo-degraded recyclate was found to fall very slightly (XRD measurements) or stay the same (DSC1 measurement) when the exposure time increased
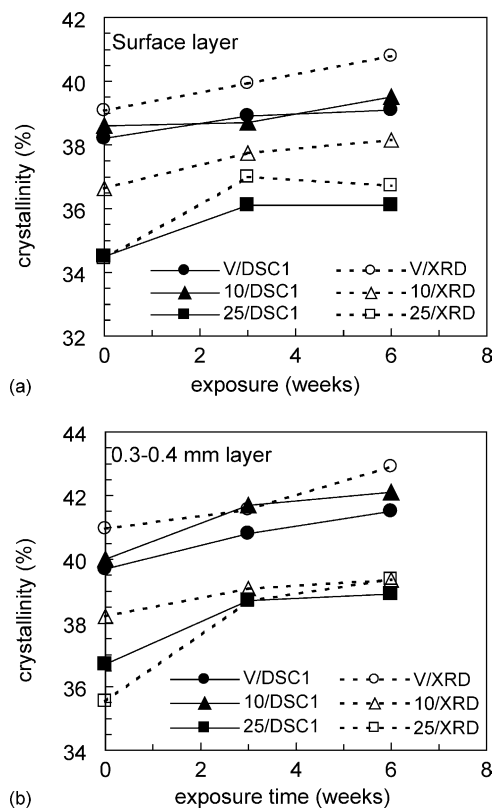
(a)

(b)

Fig. 6. Comparison of DSC1 and XRD crystallinity measurements obtained in the unexposed state for PPCO-V (V), PPCO-V+10P (10) and PPCO-V+25P (25) obtained with samples taken from (a) the surface and (b) the 0.3–0.4 mm layer. The XRD measurements were taken from (a) the exposed surface and (b) the terrace exposed by removing 0.3 mm material from the exposed surface.

from 3 weeks to 6 weeks (Fig. 6(a)). The sample exposed for 6 weeks is the most heavily degraded of all of the material studied, having the highest amount of photo-degraded recyclate content and the most potent UV exposure (surface sample with highest intensity and greatest oxygen access; longest exposure time). Perhaps some erosion of the crystal phase occurs under such severe conditions though the apparent fall in crystallinity is within measurement error. Oxidation occurs almost exclusively in the amorphous phase and it is evident that, at the exposures employed in the current work, the crystal phase shows little evidence of erosion, except at the most severe conditions.

The changes in crystallinity, Δf_{cr}, that occurred at all depths both for the first 3 weeks exposure and for the second 3 weeks exposure (i.e. the change in crystallinity from 3 weeks to 6 weeks) are given in Fig. 7, derived from the DSC1 data. The changes observed in the second 3 weeks were very small for PPCP-V+25P, of the order of the measurement error, indicating that the molecules in the amorphous phase were too defective to contribute to further crystallization even if scission released segments from entanglements. (Note that each Δf_{cr} value is the difference between two measurements, both with an estimated error of
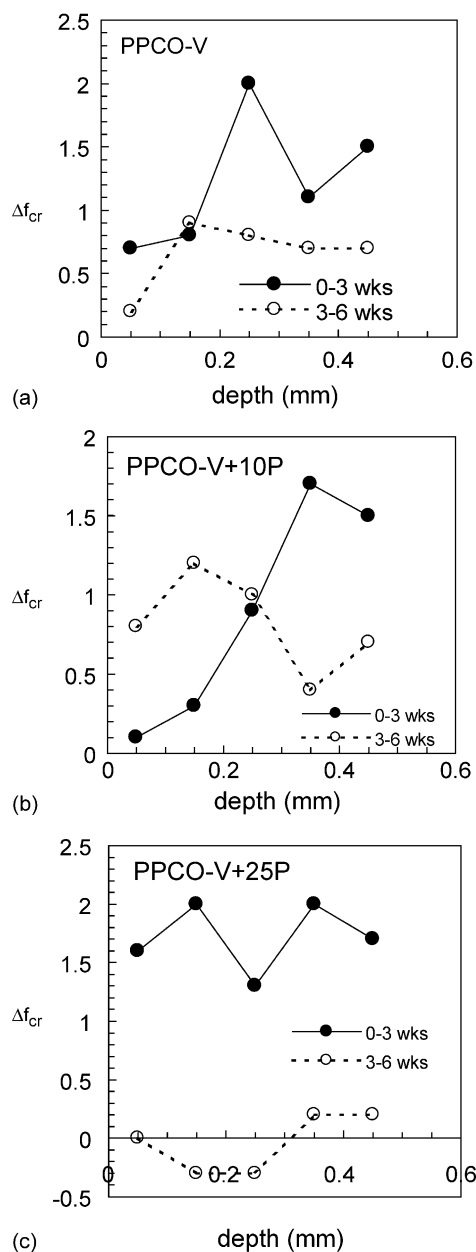

(a)

(b)

(c)

Fig. 7. Change in crystallinity Δf_{cr} obtained in the first 3 weeks UV exposure (1–3) and in the second 3 weeks exposure (3–6) for (a) PPCO-V; (b) PPCO-V+10P; (c) PPCO-V+25P. Data derived from DSC1 measurements.

$\sim 0.2\%$, and the error in the Δf_{cr} values is therefore $\sim 0.3\%$).

4.4. Crystallizability of recycled polymer

Figs. 3–5 show that in the as-moulded state, the greatest DSC1 crystallinity values were obtained for the blend containing 10% photo-degraded recyclate and the smallest ones with the blend containing 25% recyclate. The highest XRD crystallinity measurements were obtained with the as-moulded virgin polymer and the lowest again with the blend

containing 25% recyclate. That PPCO-V+25P gave the lowest crystallinities in the as-moulded state indicates that the molecular defect content was dominant when the material crystallized under the conditions applied during injection moulding. The results for PPCO-V+10P seem to indicate that the nature of the crystal phase formed is different to that obtained with virgin polymer, causing the ranking obtained by the two measurement methods to be reversed. The DSC2 data give an indication of the recrystallizability of the material, free from processing history, and these data are replotted in Fig. 8. Comparing the virgin material and the blend containing 10% recyclate, the
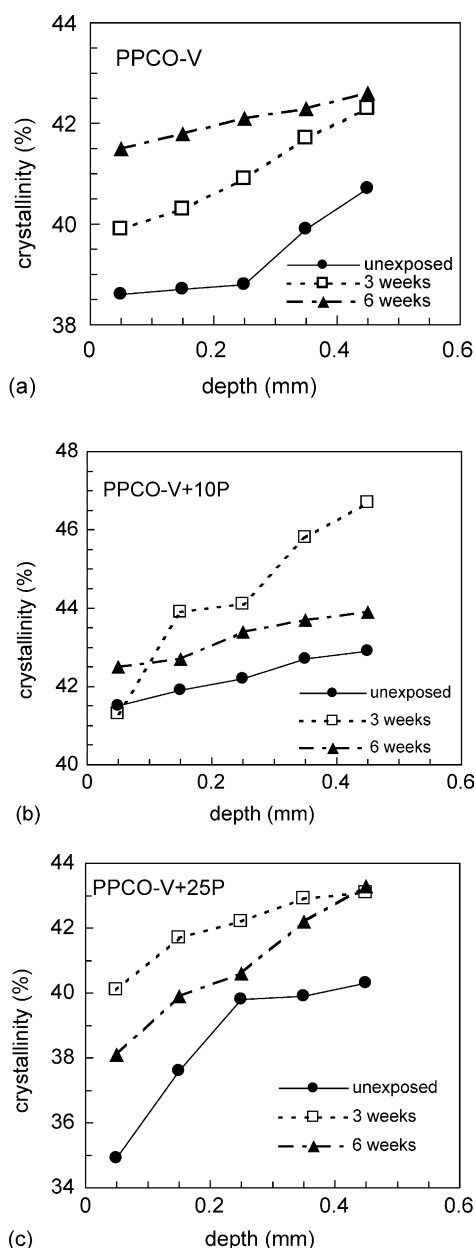

Fig. 8. Crystallinity measurements obtained from DSC2 runs for samples taken at different depths in the unexposed state and after 3 and 6 weeks UV exposure, respectively. (a) PPCO-V; (b) PPCO-V+10P; (c) PPCO-V+25P.

greater crystallinity in the latter presumably occurs because the smaller molecules (produced by chain scission during the photo-degradation of the material from which the recyclate was obtained) had smaller tendency to entangle and crystallized more readily. The same argument leads to the prediction that the blend containing 25% recyclate should yield even greater crystallinity, but this is not found to be true. Therefore it is speculated that the smaller molecules help to mobilise the virgin molecules but are prevented from crystallizing extensively themselves by defects such as carbonyl groups formed as a result of oxidation. When the recyclate content reached 25%, the amount of material that was not crystallizable because of this was large enough to have a significant effect, and this prevailed over the mobilization effect. The idea of mobilization introduced here to interpret the results represents a further level of detail compared to the simple model presented above in the Introduction.

Fig. 8(a) shows that when the virgin polymer was exposed to UV for 3 weeks, the crystallizability increased at all depths and that increasing the exposure time to 6 weeks produced a further increase. With PPCO-V+10P and PPCO-V+25P the unexposed material remained the least crystallizable (Fig. 8(b) and (c)). With these blends the material that was exposed for 6 weeks had lower crystallizability after 6 weeks exposure than after 3 weeks exposure, indicating that the molecular defect effect was beginning to have more influence than the small molecule effect.

5. Conclusions

Significant secondary crystallization was observed to occur during UV exposure of polypropylene samples made from virgin polymer and from blends containing recyclate that had been photo-degraded prior to reclamation, confirming that molecule segments in the amorphous phase of the as-moulded samples were capable of crystallizing if released from entanglements by photo-oxidative scission events. For the longest exposure (6 weeks) the material containing the most degraded material (PPCO-V+25P) appeared to have reached the limit of crystallization. This, and other more detailed inspection of the results, indicated that molecular defect content of the molecules in the amorphous phase was too high to allow further crystallization even if they were released from entanglements.

The addition of 25% photo-degraded recyclate caused the material to become less crystallizable when injection moulded, presumably because the increased defect content of the reclaimed molecules was more influential than the reduced molecular size. With the addition of 10% recyclate the changes in crystallinity for the as-moulded material measured by XRD and DSC1 were in disagreement and it is

not possible to assert whether the small molecule size or the molecular defects dominated the behaviour.

On applying further UV exposure, the crystallizability of the material (deduced from the DSC2 measurement) increased at first but with PPCO-V+25P there was evidence that for between 3 and 6 weeks UV exposure, there was no further crystallization and that the molecular defect content was too high to allow further crystallization.

The changes in crystallinity reported here are significant and will have a significant effect on the mechanical properties of the materials. In further studies, to be reported elsewhere, it was discovered that, when exposed to UV, blends containing recyclate that had been photo-degraded prior to recycling degraded faster than virgin polymer or blends with 'controlled' recyclate that had not been photo-degraded. It is unlikely that tests on recycled material conducted immediately after reprocessing will reveal this deficiency and it is essential that polymeric materials under consideration for recycling are tested for the presence of pro-degradants, especially if the new products are intended for outdoor applications or are likely to be exposed to UV from some other source.

Acknowledgements

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