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Mechanical properties of photo-degraded recycled photo-degraded polyolefins

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Test bars made from a selection of polyolefins were injection moulded from virgin polymer and from blends containing recycled photodegraded polymer of the same kind. Bars were also moulded from similar blends prepared using recycled polymer that had not been photodegraded previously. The moulded bars were subjected to ultraviolet (UV) exposure and tensile tests were conducted after various exposure times. The extensibility decreased rapidly after a period of exposure that varied with the material and with fraction of recyclate contained. The results showed that previously photodegraded material acts as a pro-degradant in all of the materials studied. The recyclability of the materials is discussed.

1. Introduction

There are many technical difficulties to overcome when recycling post-use polymers. The incompatibility of different polymers and the presence of contaminants are formidable problems. Even when the waste material has been sorted into single polymer types and thoroughly cleaned, further problems may remain. Polymer degradation often occurs during the first service life of the material. Polymers that are used outdoors suffer photo-oxidation promoted by exposure to the ultraviolet (UV) component of sunlight, leading to molecular chain scission and/or crosslinking. Some of the products of the chain reactions that occur during photo-oxidation are themselves pro-degradants. This is immediately a potential problem during recycling because they may promote thermal oxidation during moulding of the reclaimed material. Although the pro-degradants are unlikely to survive the temperatures used to re-mould the material, the reactions that destroy them are likely to generate new pro-degradant products that reach the moulding made from recyclate.

LaMantia pointed out that a photosensitive component in a polymer blend may sensitise the whole material nearly 20 years ago [1] and followed this with some studies of particular examples of recycled polymers [2, 3]. Much research has been devoted to the development of additives for the re-stabilization of recycled polymers [4–16]. Although some of the motivation for this is to combat the effects of pro-degradants produced during the service life of the material prior to recycling, re-stabilization is also required to replenish stabilizer that has been consumed during the original service life. Other contaminants, additional to those produced by chemical reaction prior to and during reprocessing, may also be present and may have a pro-degradant effect [5]. Mechanical recycling causes degradation and many studies have been conducted in which the material has been passed through successive cycles of extrusion and granulation. Although such research has significant value in developing strategies for reprocessing polymers, it does not address the sensitisation of the material to photodegradation. Conversely, although much of the work on re-stabilization concerns protection against photodegradation of the recycled material, very few studies have been devoted to the separation of the effects due to photodegradation in the original service life of the reclaimed material and to mechanical reprocessing. An exception is included in the wide-ranging investigation reported by Al-Malaika *et al.* [17] in which they observed that photodegraded recyclate had a much more detrimental effect on properties of recycled blends than recyclate that had not been photodegraded prior to reprocessing. This study [17] is a special case, however, because it concerns polyethylenes that were designed to be degradable. We have not discovered reports in the literature of any equivalent study with polymers that have not been deliberately sensitised to degrade, apart from those from our own laboratory [18, 19].

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The particular concern in the present work is the sensitisation of mouldings containing recycled polymer to photodegradation. This phenomenon was studied by Stephenson and White [18] who compared the photodegradation of bars moulded from virgin polystyrene and similar bars made from a blend of virgin polymer (80%) and recycled polymer (20%). Recycled polymer from different sources was used, including material that had been photodegraded prior to reclamation and material that had not been so treated. In the material that contained recycled photodegraded material, the deterioration of properties started as soon as it was exposed to UV irradiation whereas bars made from the virgin polymer and from blends that contained recyclate that had not been photodegraded prior to reclamation displayed an incubation time before significant deterioration was measured [18]. A pro-degradant effect was also observed in a similar study using a rubber-toughened polypropylene [19].

The present study compares the behaviour of three different polyethylenes and two polypropylenes when photodegraded recyclate was blended with the virgin polymer and has been complemented by a significant programme of molecular and structural characterization, described elsewhere [20–23]. Similar blends of virgin polymer with recyclate that was not subjected to photodegradation prior to reclamation were tested using the same procedures.

2. Experimental

2.1. General strategy

The studies presented here form part a programme designed to explore the effects of including photodegraded polymer in recyclate. Samples were injection moulded from virgin material in large batches. The mouldings were divided into four groups (of different size) and used as follows:

(i) One group was used for property measurement to characterize the virgin materials.

(ii) Another group of mouldings was regranulated to produce recyclate that had not been photodegraded. 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.

(iii) The largest group of mouldings was exposed to ultraviolet irradiation (UV) in the laboratory and used as a source of photodegraded material. Samples were removed from UV exposure periodically to measure the effect of photodegradation on the virgin bars. After a chosen period of UV exposure, the photodegraded mouldings were regranulated, mixed with virgin granules of the same polymer type, tumble mixed, and reprocessed into tensile test bars by injection moulding as before.

(iv) The fourth group of mouldings was thermally aged in a companion study that will be reported in the future [24].

2.2. Materials and sample preparation

The polymers used were all BP grades, provided by the manufacturer:

High density polyethylene (HDPE) was Rigidex HD5802GA;
Low density polyethylene (LDPE) was Novex LD1402AA;
Linear low density polyethylene (LLDPE) was Innovex 6910AA;
Polypropylene homopolymer (PPHO) was Elex 358 HV200;
Polypropylene copolymer (PPCO) was 400-GA03.

The polymers were described as free from photostabilizers; they probably contained some thermal stabilizer. More details about these materials are given by Willoughby *et al.* [25]. The virgin polymers are denoted HDPE-V, LDPE-V, LLDPE-V, PPHO-V and PPCO-V respectively. Blends containing x% photodegraded recyclate are denoted HDPE-V+xP, LDPE-V+xP, LLDPE-V+xP, PPHO-V+xP and PPCO-V+xP respectively and those containing x% recyclate that had not been photodegraded prior to reprocessing are denoted HDPE-V+xU, LDPE-V+xU, LLDPE-V+xU, PPHO-V+xU and PPCO-V+xU. Two blend compositions were used for each polymer type, with $x = 10$ and 25 respectively. Tensile test bars (ISO527 type 1B) with 3 mm thickness and 145 mm long were moulded using a single end-gated tool at University of Warwick for a collaborative project between University of Warwick, University of Newcastle upon Tyne and RAPRA (Shawbury, Shrewsbury).

The reason for using materials that were free from UV stabilizer is that European grades of polyolefins are often supplied with low levels of stabilizer, especially if intended for indoor applications or even "under the bonnet" automotive applications. Scrapped material may be exposed outdoors while awaiting reclamation and the study described here was designed to examine whether this could lead to defective recyclate. Much of the work on restabilization [4–16] is geared to the replacement of stabilizer consumed in the first life of the material, a separate issue to that under scrutiny here, in which the effect of the production of pro-degradants during the first life of the polymer and their subsequent effect during the second life, after recycling, is examined.

2.3. UV exposure conditions

The bars were exposed to UV on open racks at 30 ± 1°C using fluorescent tubes type UVA-340 (Q-Panel Company) that have spectral output matching that of terrestrial solar radiation in the wavelength range up to ∼360 nm [26]. They display a similar wavelength cut-off to solar radiation, at approximately 290 nm. At wavelengths above 360 nm the intensity falls below that of sunlight and is very much less in the visible range and effectively zero in the infrared range, and radiation heating of the samples was negligible. The intensity in the wavelength range <320 nm was 2.0 ± 0.3 Wm^{-2} for the experiments reported here. This falls within the upper range of terrestrial intensities in a hot climate [27]. Exposures were conducted uninterrupted, 24 h per day, and exposures up to 12 weeks were used. Photodegraded recyclate was obtained from bars that were exposed to UV for 3 weeks on each side then regranulated.

2.4. Structural and molecular characterization

Characterization of the materials at various stages of preparation and UV exposure was conducted using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) to measure crystallinities and by gel permeation chromatography (GPC) to investigate molecular mass changes due to chain scission and crosslinking. Samples were obtained by high speed milling, removing successive layers of 0.1 mm depth using a single point cutter with fly cutting action. The samples were used to obtain depth profiles, showing how degradation varied at different depths from the exposed surface [21, 23]. The procedures used for DSC and XRD measurements are described elsewhere [21, 23]. Crystallinity changes occurred, especially in the first 0.5 mm from the surface. Some of the data obtained by GPC were subjected to "molecular weight distribution computer analysis" to determine the scission and crosslinking concentrations and so permit the molecular changes to be followed more closely than is possible when using simply molecular mass averages [20, 22].

2.5. Mechanical testing

Tensile tests were conducted on bars exposed for various periods of time using a crosshead speed of 25 mm/min.

2.6. Fractographic observations

For the study of HDPE, selected fracture surfaces produced during the tensile testing were examined by scanning electron microscopy using the secondary electron image with a Hitachi S-2400 operated at 15 kV. The samples were gold-coated to prevent charging and to enhance contrast. The surfaces adjacent to the fracture surface were also viewed.

3. Results

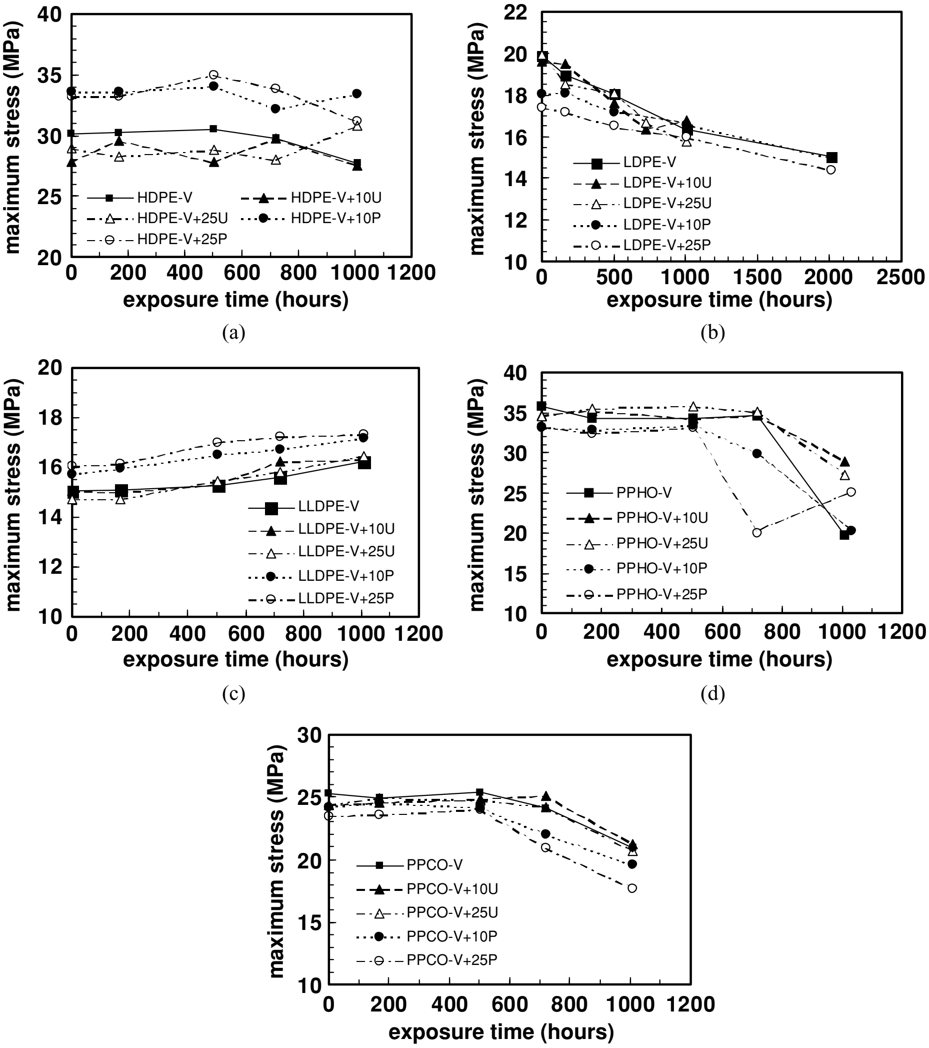
3.1. Introduction

All of the materials, in virgin form and in the form of blends of virgin material and recyclate, showed reduced ductility after prolonged UV exposure. Beyond this, it is difficult to make any other general observation. It is therefore necessary to deal separately with each polymer type (including the virgin form and the blends). Results are given for (i) the maximum engineering stress recorded in the tensile test and (ii) the strain at break. In each case, five samples were tested and the results plotted in Figs. 1 and 2 are for the averages of the five measurements. If the standard deviation (SD) of the five results is taken to be the appropriate value for the error bar amplitude then the error bars would overlap in many of the graphs presented below and they have been omitted partly for this reason, for the sake of clarity. The SD varied considerably with material and exposure state. Discussion of the variation in measurements is therefore treated below case by case. Some of the samples displayed cold drawing and did not fail even when the test machine crosshead reached the limit of its travel (at ∼250% strain). In most cases this property was shown by all of a set of five samples or by none of them. When some but not all of the samples in a set drew to the full limit, the set of maximum strain measurements can no longer be considered as part of a normal distribution and calculation of a standard deviation is impossible, another reason for refraining from plotting error bars. The load passed through a maximum before failure so this did not affect the maximum stress data. Samples that did not break before reaching the machine limit are indicated in Fig. 2 by vertical arrows.

3.2. Mechanical properties

3.2.1. HDPE

The maximum engineering stress values for HDPE are plotted in Fig. 1(a) as a function of UV exposure. The measurements for the virgin material were very consistent at all exposure states, giving SDs < 1 MPa. The maximum stress for UV-exposed HDPE-V remained approximately unchanged until the exposure time exceeded 500 h, then began to decrease steadily. The blends containing recyclate that had not been photodegraded in its first life (HDPE-V+10U and HDPE-V+25U) showed more variation (SD ≤ 3 MPa) and generally possessed lower strengths than the corresponding virgin material (HDPE-V). The only exception was that the strength measured for HDPE-V+25U after ∼1000 h exposure was significantly higher than that for the virgin material (no overlap of the error bands), indeed this measurement exceeded those for HDPE-V and its blends with undegraded recyclate at all exposure states. That more scatter is displayed in measurements made with the blends than those made with the virgin polymer is probably related to the presence of flaws generated by the recycling process. The maximum stress values recorded with the blends containing photodegraded recyclate were significantly higher than those for HDPE-V at all exposure states (Fig. 1a). Results for



(a) (b) (c) (d) (e)

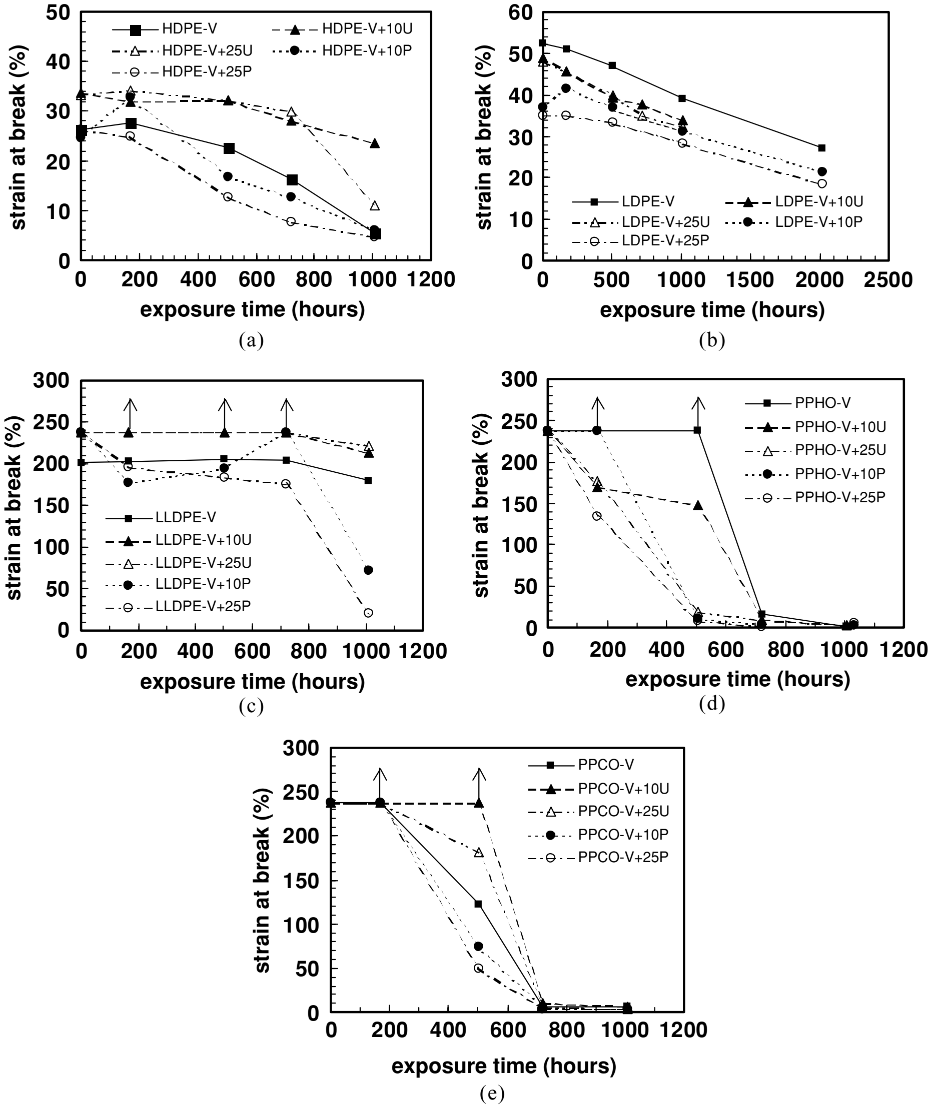
Figure 1 Maximum (engineering) stress versus UV exposure time for (a) HDPE; (b) LDPE; (c) LLDPE; (d) PPHO; (e) PPCO. The data points are the average of 5 measurements. The error bars measure less than the symbol size.

HDPE-V+10P and HDPE-V+25P were even more scattered than those for HDPE-V+10U and HDPE-V+25U, with greatest variation for HDPE-V+10P at zero exposure (SD ∼4 MPa) and for HDPE-V+25P after ∼1000 h exposure (SD ∼ 5 MPa).

The scatter in results for the strain at break was quite large, as is normal with ductile polymers. HDPE-V showed the smallest variation, with a largest SD of ∼3% (at zero exposure). The largest SD was 21%, for HDPE-V+10P after ∼180 h exposure. All other SDs were 12% or lower and declined when the exposure time exceeded 500 h. The strain at break for UV-exposed HDPE-V began to decline earlier than the strength (Fig. 2a c.f. Fig. 1a). The strain at break for the blends of HDPE-V with undegraded recyclate was higher than that for HDPE-V for all exposure states whereas the strain at break for the blends containing photodegraded recyclate was lower than that for HDPE-V in almost every case.

3.2.2. LDPE

For LDPE and all of the LDPE blends, the maximum stress showed a steady decline even at modest UV exposure times (Fig. 1b). The values for all materials are much more closely bunched than with HDPE. The standard deviations for the LDPE-V results were less than 0.4 MPa for all exposures up to 1000 h, but increased to nearly 0.7 MPa at ∼2000 h exposure. Samples containing undegraded recyclate showed much more measurement variation, with the largest SDs for LDPE-V+25U of 1.8 MPa (at zero exposure) and LDPE-V+10U of ∼1.5 MPa (after ∼500 h exposure). Smaller variation was observed with the samples containing photodegraded polymers, the largest SD being 0.8 MPa (after ∼500 h exposure); all other sets gave SD < 0.6 MPa. For LDPE, the blends with photodegraded polymer gave the lowest maximum stress values, with LDPE-V+25P performing worse than LDPE-V+10P at all exposures.



(a)

(b)

(c)

(d)

(e)

Figure 2 Maximum strain versus UV exposure time for (a) HDPE; (b) LDPE; (c) LLDPE; (d) PPHO; (e) PPCO. A vertical arrow denotes samples that did not break before the tensile machine crosshead reached the limit of its travel (at ~250% strain) and would have recorded a higher value if allowed to continue to break.

The strain at break showed less variation than was observed with HDPE. The highest SD value was < 7%, for LDPE-V+10P (after ~180 h exposure). No other SD greater than 5% was recorded. Somewhat surprisingly two of the three examples at this level were for LDPE-V (at zero exposure and after ~500 h exposure). The highest values of strain at break were obtained with LDPE-V at all exposures (Fig. 2b) and the blend LDPE-V+25P gave the lowest values at all exposures.

3.2.3. LLDPE

The maximum stress values recorded with all of the LLDPE materials showed modest increases with UV exposure time (Fig. 1c). This was the only polymer to display this characteristic. The variation in the maximum stress was fairly small for all blends. The greatest SD was ~0.5 MPa, for LLDPE-V+10P after ~1000 h exposure and LLDPE-V+25U after 720 h exposure. For most sets of data SD was <0.3 MPa. The highest values of maximum stress were recorded for the blends containing photodegraded recyclate, with LLDPE-V+25P giving slightly higher values than LLDPE-V+10P. The results for LLDPE-V and its blends with recyclate that had not been exposed to UV prior to reclamation were hardly separable.

The dependence of ductility on UV exposure varied according to the composition of the materials based on LLDPE-V. The virgin material showed very little change in strain at break until ~800 h exposure had elapsed and the value was not much smaller even after extending the exposure beyond 1000 h (Fig. 2c). The largest SD for

LLDPE-V was ∼50% for ∼1000 h exposure; the other SD values for LLDPE-V were ≤30%.

The blends containing recyclate that had not been photodegraded prior to reclamation showed greater ductility, cold drawing to the tensile test machine travel limit for all tests up to 800 h UV exposure, and even after 1000 h UV exposure they failed at a greater strain than that recorded for LLDPE-V. The blends containing photodegraded recyclate showed a catastrophic reduction in the strain at break after 1000 h UV exposure. Prior to this there was no discernible pattern to the observed behaviour. Both LLDPE-V+10P and LLDPE-V+25P displayed a significant fall in ductility in the first 200 h exposure but from then until 800 h exposure the strain at break for LLDPE-V+10P increased with exposure whereas that for LLDPE-V+25P decreased (Fig. 2c). Curiously, some samples containing photodegraded recyclate increased drawability after 500 h exposure, with more examples for LLDPE-V+10P than for LLDPE-V+25P. That some samples reached the draw limit without failure means that the calculated average strain-at-break values are artificially depressed.

3.2.4. PPHO

The maximum stress values recorded for the PPHO-V series of samples were bunched fairly closely in the as-moulded state and remained so until 500 h UV exposure (Fig. 1d). The SDs were small in this range, <1 MPa. Much larger variations were recorded for exposures of 720 h and more, including SDs of 3.5 MPa after 720 h and 4.3 MPa after ∼1000 h for PPHO-V+10P. All other SDs were 2 MPa or less. After 500 h exposure, the measurements for the blends containing photodegraded recyclate fell steeply. The maximum stress recorded for PPHO-V and the blends with undegraded recyclate remained steady up to ∼800 h UV exposure. Thereafter the maximum stress values fell significantly, with PPHO-V showing the biggest drop.

Fig. 2d shows that PPHO-V retained ductility the longest (past 500 h UV exposure). Although PPHO-V+10P remained ductile up to ∼200 h UV exposure, it had become very brittle by 500 h exposure. The fall in ductility was much more sudden and advanced than that observed with HDPE and LDPE blends. As such the behaviour was more like that of LLDPE-V+xP but with catastrophic failure occurring at an earlier time. The only blend showing significant ductility after 500 h UV exposure was PPHO-V+10U. PPHO-V+25P and PPHO-V+25U both began to lose ductility at low exposure times and had become very brittle by 500 h exposure. After ∼180 h exposure, PPHO-V+10U, PPHO-V+25U and PPHO-V+25P all had a mixture of samples that drew to the limit of the tensile machine travel and samples that did not.

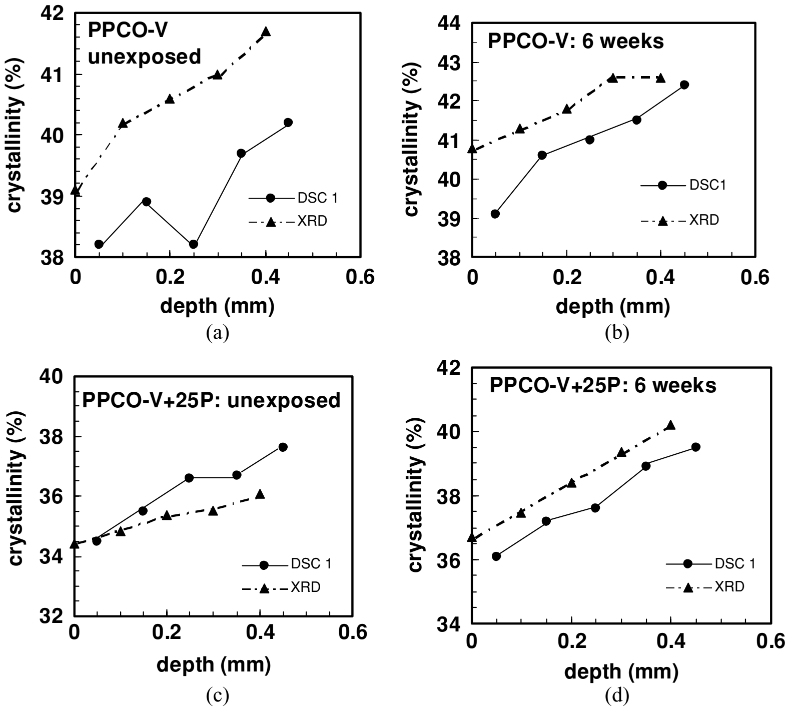
3.2.5. PPCO

The maximum stress data for the materials based on PPCO-V were bunched fairly closely up to 500 h UV exposure (Fig. 1e) but then significant strength decline set in with the most rapid fall shown by the blends containing photodegraded recyclate. The results for the blends with undegraded recyclate are difficult to separate from those for PPCO-V. The variation in measurements was not particularly great. The largest variation was observed with the blends containing photodegraded recyclate with highest SD values of ∼1 MPa for PPCO-V+10P after ∼1000 h and ∼0.8 MPa for PPCO-V+10P. The variation in results for PPCO-V and PPCO-V+10U was quite small, with SD <0.4 MPa at all exposures.

The ductility measurements for the materials based on PPCO-V show interesting partitioning (Fig. 2e). PPCO-V and all of the blends showed high ductility even after 200 h UV exposure. After that, only PPCO-V+10U retained the ability to draw beyond the tensile test machine crosshead travel limit. After 500 h UV exposure, the second most ductile PPCO material was PPCO-V+25U. The least ductile materials at this level of exposure were the two blends with photodegraded recyclate, with PPCO-V+25P recording the lowest value. PPCO-V was intermediate between the pair of blends with undegraded recyclate and the pair with photodegraded recylcate (Fig. 2e). The results measured at ∼500 h exposure were quite scattered, with SDs of ∼35% for all except PPCO-V+25U for which SD was ∼55%. Although this means that there is some overlap of the error bars, the separation of the averages is sufficiently large to indicate that there is probably a significant effect here. It is noted that the following specimen types showed a mixture of samples that drew to the limit and those that did not: PPCO-V after ∼200 h and PPCO-V+10U after ∼200 h and after ∼500 h. All blends reached an advanced state of embrittlement by 720 h UV exposure (Fig. 2e).

3.3. Crystallinity measurements

Crystallinity depth profiles obtained using DSC and XRD measurements on samples extracted at 0.1 mm thickness intervals have been reported previously [21, 23]. Photo-oxidation leads to changes in crystallinity; the largest changes in crystallinity occurred in the 0.5 mm depth closest to the exposed surface. This is illustrated for the case of PPCO in Fig. 3 in which both DSC and XRD results are given for the virgin material in the unexposed state (Fig. 3a) and after 6 weeks UV exposure (Fig. 3b), and for the blend containing 25% photodegraded recyclate unexposed (Fig. 3c) and after 6 weeks exposure (Fig. 3d). The DSC results were obtained in the first heating run ("DSC1"); results obtained from a second, reheating, run are given elsewhere [21] and can be used to assess the crystallizability of the material (as op-



(a) (b) (c) (d)

Figure 3 Crystallinity measurements made at various depths from the surface using XRD and DSC for virgin PPCO (a, b) and for its blend with 25% recyclate, PPCO-V+25P (c, d). Results are given for the unexposed state (a, c) and after 6 weeks UV exposure (b, d).

posed to the crystallinity of the processed and UV-exposed material that is the concern in the current paper). The absolute crystallinity values measured by the two methods are not in exact agreement, for reasons discussed elsewhere [21], but the trends are the same. Therefore in the current paper only data obtained using DSC will be used to show the changes occurring in the samples on UV exposure from here on. Because the first 0.5 mm depth from the exposed surface is the part that is most severely embrittled and generally leads to changes in the tensile failure properties, the results are summarised by taking the average of the crystallinity values measured for the depths 0.1–0.2, 0.2–0.3, 0.3–0.4 and 0.4–0.5 mm respectively (i.e. for 0.1–0.5 mm depth), Fig. 4. The results for the first layer (0–0.1 mm) were quite erratic for some of the materials, possibly because of a very advanced state of degradation in this layer, and the results for this layer have been ignored. In some cases (denoted in the caption of Fig. 4) crystallinity measurements were made only at three locations: the surface layer (0–0.1 mm); the 0.3–0.4 mm layer; and a layer near to the centre of the bar. In these cases the results for the 0.3–0.4 mm layer are used in place of the average for the 0.1–0.5 mm region.

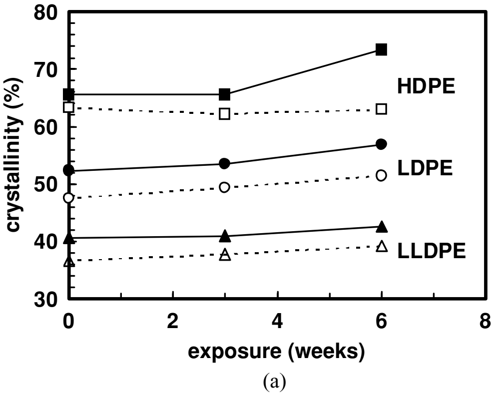
3.4. Scanning electron microscopy: HDPE

It was observed above that HDPE-V showed a significant drop in ductility between 500 h and 1000 h UV exposure. Highly ductile zones were present on the fracture surface after ∼500 h exposure (Fig. 5a) whereas ductile features were very restricted in size and abundance after 1000 h exposure (fig. 5b). The as-moulded face of a sample tensile tested after ∼500 h exposure showed multiple cracks in a "crazy paving" pattern (Fig. 6a). The cracks were apparently fairly shallow. In a similar location in a bar exposed for ∼1000 h before tensile testing, just one crack is visible apart from the one that caused failure (Fig. 6b). This crack is much deeper than those shown in Fig. 6a. An intermediate state of ductility was observed in a sample tensile tested after 720 h exposure (Fig. 7). A HDPE-V+10P sample that was tensile tested after ∼500 h exposure showed many features reminiscent of Fig. 7 (Fig. 8); the average failure strain for such samples is similar (Fig. 2a). Even less ductility is in evidence on the fracture surface of HDPE-V+25P tensile tested after ∼500 h exposure (Fig. 9). This correlates with the lower strain at break of such samples (Fig. 2a). Another sample of HDPE-V+25P, tensile tested after 720 h exposure, was heavily cratered (Fig. 10a). The craters seemed to be nucleated by flaws, some of them quite large (Fig. 10b).

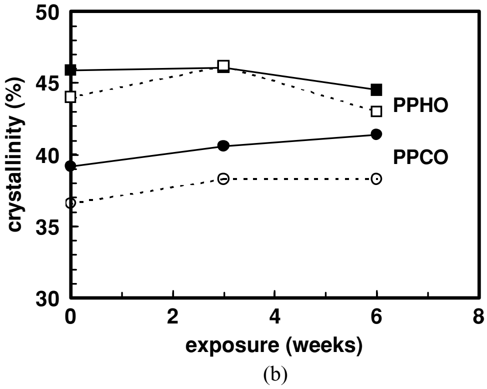
4. Discussion

4.1. Molecular composition of recycled polymer

It is worth reflecting on the molecular composition of the materials generated by blending recyclate and virgin



(a)



(b)

Figure 4 Average crystallinity measurements for the material between 0.1 mm and 0.5 mm below the exposed surface for samples made from virgin polymer (solid symbols) and blends of virgin polymer (75%) with photodegraded recyclate (25%) (open symbols). (a) HDPE, LDPE and LLDPE; (b) PPHO and PPCO. The unexposed virgin polyethylenes and unexposed virgin PPHO are represented by the value measured using the layer 0.3 mm–0.4 mm from the surface instead of the average defined previously. Data from DSC measurements.

polymer in the manner employed here. Photodegradation and the thermo-mechanical degradation that occurs during re-processing are both oxidation processes that produce shorter molecules, crosslinking between molecules, and molecular defects (such as carbonyl groups). During photodegradation of thick mouldings of the kind used in this study the molecules that were located near the exposed surface become heavily degraded, broken into smaller fragments and with crosslinks also introduced. The molecules in this component of the recyclate will also have a high concentration of carbonyl groups and other molecular defects prior to re-processing. Small molecules generally crystallize more readily than long ones because they are less inhibited by entanglements, but the defects on the molecules in the heavily degraded recycled component will discourage crystallization because they will not fit into the crystal lattice [23, 28]. Therefore, there are two major characteristics (molecule size reduction and the introduction of molecular defects) that affect the crystallinity in opposite senses when polymer containing degraded molecules is recrystallized. Higher crystallinity will favour higher stiffness and strength but lower ductility. The data for the as-moulded samples given in Fig. 4 (at zero exposure time) show that for all of the materials dealt with in this investigation, the effect of including recyclate was to reduce the crystallinity. If this were the only effect, it would lead to a fall in strength and, probably, an increase in ductility. None of the polymers for which crystallinity data are available displayed this behaviour. HDPE-V blends with recyclate that had not been photodegraded appear to behave in the predicted manner but no crystallinity measurements were made and the correlation remains unproven.

Because crystallinity measurements for the blends containing photodegraded recyclate were lower than those obtained with the virgin polymers it is deduced that the change in crystallinity was dominated by molecular defects rather than the small molecule effect. The introduction of the short molecules will, of course, have a direct effect on the mechanical properties because they will reduce the number of entanglements and this will reduce the strain at break.

4.2. Effect of the presence of recyclate in as-moulded blends

Some of the blends with recyclate possessed tensile properties that were significantly different to those of the virgin polymer in the as-moulded state. Interestingly, in most cases, the differences in property correlated most closely with the kind of recyclate (photodegraded or undegraded) than with the quantity (10% or 25%). Thus it is observed that the maximum stress recorded with the blends with photodegraded polymer was higher than for the virgin polymer with HDPE (Fig. 1a) and LLDPE (Fig. 1c) whereas it was lower than for the virgin polymer with LDPE (Fig. 1b), PPHO (Fig. 1d) and PPCO (Fig. 1e); the margin is smaller with PPHO and PPCO than for LDPE. The maximum stress values for blends with undegraded polymer were lower than for the virgin polymer with HDPE, LDPE and LLDPE (slightly). Therefore, for HDPE the effect on the maximum stress when photodegraded recyclate was added was opposite to that observed when undegraded recyclate was added. LLDPE gave a similar result.

The ranking of the materials based on strain at break is quite different to that based on the maximum stress recorded in the tensile tests. The lowest values of the strain at break were recorded with blends containing photodegraded polymer for HDPE (equal with HDPE-V) and LDPE. The lowest values recorded for LLDPE were obtained with the virgin polymer. With both polypropylenes, the virgin material and all blends were sufficiently ductile to resist failure up to the limit of crosshead travel in the tensile test and could not be ranked using this parameter.

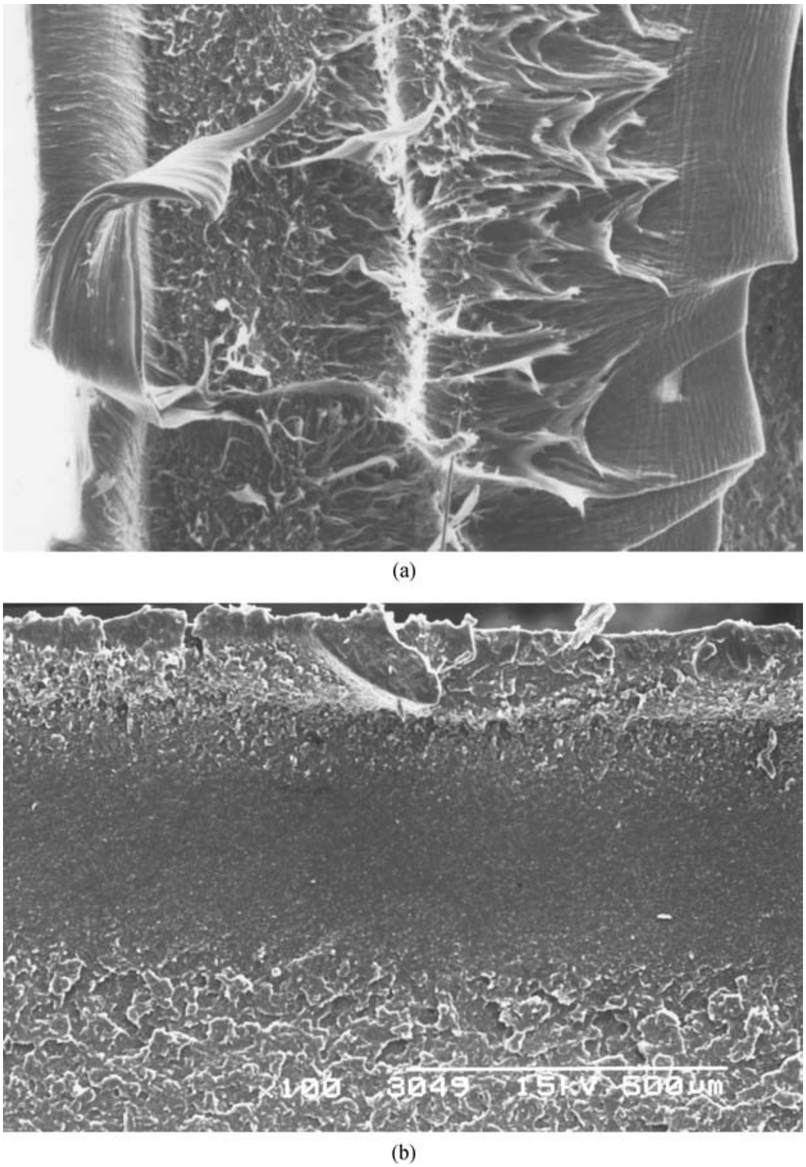


Figure 5 Fracture surfaces from HDPE-V samples tensile tested after (a) ∼500 h and (b) ∼1000 h UV exposure. In (b) the exposed surface is at the top, in (a) the exposed surface is on the left. SEM images at same magnification.

4.3. Effect of the presence of recyclate on photodegradation rate

The most important result in this study is that for all five polymers, the blends containing photodegraded recyclate were the first to reach an advanced state of embrittlement, as judged by the strain-at-break data. The ductility is closely related to the toughness of the material and this, rather than the strength, is the property that is most likely to determine whether or not a component fails. This is a very positive identification of the pro-degradant nature of photodegraded material present in a recyclate. It is noted that in the experiments reported here, the material that had suffered significant photodegradation prior to recycling was contained in the surface regions of the bars that were then recycled. Much of the material contained in the interior of the bars did not suffer advanced photodegradation, because of oxygen-diffusion limitation that leads to a steep depth profile of degradation [26, 33–39]. The severely-degraded component was then further diluted by blending (90% virgin + 10% recyclate and 75% virgin + 25% recyclate). The pro-degradant fraction is therefore quite small, but its effect on ductility is clear to see. Recyclate obtained from polymer films that can suffer photodegradation through the entire depth can be expected to be more potent. Comparison of the behaviour of the blends containing photodegraded recyclate with that of the blends with recyclate obtained from bars that had not been photodegraded showed that the effect could not be explained simply by defects produced by the thermomechanical

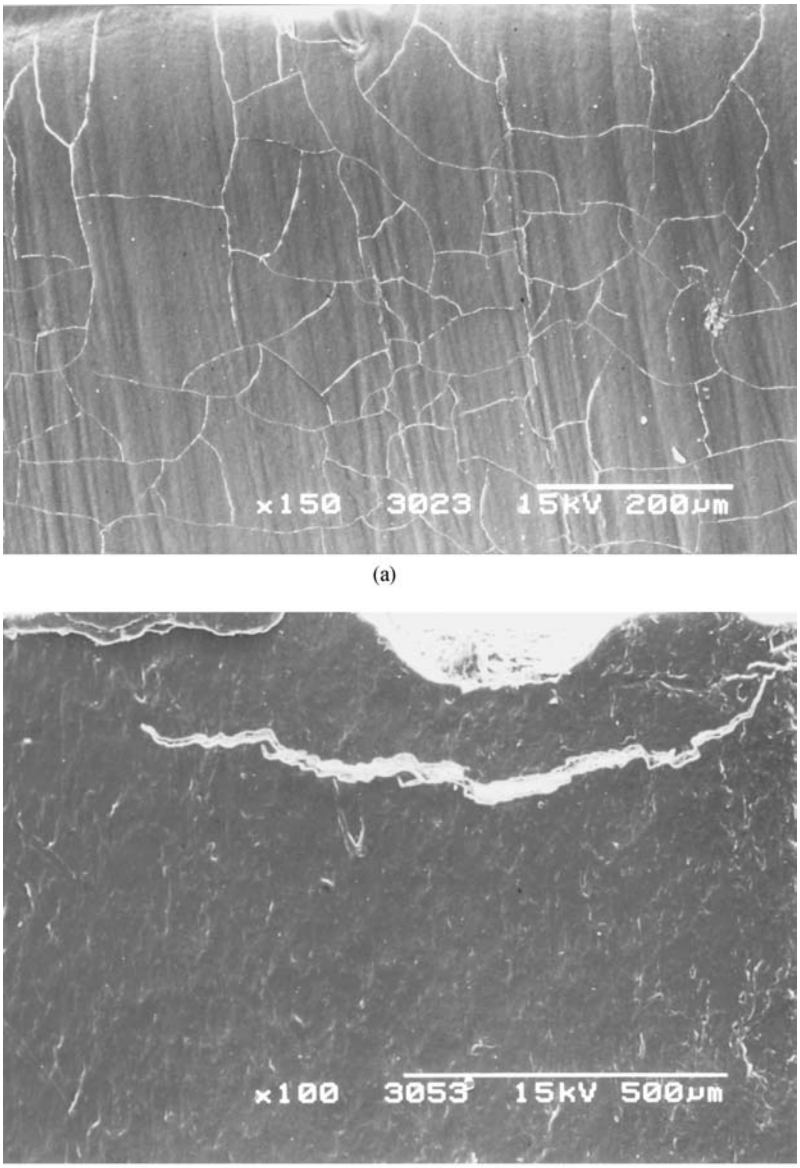


Figure 6 Irradiated surfaces of HDPE-V samples that were tensile tested after UV exposure for (a) ~500 h; (b) ~1000 h. Note the difference in magnification.

recycling action, even though this caused additional effects.

UV exposure caused more discrimination between the different blends than was observed in the as-moulded state. The greatest discrimination was generally apparent after ~500 h UV exposure. At this time it was observed in some of the families of materials that the maximum stress and strain at break measurements obtained with some blends had not changed while for others a significant fall in property was recorded. For all of the polymer types, the "V+xP" blends showed the lowest ductility; with HDPE, LLDPE and PPCO, the blends containing undegraded recyclate gave the highest values. The decline in the measured ductility of the HDPE blends with UV exposure correlated well with features observed by scanning electron microscope inspection of the fracture surfaces (Section 3.4).

These results show that the inclusion of photodegraded material in recyclate is potentially very detrimental. It is clearly advisable to analyse any source of recycled material to check for the presence of pro-degradants before utilising it in a critical application in which it may be exposed to UV.

4.4. Changes in crystallinity during UV exposure (chemi-crystallization)

Crystallinity measurements were made with the virgin materials and with the blends containing 25% photodegraded recyclate in the as-moulded state and after UV ex-

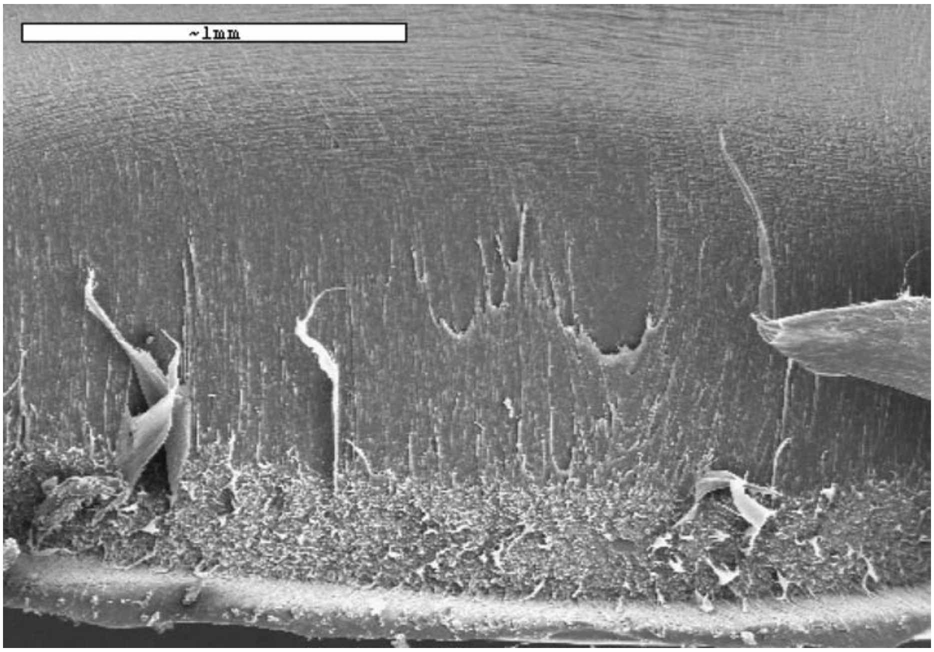


Figure 7 Fracture surface of HDPE-V sample that was tensile tested after 720 h UV exposure.

posures of 3 weeks and 6 weeks respectively. The changes in crystallinity depth profile caused by photoageing these materials have been given previously [21, 23] and average values for the material near to the exposed surface taken from these studies are given in Fig. 4. It is noted that, in every case, prior to exposure, the blend containing photodegraded recyclate had lower crystallinity than the virgin material, indicating that the molecular defect effect dominated over the small molecule effect. In almost every case, UV exposure caused an increase in the crystallinity of the polymer near to the surface ("chemi-crystallization" [21, 23, 29]). The increase in crystallinity is, of course, accompanied by a corresponding decrease in the amorphous content. For semi-crystalline polymers such as polyethylene and polypropylene for which the glass transition temperature is below room temperature, the amorphous phase is very deformable and the reduction in the fraction of the material that is in this state will inevitably reduce the overall deformability of the material and cause it to become more brittle. The increasing number of crosslinks [20, 22] also reduces ductility, and the increase in chain scission reduces the network of entanglements that the amorphous phase requires for its mechanical integrity. Therefore progressive photodegradation can be expected to cause increasing embrittlement of the material. Furthermore, because the crystals are denser than the amorphous phase, the increase in crystallinity is accompanied by a reduction in volume. If the change in crystallinity occurs primarily near to the surface, this results in the material in this region shrinking more than that in the underlying zone nearer to the centre of the moulded bar, producing an increment of tensile residual stress near to the surface [30, 31]. Most injection mouldings made from thermoplastics have residual compressive stresses near to the surface in the as-moulded state [32] and the tensile increment caused by chemi-crystallization will reduce the compressive stress, or, if large enough, will reverse it so that tensile stresses develop near to the exposed surface. This has been analysed quantitatively for data obtained with polypropylene [31]. The presence of compressive stresses near to the surface discourages the initiation and growth of cracks but the development of tensile stress has the opposite effect, providing the driving force for crack initiation and propagation in the material that has already become weakened by the photochemical changes. Therefore the increase in crystallinity will increase the tendency to brittle behaviour indirectly through this mechanism as well as directly, through the reduction in the deformable amorphous phase content.

Fig. 4a shows that, for the polyethylenes, the crystallinity increased with exposure except, perhaps, for HDPE containing 25% recycled photodegraded polymer, for which very little change is evident. HDPE-V did not change much in the first 3 weeks of UV exposure but the crystallinity increased markedly between 3 and 6 weeks exposure. Correspondingly, in Fig. 2a, the fall in strain at break between 3 and 6 weeks exposure was much greater than that observed to occur in the first 3 weeks. On the other hand, HDPE-V+25P showed a similar fall in the strain at break from 0-3 weeks exposure and from 3–6 weeks respectively (Fig. 2a). Therefore the change in ductility could be connected with embrittlement associated with an increase in crystallinity with exposure (Fig. 4a).

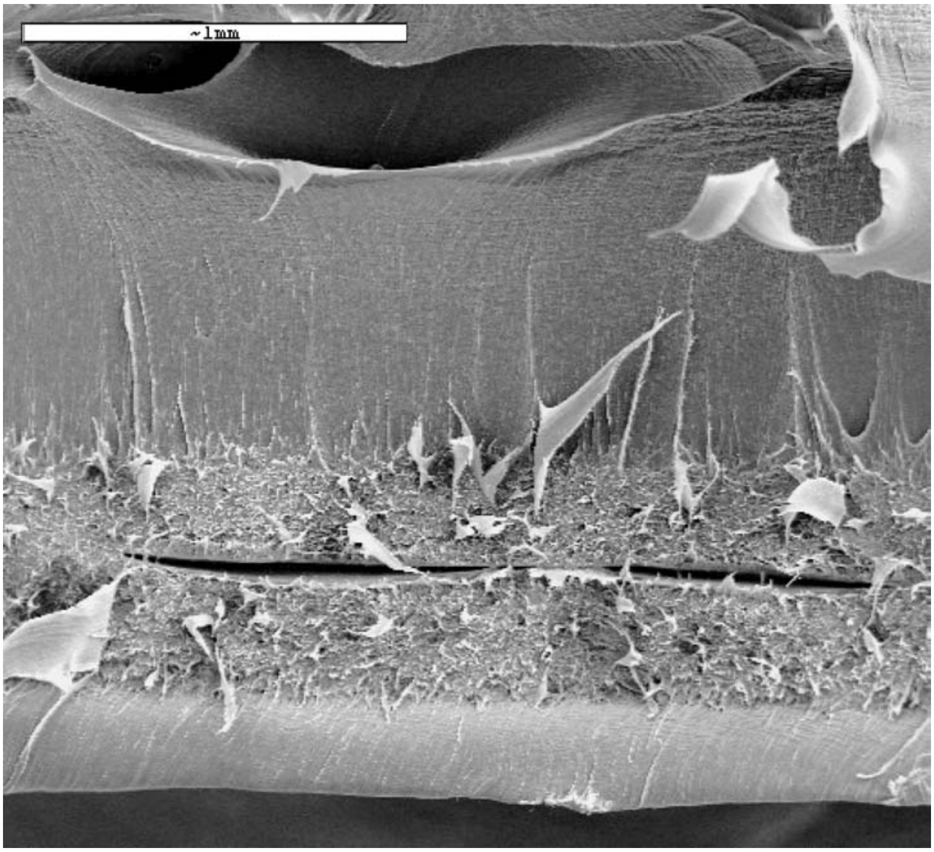


Figure 8 Fracture surface of HDPE-V+10P tensile tested after ∼500 h UV exposure.

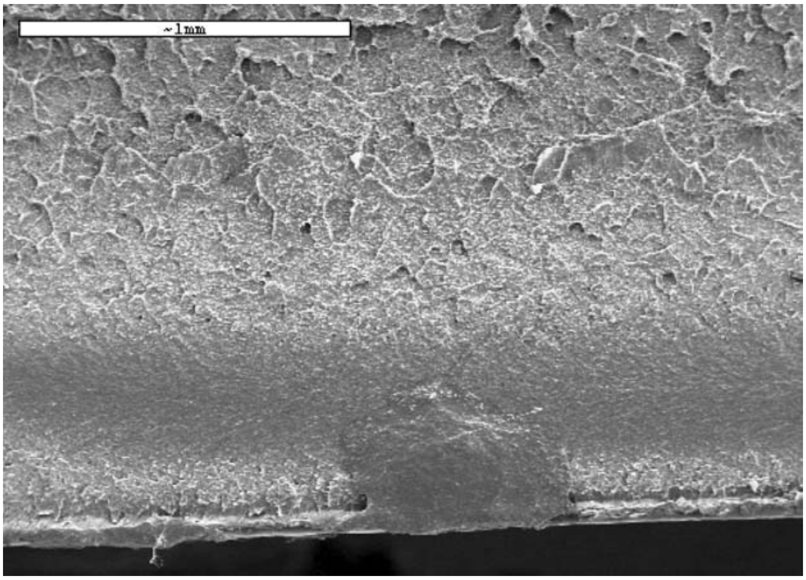
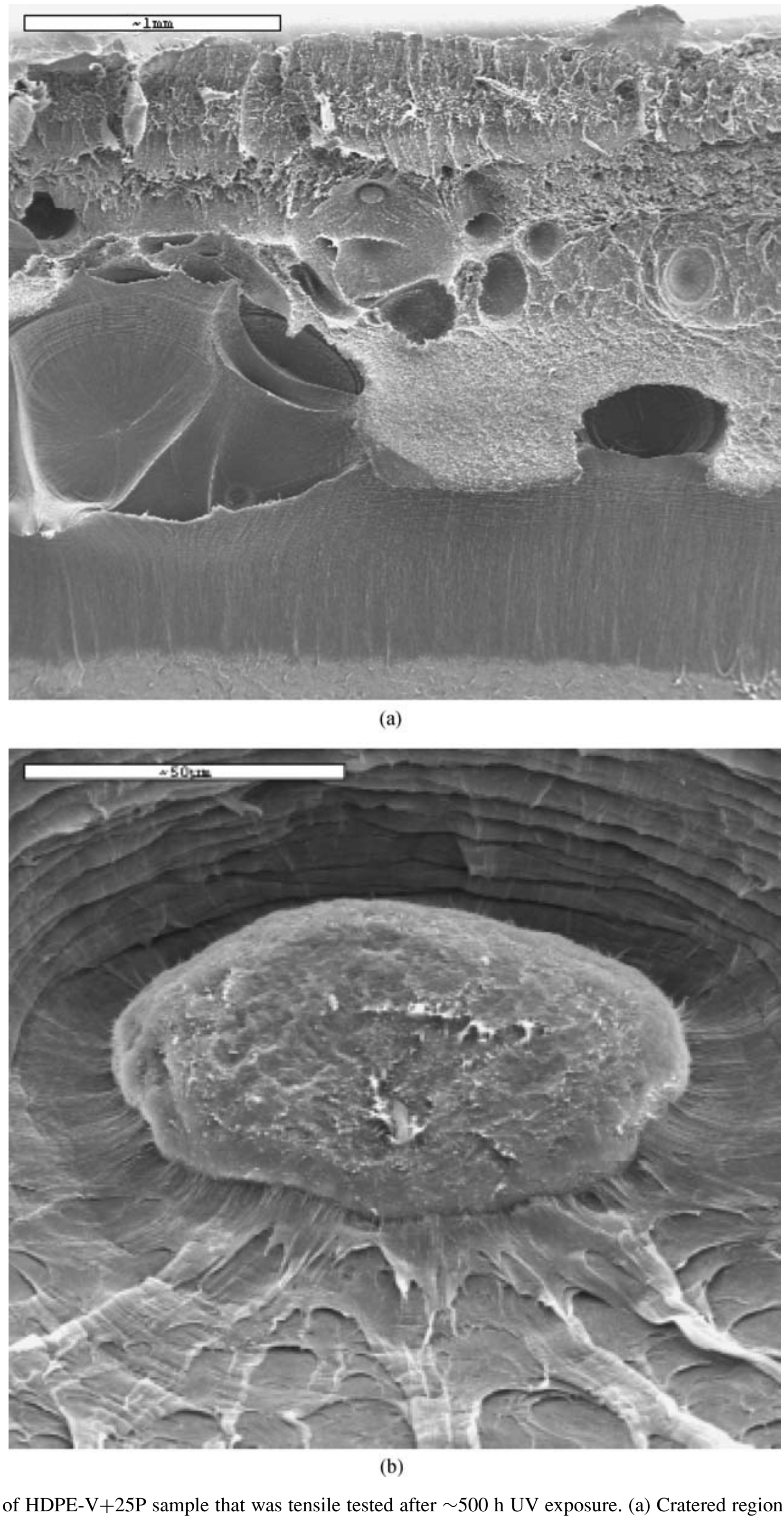


Figure 9 Fracture surface of HDPE-V+25P sample that was tensile tested after ∼500 h UV exposure.

Both LDPE-V and LDPE-V+25P showed steady increase in crystallinity with exposure (Fig. 4a) and steady decrease in strain at break (Fig. 2b). Again, this is consistent with the hypothesis that increasing crystallinity correlates with decreased ductility.

The crystallinity changes are fairly similar in LLDPE-V and LLDPE-V+25P in the 6 weeks exposure period, whereas the changes in the ductility of LLDPE-V and LLDPE-V+25P were very different over the 6 week exposure period (Figs. 4a and 2c). The strain at break for



(a)

(b)

Figure 10 Fracture surface of HDPE-V+25P sample that was tensile tested after ∼500 h UV exposure. (a) Cratered region; (b) Flaw at centre of one of craters.

LLDPE-V did not change much for exposures ≤ 6 weeks duration whereas for LLDPE-V+25P it fell significantly in the first 3 weeks and fell much more during the second 3 week period (Fig. 2c). It seems that for LLDPE-V and LLDPE-V+25P, factors other than crystallinity dominated the ductility changes caused by UV exposure.

PPCO-V and PPCO-V+25P both increased crystallinity with UV exposure and displayed greater change in weeks 0–3 than in weeks 3–6. Both showed steep reductions in strain at break over the period 1–4 weeks (Fig. 2e), seemingly correlating with increased crystallinity.

Unlike all of the other materials, PPHO showed lower crystallinity after 6 weeks UV exposure than previously (Fig. 4b). All blends based on PPHO-V failed catastrophically after UV exposures of 6 weeks and above (Fig. 2).

5. Conclusions

The studies presented here were performed as part of an investigation into the recyclability of polymers that had been photodegraded prior to reclamation. It has been shown that bars made from blends containing photodegraded recyclate developed very brittle behaviour much more rapidly when exposed to UV irradiation than bars made from the corresponding virgin polymer or blends containing undegraded recyclate. The pro-degradant nature of the previously photodegraded polymer was thus demonstrated. It is noted that the recycled material was obtained from bars that were 3 mm thick and were heavily photodegraded near the surface but much less degraded in the interior, and that a relatively small fraction of the material was therefore responsible for the enhanced sensitivity. The strength of blends of virgin polymer with recycled polymer did not follow any particular pattern.

Some of the effects produced by UV exposure could be correlated with changes in crystallinity (chemi-crystallization) in HDPE, LDPE, PPHO and PPCO but there were evidently additional effects influencing property change with LLDPE.

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References

1. F. P. LAMANTIA, *Polym. Degrad. Stab.* **14** (1986) 241
2. F. P. LAMANTIA and D. CURTO, *ibid.* **36** (1992) 131
3. F. P. LAMANTIA, *ibid.* **37** (1992) 145
4. H. HERBST, K. HOFFMANN, R. PFAENDNER and F. SITEK, *Kunststoffe* **82** (1992) 783.
5. J. POSPÍŠIL, F. A. SITEK and R. PFAENDNER, *Polym. Degrad. Stab.* **48** (1995) 351.
6. R. PFAENDNER, H. HERBST, K. HOFFMANN and F. SITEK, *Angew. Makromol. Chem.* **232** (1995) 193.
7. R. PFAENDNER, H. HERBST and K. HOFFMANN, *Engineering Plastics* **9** (1996) 249.
8. J. POSPÍŠIL, S. NEŠPŮREK, R. PFAENDNER and H. ZWEIFEL, *Trends in Polymer Science* **5** (1997) 294.
9. N. TZANKOVA DINTCHEVA, N. JILOV and F. P. LA MANTIA, *Polym. Degrad. Stab.* **57** (1997) 191.
10. R. PFAENDNER, H. HERBST and K. HOFFMANN, *Macromol. Symp.* **135** (1998) 97.
11. H. HERBST and R. PFAENDNER, *Polymer Recycling* **4** (1999) 75.
12. C. N. KARTALIS, C. D. PAPASPYRIDES and R. PFAENDNER, *Polym. Degrad. Stab.* **70** (2000) 189.
13. C. N. KARTALIS, C. D. PAPASPYRIDES, R. PFAENDNER, K. HOFFMANN and H. HERBST, *J. Appl. Polym. Sci.* **77** (2000) 1118.
14. C. N. KARTALIS, C. D. PAPASPYRIDES, R. PFAENDNER, K. HOFFMANN and H. HERBST, *Polym. Eng. Sci.* **41** (2001) 771.
15. C. D. PAPASPYRIDES, C. N. KARTALIS and R. PFAENDNER, *Polymer Recycling* **6** (2001) 1.
16. R. PFAENDER, Chap.19 in Plastics Additives Handbook, 5th ed. edited by H. Zweifel (Hanser, Munich, 2001) 973.
17. S. AL-MALAIKA, S. CHOHAN, M. COKER, G. SCOTT, R. ARNAUD, P. DABIN, A. FAUVE and J. LEMAIRE, *J.M.S. Pure Appl.Chem.* **A32** (1995) 709.
18. W. STEVENSON and J. R. WHITE, *J. Mater. Sci.* **37** (2002) 1091.
19. E. LOYD and J. R. WHITE, *J. Mater. Sci. Lett.* **21** (2002) 627.
20. I. H. CRAIG, J. R. WHITE, A. V. SHYICHUK and I. D. SYROTYNSKA, *Polym. Eng. Sci.* **45** (2005) 579.
21. J. R. WHITE, I. H. CRAIG and PHUA CHAI KIN, *Polymer* **46** (2005) 505.
22. A. V. SHYICHUK, J. R. WHITE, I. H. CRAIG and I. D. SYROTYNSKA, *Polym. Degrad. Stab.* **88** (2005) 415.
23. I. H. CRAIG and J. R. WHITE, *Polym. Eng. Sci.* **45** (2005) 588.
24. R. STEWART, G. SMITH, I. H. CRAIG and J. R. WHITE, unpublished studies.
25. B. G. WILLOUGHBY, A. GOLBY, J. DAVIES and R. CAIN, *Polymer Test.* **22** (2003) 553.
26. B. O'DONNELL and J. R. WHITE, *J. Mater.Sci.* **29** (1994) 3955.
27. M. M. QAYYUM and A. DAVIS, *Polym.Degrad.Stab.* **6** (1984) 201.
28. M. S. RABELLO and J. R. WHITE, *Polymer* **38** (1997) 6389.
29. *Idem.*, *ibid.* **38** (1997) 6379.
30. LI TONG and J. R. WHITE, *Plast. Rubb. Compos. Procs. Applics.* **25** (1996) 226.
31. LI TONG and J. R. WHITE, *Polym. Eng. Sci.* **37** (1997) 321.
32. J. R. WHITE, *Polymer Test.* **4** (1984) 165 [Also appeared as Chapter 8 in Measurement Techniques for Polymeric Solids, edited by R. P. Brown and B. E. Read (Elsevier, Barking, 1984)]
33. L. AUDOUIN, V. LANGLOIS, J. VERDU and J. C.M. DE BRUIJN, *J. Mater. Sci.* **29** (1994) 569.
34. K. T. GILLEN, J. WISE and R. L. CLOUGH, *Polym. Degrad. Stab.* **47** (1995) 149.
35. J. WISE, K. T. GILLEN and R. L. CLOUGH, *Polymer* **38** (1997) 1929.
36. J. C. M. DE BRUIJN, *Adv. Chem. Sers.* **249** (1996) 599.
37. G. E. SCHOOLENBERG and P. VINK, *Polymer* **32** (1991) 432.
38. T. J. TURTON and J. R. WHITE, *J. Mater.Sci.* **36** (2001) 4617.
39. *Idem.*, *Polym. Degrad. Stab.* **74** (2001) 559.