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Observation of different photo-degradation behaviour in two similar polypropylenes

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The photodegradation properties of injection moulded bars 3 mm thick made from two nominally similar toughened polypropylene compounds (PP and MPP) have been found to differ remarkably in some aspects. In both of them the plot of the mass average molecular mass (M_w) versus distance from the exposed surface displayed a steep sigmoidal shape with very low values near the surface and values close to the undegraded value near the bar centre. With PP the steepest part of the M_w versus depth plot remained at almost the same position irrespective of exposure time for tests carried out for periods up to 64 weeks whereas with MPP the steepest part of the plot shifted progressively in from the exposed surface as exposure increased. The tensile strength fell rapidly with exposure time in both PP and MPP but with PP partial recovery was observed whereas with MPP the fall in strength appeared to be monotonic with exposure time.

1. Introduction

From the literature on photo-degradation of polymers it is evident that different generic types behave quite differently from one another. Studies of the behaviour of particular generic types generally concentrate on the mechanisms of degradation or on the effect of additives such as stabilizers or pigments. A few studies have revealed differences in behaviour of polymers within a single generic type. An example is the observation that synergistic effects occurred in Ziegler type polyethylene having a stabilizer system containing both hindered phenols and phosphites in UV exposure whereas under some conditions antagonism was observed when a Philips type polyethylene with the same stabilizer system was tested [1]. This was attributed to the higher level of unsaturation in the Philips polymer. Different polyethylenes give different decomposition products even when they are additive-free [2, 3]. In the work presented here the observations were obtained as part of a study of the effect of stabilizer and pigment on the degradation profiles in photo-degraded polypropylene [4, 5]. Two very similar polymers were used in the course of this work. We were surprised to discover some significant differences in their degradation behaviour and this is the subject of this report.

2. Experimental

2.1. Materials and specimen preparation

The materials used in this study were based on Montell Moplen polypropylene grade EPF 30U which was provided in both unstabilized (PP) and stabilized (PPS) form. Moplen EPF 30U is toughened by a rubbery ethylene–propylene copolymer which separates as spherical inclusions. A second similar polymer made by a different route but possessing properties similar to that of EPF 30U was supplied by the manufacturer as X-EPF 30U (= MPP in the coding used below). It was provided in both unstabilized (MPP) and stabilized (MPPS) form. The stabilizer system for both PPS and MPPS was formulated from the Ciba-Geigy range and consisted of 0.3% Tinuvin 770, a monomeric hindered amine light stabilizer (HALS), 0.3% Chimassorb 944 (an oligomeric HALS), and 0.3% Irganox B215 (a phenolic antioxidant). The manufacturer prepared the MPP and MPPS grades in response to our request for extra supplies of PP and PPS after the project was in progress and after production of EPF 30U has ceased. MPP was designed to replicate EPF 30U and most of the main characteristics, including ethylene content and viscosity, were a good match. The molecular mass distribution of MPP was skewed towards higher sizes and was slightly broader than that of PP (Fig. 1). The size and distribution of the rubbery phase was similar for the two materials (Fig. 2).

The polymers were injection moulded into tensile test bars (190 mm × 12.7 mm) with thickness 3 mm using a tool with an end-gated cavity.

2.2. Photo-degradation and characterization

Photo-degradation was conducted in the laboratory at 30 ± 1°C using *Q-Panel UVA-340* tubes with output in

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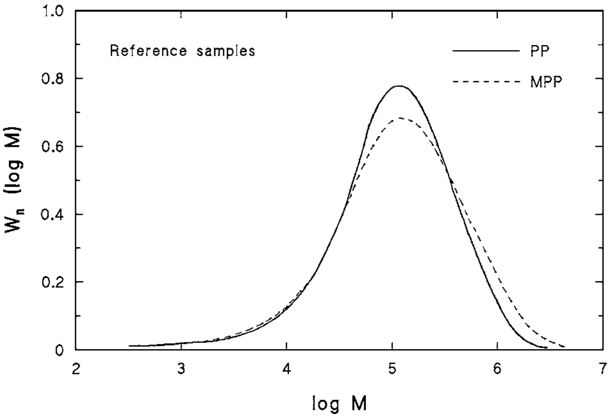
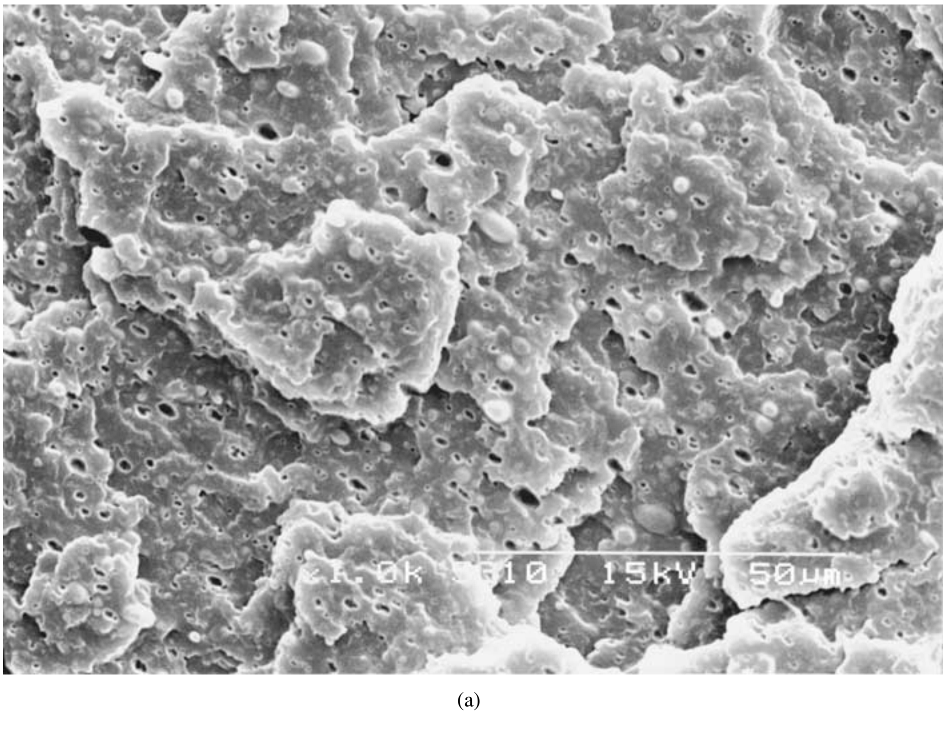
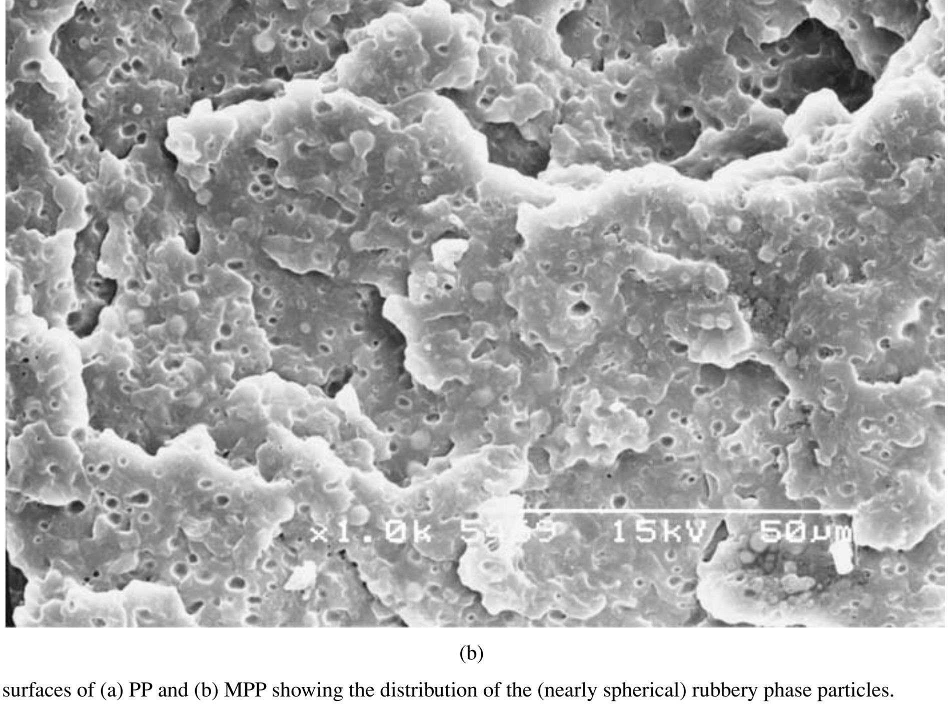


Figure 1 Molecular mass distributions for PP and MPP.

the ultraviolet (UV) region matching the solar radiation spectrum at the Earth's surface fairly closely in the wavelength range below 360 nm down to the cut-off at approximately 295 nm and using equatorial intensities [4–8]. After exposures for varying periods samples were removed from the bars by milling and the molecular weight distributions and molecular mass averages were obtained by gel permeation chromatography (GPC) at RAPRA (Shawbury, Shrewsbury) using conditions and procedures described elsewhere [4–7, 9]. The residual stress distributions in bars made from PP, PPS, MPP and MPPS were measured using the layer removal procedure [4, 10, 11]. Residual stress distributions were measured in as-moulded bars and in some other bars after a period of UV exposure.



(a)



(b)

Figure 2 Fracture surfaces of (a) PP and (b) MPP showing the distribution of the (nearly spherical) rubbery phase particles.

Tensile tests were conducted on selected samples using a crosshead speed of 50 mm min^{-1}. The fractured ends were cut from selected samples, mounted on SEM stubs and goldcoated in preparation for inspection in the scanning electron microscope (SEM).

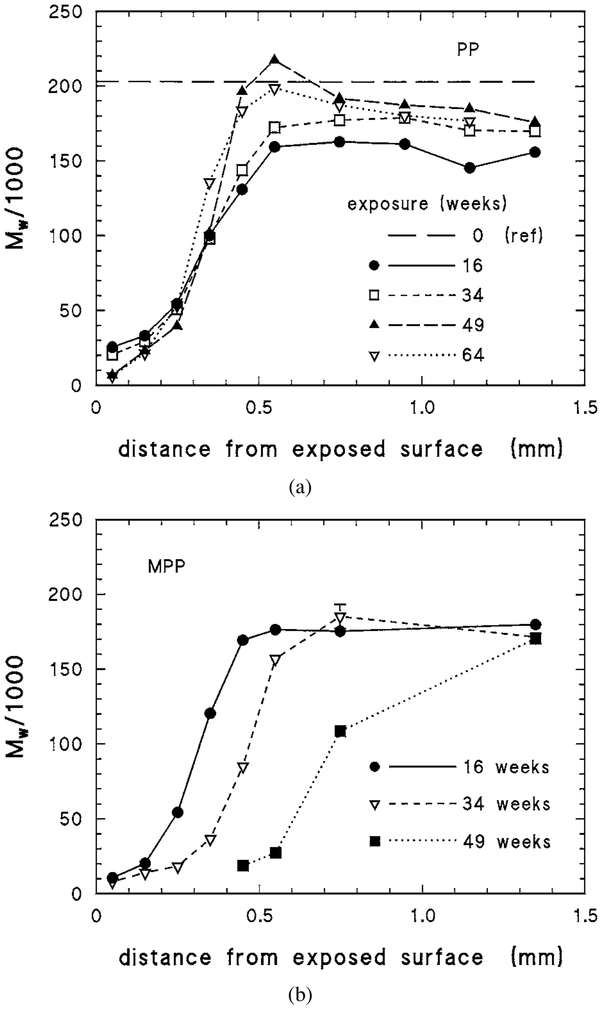
3. Results

3.1. Molecular mass

Fig. 3a shows the variation of the mass average molecular mass, M_w with depth in (unstabilized) PP for exposure times of 16, 34, 49 and 64 weeks. It is evident that the major changes take place within 0.5 mm of the surface. The M_w distributions for all exposure times show a steep change from approximately 0.25 mm to 0.55 mm. A quite different result is shown for MPP where the steep change is found to move towards the interior of the bar as the exposure time is increased (Fig. 3b). Stabilized PPS and MPPS both showed a progressive fall in M_w with exposure time, maintaining a fairly flat profile through the bar depth (Fig. 4).

3.2. Residual stress distributions

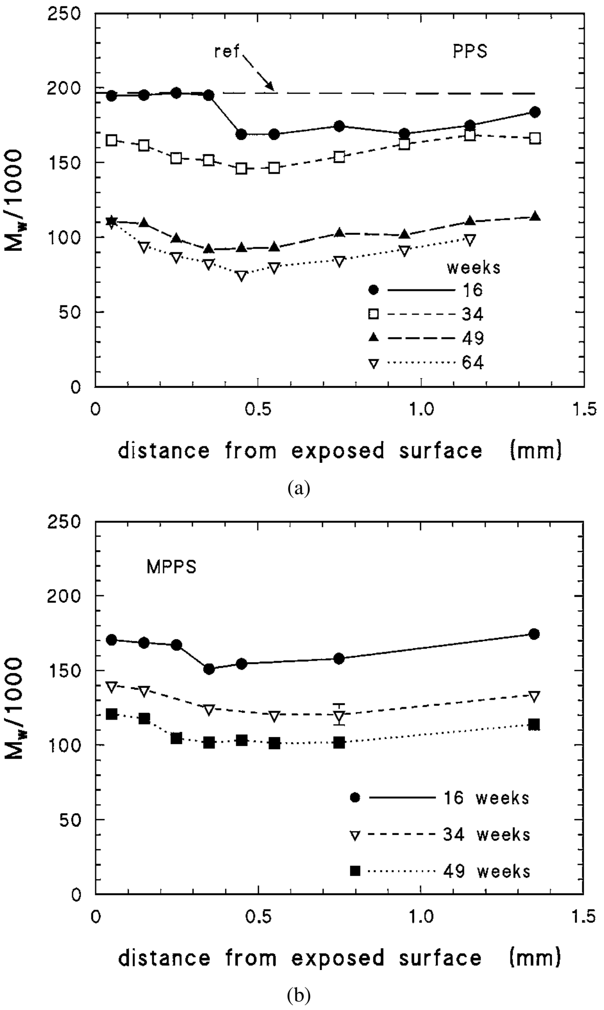
Residual stress distributions for PP and PPS as-moulded and after 34 weeks UV exposure are shown in Fig. 5. The distributions are very conventional with compressive stresses near the surface balancing weaker tensile stresses which are present in the interior, occupying a larger proportion of the bar section. The tensile stress is nowhere above 1 MPa in any of the samples and the maximum compressive stress, observed near the bar surface, is less than 2 MPa. At such modest



(a)

(b)

Figure 3 M_w versus depth for unstabilized polypropylene samples after UV exposure for various times: (a) PP; (b) MPP.



(a)

(b)

Figure 4 M_w versus depth for stabilized polypropylene samples after UV exposure for various times: (a) PPS; (b) MPPS.

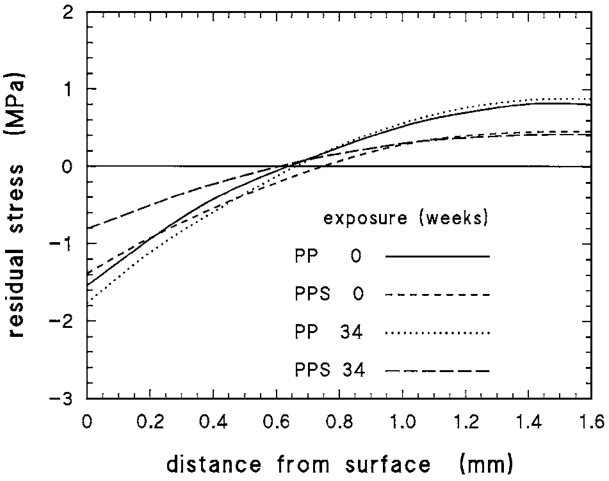
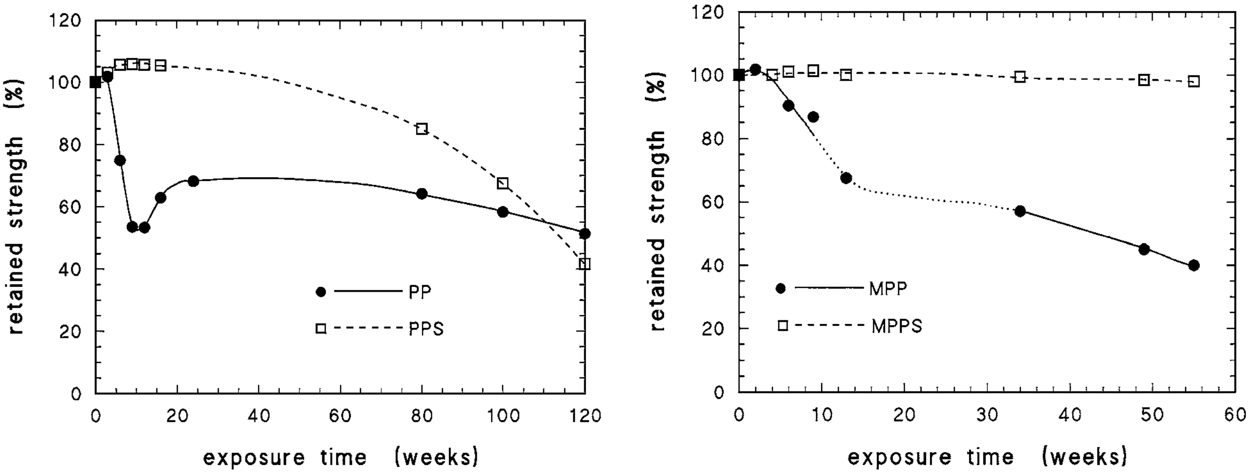
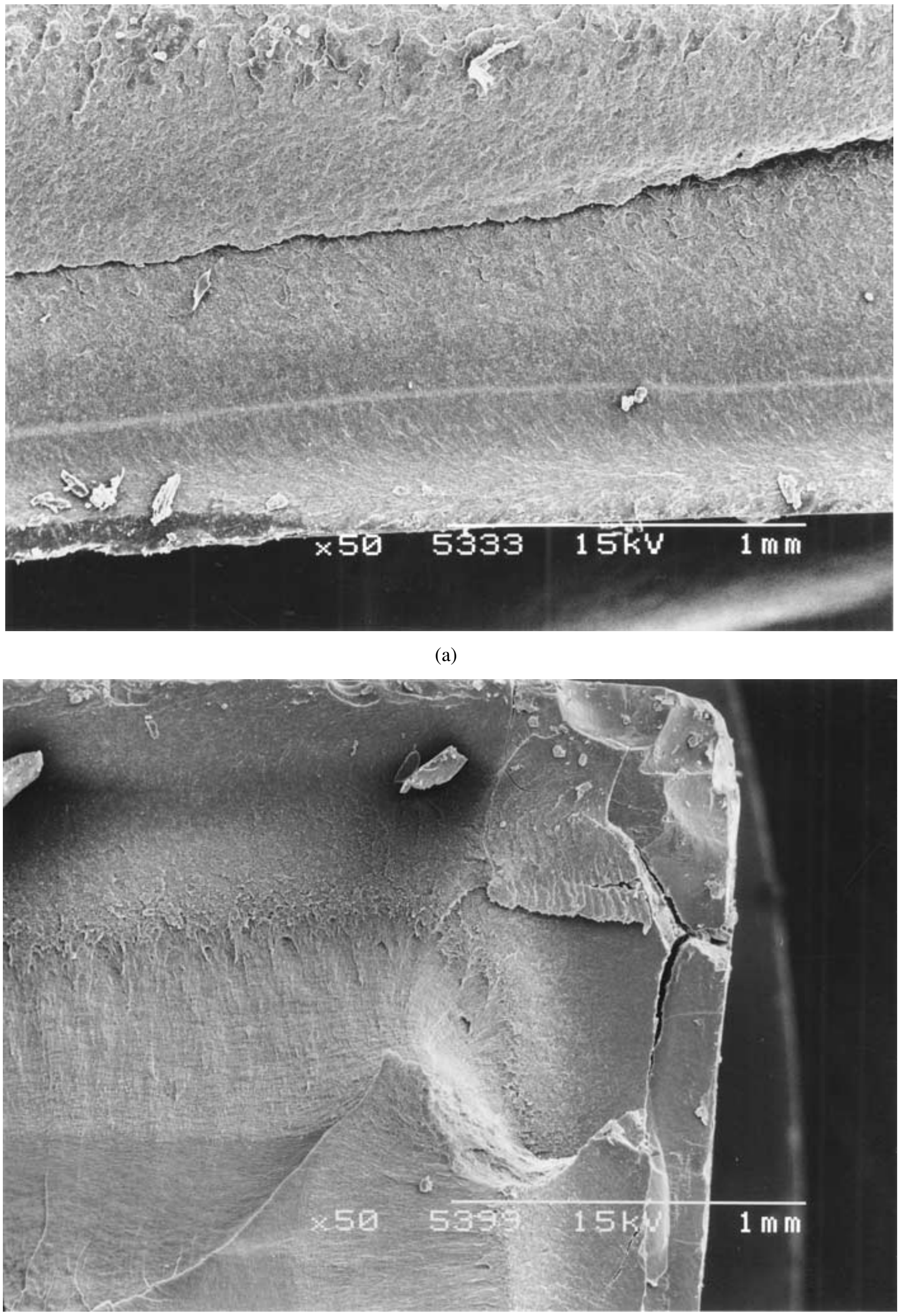


Figure 5 Residual stress distributions in PP and PPS bars, as-moulded and after 34 weeks UV exposure. The analysis is shown for approximately half of the bar (total thickness ∼3 mm). Tensile stresses (positive) dominate in the interior. In the case of UV- exposed samples the reference surface from which layers were removed was the exposed surface: the stress distribution may not have been symmetrical about the midplane in such samples but it is evident that UV exposure did not produce major changes in these materials.



(a) (b)

Figure 6 Strength (relative to the unexposed value) as a function of UV exposure time for (a) PP and PPS; (b) MPP and MPPS.



(a)

(b)

Figure 7 Fracture surface of PP after (a) 20 weeks exposure; (b) 80 weeks exposure.

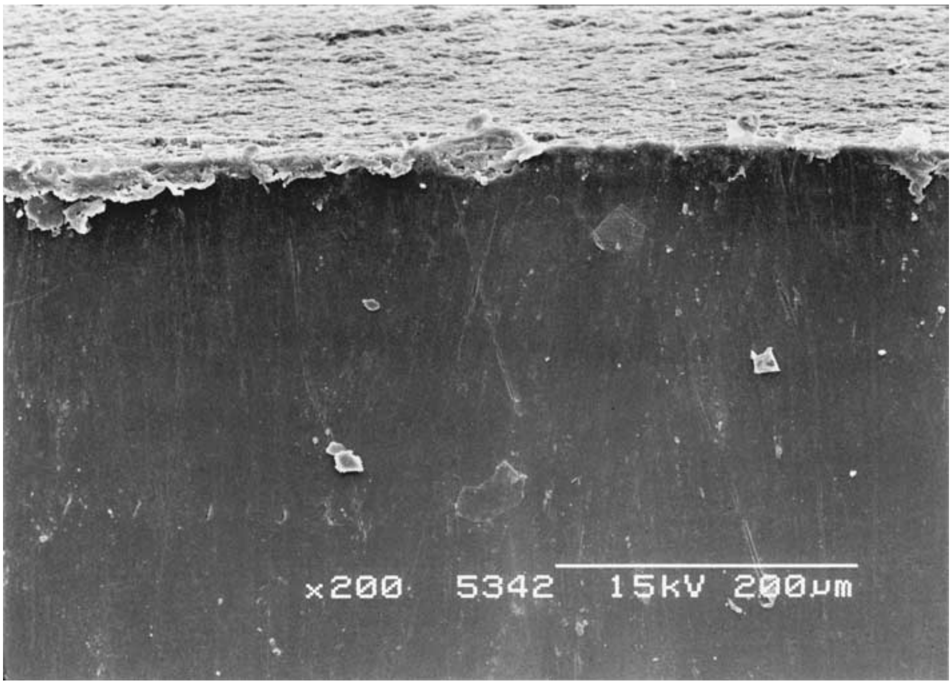


Figure 8 Oblique view of fracture surface of PP after tensile testing following 20 weeks exposure, showing moulded surface (with no signs of cracking).

Figure 9 Cracking in surface of PP after tensile testing following 80 weeks exposure.

levels of stress, it is unlikely that residual stress has any significant influence on photo-degradation. Similar small values of residual stress were measured in MPP-series mouldings [4, 5].

3.3. Tensile behaviour

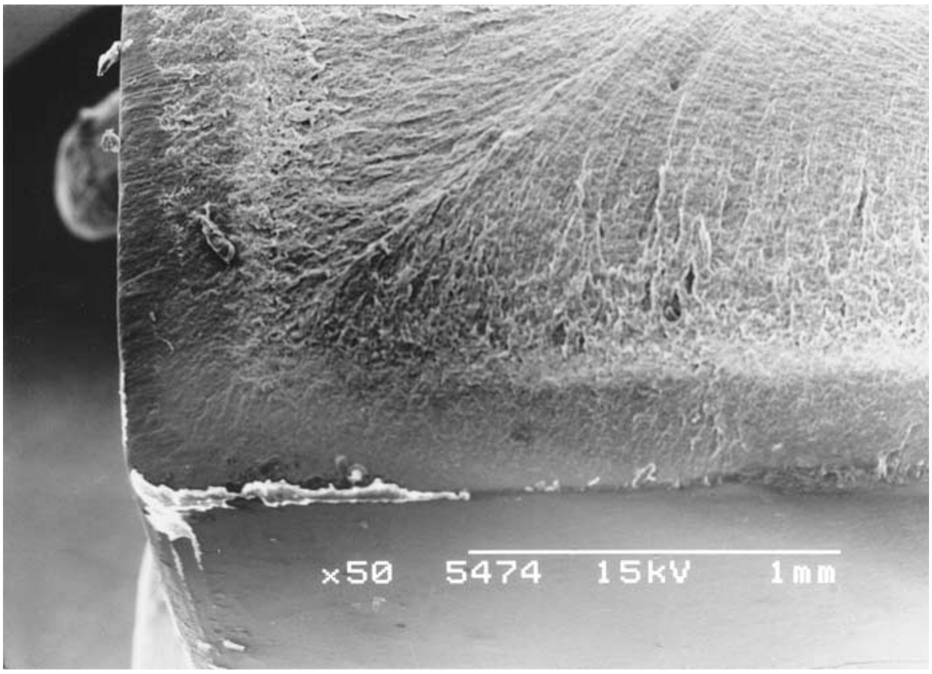
Another difference between the two polymers was found in the tensile behaviour of UV exposed bars. Fig. 6a shows the tensile strength variation with exposure time for PP and PPS and Fig. 6b the corresponding data for MPP and MPPS. Both stabilized grades (PPS and MPPS) show very little change with exposure time. Both unstabilized grades show marked reductions in strength with exposure time but the characteristics are quite different. MPP showed a monotonic fall in strength with exposure time whereas the strength of PP fell very rapidly to about 50% of the unexposed value in about 10 weeks then recovered somewhat (reaching a value about 65% of the unexposed value after 24 weeks exposure) before falling slowly again.

3.4. Scanning electron microscopy

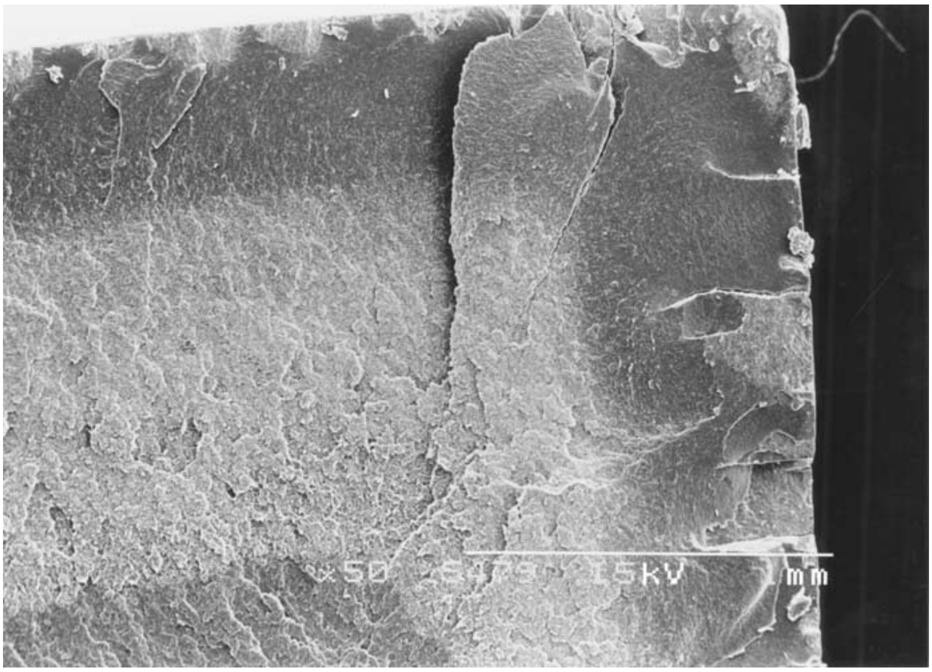
Part of the fracture surface of a PP bar tensile tested after 20 weeks exposure is shown in Fig. 7a. There is a distinct boundary at 0.35–0.4 mm from the surface. This corresponds to the depth at which the steep rise in M_w occurs and we speculate that it is the position at which the crack growing through the heavily degraded surface zone was arrested when reaching the ductile, relatively undamaged material underneath. A less distinct boundary at approximately the same depth is visible on the fracture surface of the sample tested after 80 weeks exposure (Fig. 7b); the surface region now appears to be very much more brittle, with cracking parallel to the moulded surface fairly well developed. Not much cracking was found in the surface of PP after 20 weeks exposure even after conducting a tensile test (Fig. 8). The sample tensile tested after 80 weeks exposure contained a dense pattern of cracks (Fig. 9). The degraded surface layer appears to be about to flake off; some parts of the surface charged quite badly in the SEM. With MPP the degraded surface zone, in which the flat brittle fracture propagates, grew in depth as the exposure time increased (Fig. 10). The depths of the flat fracture zones shown in Fig. 10 are approximately (a) 0.3 mm (6 weeks exposure); (b) 0.5 mm (34 weeks); and 0.85 mm (55 weeks). These measurements correspond approximately to the steepest part of the graphs in Fig. 3b for 16, 34 and 49 weeks exposure respectively.

4. Discussion

The reason for the steep degradation profile in the unstabilized material is generally accepted to be caused by oxygen diffusion limited reaction: the reaction rate near the surface is very high with UV levels of the magnitudes used in these experiments and most of the oxygen is consumed before it can penetrate far into

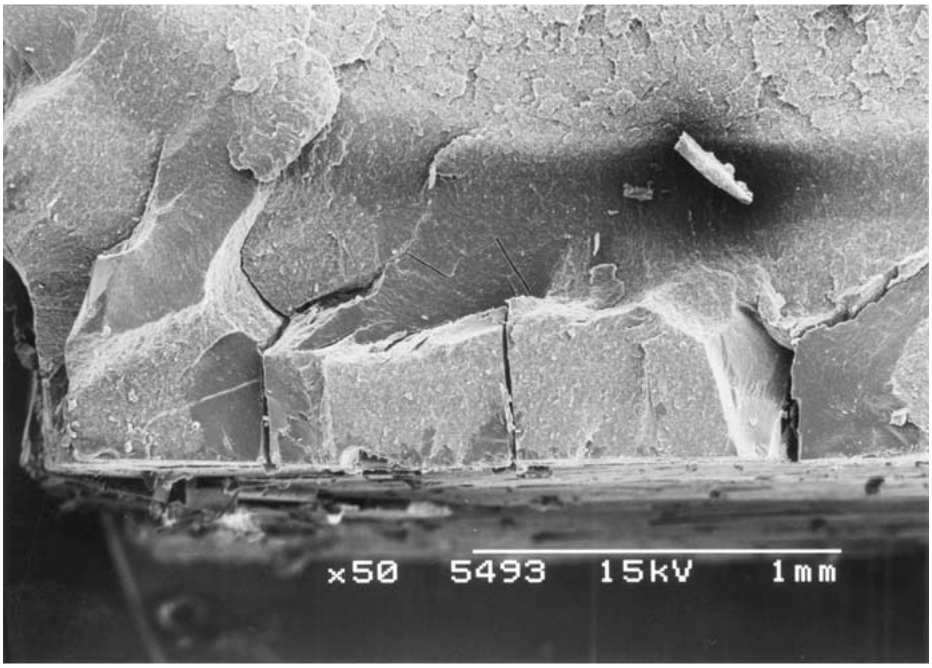


(a)



(b)

Figure 10 Fracture surfaces of MPP after tensile testing following exposures of (a) 6 weeks; (b) 34 weeks; and (c) 55 weeks. (*Continued*.)



(c)

Figure 10 (*Continued.*)

the material [12–15]. This does not explain why there is a difference in the behaviour observed with PP and MPP respectively. In the stabilized grades the rate of reaction is much lower, permitting penetration of oxygen into the interior and allowing photodegradation reaction to proceed even though the UV intensity is lower there than at the exposed surface.

The kind of recovery displayed by PP in Fig. 6a has been found with many different types of polypropylene [16–19]. The general recovery behaviour has been explained as follows [19]. After a short period of photodegradation a brittle layer of degraded polymer forms on the surface of the exposed bar. Cracks form easily in this layer and under high loading conditions may propagate into and through the interior. After longer periods of exposure the surface layer becomes so fragile it may flake off, or cracks within it do not propagate into the interior because load transfer cannot occur from the surface layer into the interior because of its weakness. Then recovery of strength is observed. [This is only observed under well controlled testing conditions in which the mechanical test is conducted separate to and after the completion of the UV exposure; it is of little practical value because a component in service is likely to fail the first time it is stressed significantly when near the minimum strength state and will never proceed to the recovered state.] In earlier studies it was observed that the minimum can sometimes persist for a short range of exposure times only. Thus it is possible that a minimum in strength followed by recovery might have been observed with MPP had the exposure time interval between testing been shorter (say 1 week or less instead of 3 weeks or more) over the critical period. For reasons discussed below we tend to believe that this would not have been so; in any case, the strength-exposure time data for PP and MPP are still very different.

The type of molecular mass degradation observed with PP (Fig. 3a) is consistent with the explanation for recovery given above because the degraded zone is seen to remain almost unchanged in depth; presumably the mechanical properties of the degraded surface continue to deteriorate progressively as exposure continues, leading to the sequence of events described. On the other hand, with MPP the location of the boundary between the severely degraded material near the surface and the relatively undegraded material in the interior shifted progressively inwards from the surface as exposure continued (Fig. 3b). Therefore, if the depth of the degraded zone is taken to be the flaw size, then fracture mechanics predicts that the strength will fall progressively with exposure. Presumably the newly degraded region close to the (still) less degraded interior will retain its potency for stress transfer, making recovery unlikely. Even if the region near to the surface becomes very fragile at long exposure times, the degraded region in contact with the relatively undegraded (and ductile) zone is continually "refreshed" and does not lose its potency. This idea is supported by the apparent changes in the depth of the smooth fracture zone near the surface, which increases with the exposure time in MPP (Fig. 10).

Thus the correlation between the observed photo-induced changes in molecular weight and mechanical properties is good for both materials, but we do not know why such large differences in the behaviour of the two materials occurs. It is hard to understand why two such similar polymers behave so differently. It challenges our understanding of degradation considerably if the source of the difference relates to the structure or morphology. Perhaps, on the other hand, a small amount of stabilizer was accidentally present in MPP and accounted for the difference. A fairly small batch of material was made so that any trace of stabilizer picked up from the processing machinery would be relatively important, but greater care was taken over the preparation of this (laboratory scale) sample than is normally possible on an industrial scale. Therefore we present these results not only for their intrinsic interest but also as a warning that even with a relatively well-understood polymer such as polypropylene, subtle changes in composition may have a significant effect not only on failure strength but on the mechanism of failure under photo-degradation.

5. Conclusions

The development of degradation near the surface of two similar polypropylenes (PP and MPP) when exposed to ultraviolet light (UV) has been found to differ considerably. In PP the depth of degradation did not change much even when exposures were continued for about a year whereas in MPP the degraded zone deepened progressively with exposure time. This lead to differences in fracture behaviour of the two materials. In MPP the progressive increase in the depth of the degraded zone caused the fracture strength to fall monotonically. In PP the main effect of photo-oxidation was to increase the extent of degradation progressively in a zone that remained almost unchanged in depth over an extended period of time. This produced the conditions in which recovery can occur and this was observed to occur after about 6 weeks exposure.

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