JOURNAL OF MATERIALS SCIENCE **37** (2002) 1091–1100

Photo-sensitivity of recycled photo-degraded polystyrene

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Blends have been made containing various combinations of (polystyrene) virgin polymer, recycled polymer and photo-degraded polymer to investigate whether recycled polymer prepared from photo-degraded waste has increased sensitivity to photo-degradation after recycling. Bars injection moulded from virgin material were used to generate photo-degraded material using laboratory ultraviolet (UV) exposure. Recycled polystyrene was prepared from (i) sprues and runners from the mouldings made with virgin material and (ii) single polymer waste that contained other grades and some material that had already been recycled at least once. Mixtures of virgin polymer and photo-degraded polymer showed accelerated degradation when compared with similar blends of virgin polymer with recyclate from mouldings that had not been exposed to UV. This effect was greatest for short exposure times (<6 weeks) but the seeding effect of the photo-degraded material was less severe at longer exposure times. © *2002 Kluwer Academic Publishers*

1. Introduction

There are considerable commercial and environmental benefits to be gained if satisfactory methods can be developed for recycling polymers. Recycling factory-generated thermoplastics waste such as sprues and runners and rejects usually presents no problem provided that any degraded material (produced by inadvertent use of excessively high temperatures or times during processing) is excluded and provided that care is taken to keep the material clean at all stages of the reprocessing chain. In a well run factory the fraction of recycled material is quite small and it can usually be mixed with virgin material without any significant deterioration in property (at a level of say 5% or less of recycled material). At the other end of the scale lies mixed waste with unknown history and contamination. Methods to recycle this have been investigated for over 20 years with limited success but no procedures have yet been developed that can produce high value products at an economical price. Between these two extremes lies an important category of plastics waste in which the source is a single high-volume product in which the problems of recovery and identification are easily resolved and for which the history and therefore the likely contaminants are known. Examples are carbonated drinks bottles and car battery cases. Polypropylene battery cases are put through a thorough cleaning process then regranulated. Re-use of this reclaimed material can involve mixing it with virgin material or adding a filler. The latter option is often beneficial because the appearance of the unfilled recycled material (which will always contain traces of degraded material and contaminants) is usually inferior to that of the virgin material whereas in the presence of filler the appearance is hardly altered when recycled material is included. Compounds containing recycled material must be subjected to rigorous tests to determine the effect of including reclaimed material on properties.

Investigations of the effect of recycling on polymer properties have concentrated primarily on studying material that has been processed repeatedly (for example, extruded-regranulated, extruded-regranulated etc); some recent examples are given as references [1–7]. The properties of such material degrade progressively but the effect on the photo-sensitivity has been largely ignored. Some studies have looked at the effect of recycling weathered polymers and at the prospects for re-stabilizing degraded material against thermal degradation during subsequent use [8–13]. Despite an early report that, in blends, a photo-sensitive polymer may act as a pro-degradant for a less sensitive polymer [14], very little attention has been paid to the weatherability of recycled weathered polymers. There is hardly any mention of this topic in the substantial review by Brandrup *et al.* [15]. Notable exceptions are the papers by Abdel-Bary *et al.* [16] and Al-Malaika *et al.* [17] though the latter concerns recycling bio-degradable materials which are a special group of materials.

Unless protected by a suitable stabilizer, thermoplastics suffer severe degradation when used outdoors, mainly through photo-oxidation promoted by the ultraviolet (UV) component of solar radiation [18, 19]. Recycled plastics products that have spent part of their service life outdoors will therefore contain degraded polymer. Degradation usually involves chain scission, though crosslinking may also occur.

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With polypropylene and polystyrene both scission and crosslinking are present. The rates of formation of both scissions and crosslinks depend on the amount of oxygen available, which is in turn determined by the rate of reaction and the rate of diffusion [20, 21]. Thus the amount and nature of the degraded polymer will depend on the thickness of the original product as well as the temperature and the UV intensity during service. The testing programme referred to above is normally designed to check the effect of contaminants and degraded polymer on the properties of the recycled plastic. The mechanical properties of central concern are normally strength (often assessed by a tensile test) and toughness (usually assessed by an impact test). These tests will reveal property deficiencies caused by contaminants acting as stress concentrations (which nucleate cracks) but do not necessarily indicate the long-term serviceability of the material.

Of concern in the study described here is whether polymer degraded during service can act as a pro-degradant when recycled. The chemical degradation of polymers in outdoor service occurs through chain reactions that involve products of reaction such as free radicals and hydroperoxides [18, 19, 22–28]. Thus if recycled material contains such products of reaction they may be able to seed degradation in the recycled product. It might be argued that such reagents would react during the reprocessing stage and would not be present in the product made from the reclaimed material. If such reactions occur during processing the products are just as likely to be pro-degradants as those produced during the original chemical degradation of the material, however. Thus they may act in the same way and render the re-processed material more vulnerable to degradation in service than a similar material made from polymer that had not suffered photo-degradation. Finally it is worth noting that products such as polypropylene car battery cases may be shielded from UV for most of their service life and will not require photo-stabilization but they will usually be exposed outdoors on a dump while awaiting recycling.

2. Experimental

2.1. General introduction

Polystyrene was chosen for study because its photo-degradation characteristics were known from previous studies [29–33]. Batches of tensile test bars were injection moulded from virgin polymer then some of these bars were photo-degraded by UV exposure in the laboratory. Photo-degraded polymer was then removed from the UV-exposed bars and mixed with virgin polymer and new bars were moulded from this compound. Such bars can be expected to have inferior properties because of the reprocessing step suffered by the photo-degraded material as well as the chemical degradation that it suffered before reprocessing. To generate samples to assess the relative importance of these two effects a further batch of bars was moulded using reprocessed polymer that had not been photo-degraded, again mixing it with virgin polymer in the same proportion as used for the photo-degraded material. The polymer that was reprocessed without photo-degradation was generated from the sprues and runners from the original batch of bars made from virgin polymer. These were kept clean and stored in the dark until required so that they were representative of the best uncontaminated sources of reprocessed material. Further batches of bars were made using scrap polymer that was kept in the processing laboratory, sorted into bins by generic type. These bins contained polymer of different grades, some of which had already been reprocessed at least once. The material in the bins was not retained under scrupulously supervised clean conditions but is expected to be at least as good as cleaned waste in a well organised reclaim operation. The reclaimed material was used both undiluted and in mixtures made with virgin material.

Samples of all of the batches of injection moulded bars were exposed to UV in the laboratory for varying periods of time then subjected to tensile tests. The fractured samples were inspected using light microscopy and/or scanning electron microscopy to determine the fracture mechanism.

2.2. Materials and sample preparation

The grade of virgin polystyrene used was Dow Styron 634, provided by the manufacturer as free from photo-stabilizers but probably contained some thermal stabilizer. The compositions of the compounds based on this polymer (both as virgin polymer and as "controlled recyclate" from the carefully preserved sprues and runners) and on the materials derived from the recycling bins ("uncontrolled recyclate") are given in Table I.

The photo-degraded material was removed from the surface of the UV-exposed bars by high speed milling using a single point cutter and fly cutting action. This has been shown in previous studies to cause minimal chemical and thermal degradation of the polymer [30, 34] so although it represents a processing step that would not be used in a commercial recycling operation it is believed to have no effect on the results presented here. Material was removed to a depth of 0.5 mm from the exposed surface since it has been shown that most of the photo-degradation occurs within this zone [29–31, 34]. Regranulation of sprues, runners and scrap mouldings was conducted using a Spruemaster which was cleaned carefully prior to the preparation of each material type. The compositions given in Table I were weighed then tumble-mixed in a plastic bag prior to feeding into the hopper of the injection moulding machine.

The tensile test bars were made using a tool with an end-gated cavity and measured approximately 190 mm × 12.7 mm × 3.1 mm. Samples were moulded

TABLE I Composition of polystyrene compounds

Code	Virgin	Photo-degraded	Controlled recyclate	Uncontrolled recyclate
PS-V	100			
PS-V + P	80	20		
PS-V + C	80		20	
PS-V + U	80			20
PS-C			100	
PS-U				100

in large batches; several mouldings were rejected at the beginning of each run to ensure that the previous compound had been completely removed and that the moulding machine had reached cyclic equilibrium. The mouldings were made with temperatures Barrel Zone 1/Zone 2/Nozzle/Mould of 170/230/180/39°C and injection pressure 72 MPa. The bars were allowed to cool in air after removal from the moulding machine. The sprues and runners from bars made from virgin polymer were removed and laid aside for separate storage and re-processing.

2.3. UV exposure conditions

UV exposures were conducted in a constant temperature room set at 30°C and maintaining $30^\circ \pm 1^\circ$C. Fluorescent tubes type *UVA-340 (Q-Panel Company)* were used as the UV radiation source. The tubes used were chosen because their output in the UV range at wavelengths below about 360 nm matches the spectrum of solar radiation at the Earth's surface fairly closely [30]. The tubes are approximately 1.2 m long with a fairly uniform output over the central metre. They are used in pairs and measurements have shown that the illumination falling onto a flat testpiece with its axis perpendicular to the tube axes is fairly uniform over the gauge-length. The intensity used was in the range 2–3 Wm^{-2} in the wavelength range 295–320 nm, that is the total radiation below 320 nm wavelength. Low wavelengths generally cause the most damage and this wavelength range is often used as a measure of the severity of the UV exposure. The intensity level corresponds approximately to outdoor conditions in Jeddah, Saudi Arabia, which has one of the most severe climates in which polymer weathering trials have been conducted [35–37]. The bars were exposed on one side only. Samples used to produce photo-degraded material were exposed for six weeks before milling away the exposed surface, as described above. Previous studies showed that very significant molecular degradation occurs within the chosen periods when using the conditions employed here [29–31, 34]. Photo-degradation exposures for all types of samples were conducted for a range of times from 1–10 weeks.

2.4. Testing and characterization

Tensile tests were conducted using an Instron 4505 machine. The crosshead speed was 30 mm/min. The fracture surfaces and the moulded surfaces adjacent to the fracture surface were inspected in the light optical microscope. Some samples were also examined in the scanning electron microscope after gold coating to prevent charging. Crazes were observed to form during the tensile tests. The crazing patterns observed in the broken halves of the different samples after the tensile tests had different appearance, depending on the blend used and on the exposure conditions. The different characteristics were as follows:

(1) extensive crazing, through the whole section;
(2) long tongue-shaped crazes, starting near the bar edge;
(3) large internal crazes, in the form of isolated discs;
(4) small internal crazes;
(5) no visible crazes: this condition corresponded to a very rough fracture surface.

The numbers listed above were used to rank the crazing type with (1) corresponding to the materials with best properties and (5) to those with the worst properties. The numbers assigned to the intermediate levels were chosen according to the craze size and did not always reflect the property ranking. Some samples contained a mixture of two crazing modes: they were given a corresponding intermediate ranking number.

3. Results

3.1. Tensile tests

Stress-strain data for virgin polystyrene (PS-V) after various exposure times are given in Fig. 1. They reflect the brittle behaviour of this material, showing an almost linear increase in stress with strain up to a maximum then an abrupt failure with minimal plastic deformation. The bars crazed before breaking, so a limited amount of inelastic deformation occurred, but the final stages of failure were too rapid to be followed by the testing machine and differences in steepness of the stress-strain characteristics beyond the stress maximum should be disregarded. Thus the major result displayed in Fig. 1 is the progressive reduction in maximum stress with increase in UV exposure (see later discussion of Fig. 3). After 10 weeks exposure the maximum load fell to approximately 40% of that for the virgin unexposed polymer. Given the shape of the stress-strain relationship this means that the energy absorbed during the tensile test to break of the 10 week exposed bars was less than 20% of that for the unexposed bars.

Fig. 2 shows a similar set of results for samples made from polystyrene containing photo-degraded material (PS-V + P). The properties are inferior to those of PS-V at all exposure times and the general trend of reduction in maximum stress with increase in exposure time is again observed (see below). One small departure from the trend shown in Fig. 1 is an apparent steepening of the stress-strain curves for 5 and 6 weeks exposure.

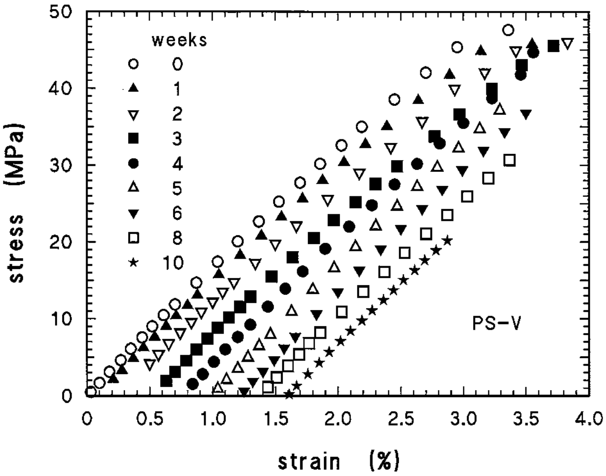


Figure 1 Stress strain data for PS-V bars tested in the as-moulded state (0 weeks) and after exposures of 1, 2, 3, 4, 5, 6, 8 and 10 weeks. Successive sets of data are displaced along the strain axis in increments of 0.2%.

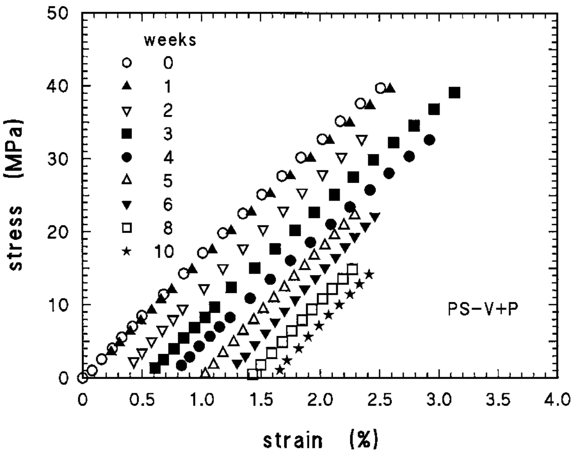


Figure 2 Stress strain data for PS-V + P bars tested in the as-moulded state (0 weeks) and after exposures of 1, 2, 3, 4, 5, 6, 8 and 10 weeks. Successive sets of data are displaced along the strain axis in increments of 0.2%.

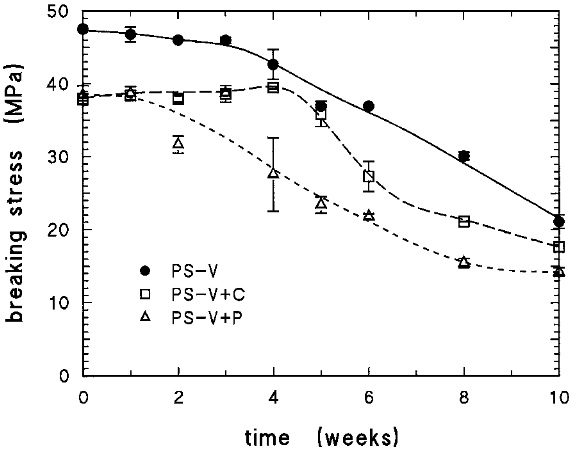


Figure 3 Breaking stress versus exposure time for PS-V, PS-V + C and PS-V + P bars (averages of 2 or 3 tests).

The general characteristics of the stress-strain behaviour of the other sets of samples derived from batches PS-V + C, PS-V + U, PS-C and PS-U were similar to those displayed in Figs 1 and 2, and the properties can be characterized by the maximum stress recorded in the test. Thus the key differences between samples that are illustrated in Figs 1 and 2 can be summarised as in Fig. 3. Results from tests conducted on samples containing controlled recyclate (PS-V + C) are also shown in Fig. 3. PS-V performed the best at all exposure times and the material containing previously photo-degraded material (PS-V + P) performed the worst. Deterioration of PS-V + P samples was evident within 2 weeks whereas it took much longer for a significant fall in breaking stress to occur in PS-V (4–5 weeks) and PS-V + C (5–6 weeks). Fig. 4 shows the results for samples containing uncontrolled recyclate (PS-V + U) again compared with those for PS-V and PS-V + C. The presence of the uncontrolled recyclate in PS-V + U resulted in property deterioration similar to that observed with PS-V + P with a steady fall in breaking stress evident almost immediately (compare Figs 3 and 4). The properties for the mixtures (PS-V + P, PS-V + C and PS-V + U) all show more scatter than those observed with virgin material (PS-V). The greatest scatter occurred in the exposure range 2–6 weeks; it was in this range that the largest disagreement was found between repeat measurements, as indicated by the size of the error bars.

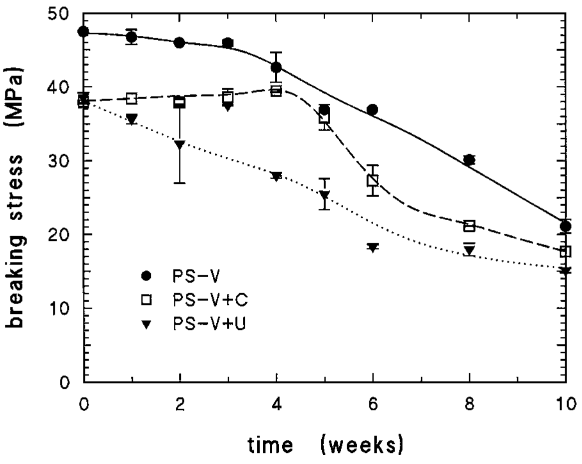


Figure 4 Breaking stress versus exposure time for PS-V, PS-V + C and PS-V + U bars (averages of 2 or 3 tests).

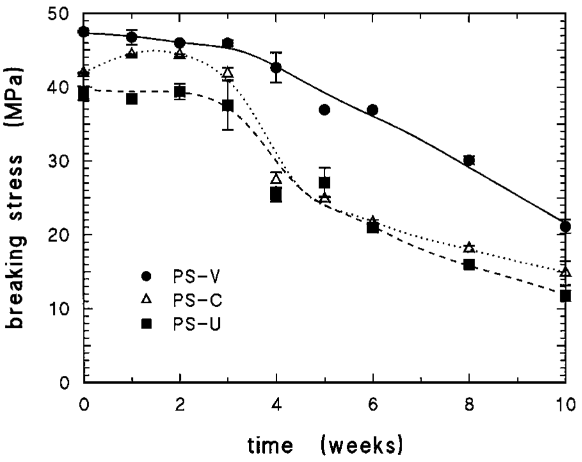


Figure 5 Breaking stress versus exposure time for PS-V, PS-C and PS-U bars (averages of 2 or 3 tests).

Results for bars made from 100% recyclate (PS-C and PS-U) are shown in Fig. 5. The results for PS-V are repeated for ease of comparison. PS-C performed somewhat better than PS-U for exposures up to 3 weeks. PS-C showed a modest increase in breaking strength for short exposure times but a sudden fall occurred after 4 weeks exposure. PS-U showed almost no change for 1 week and 2 weeks exposure but the results for 3 weeks exposure were very scattered, then a sudden drop in breaking strength was observed for 4 weeks exposure. Thereafter the results for PS-C and PS-U were not very different, though PS-C still registered the higher values. PS-V + U gave the lowest breaking strengths for short exposure times and PS-U the lowest for times greater than 6 weeks, though PS-V + P was not far from the worst over the whole exposure range.

The craze ranking results are given in Fig. 6. It is evident that the ranking increases with exposure and that movement to a higher rank corresponds to the changes in strength discussed above. The only blend to show a significant change after just one week UV exposure was PS-V + P. In the other blends there was an incubation time before significant changes were observed; thereafter the progression to higher ranks was

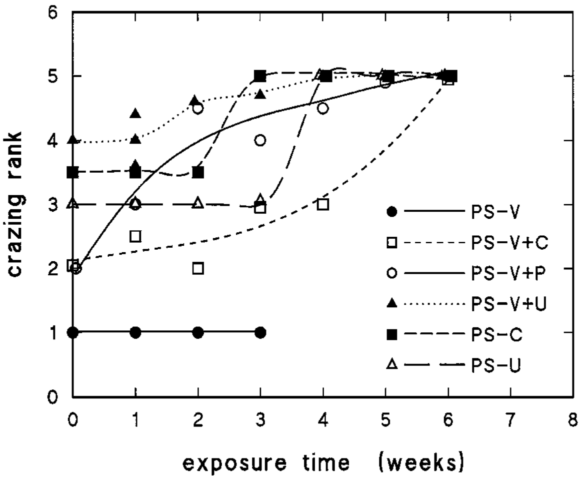


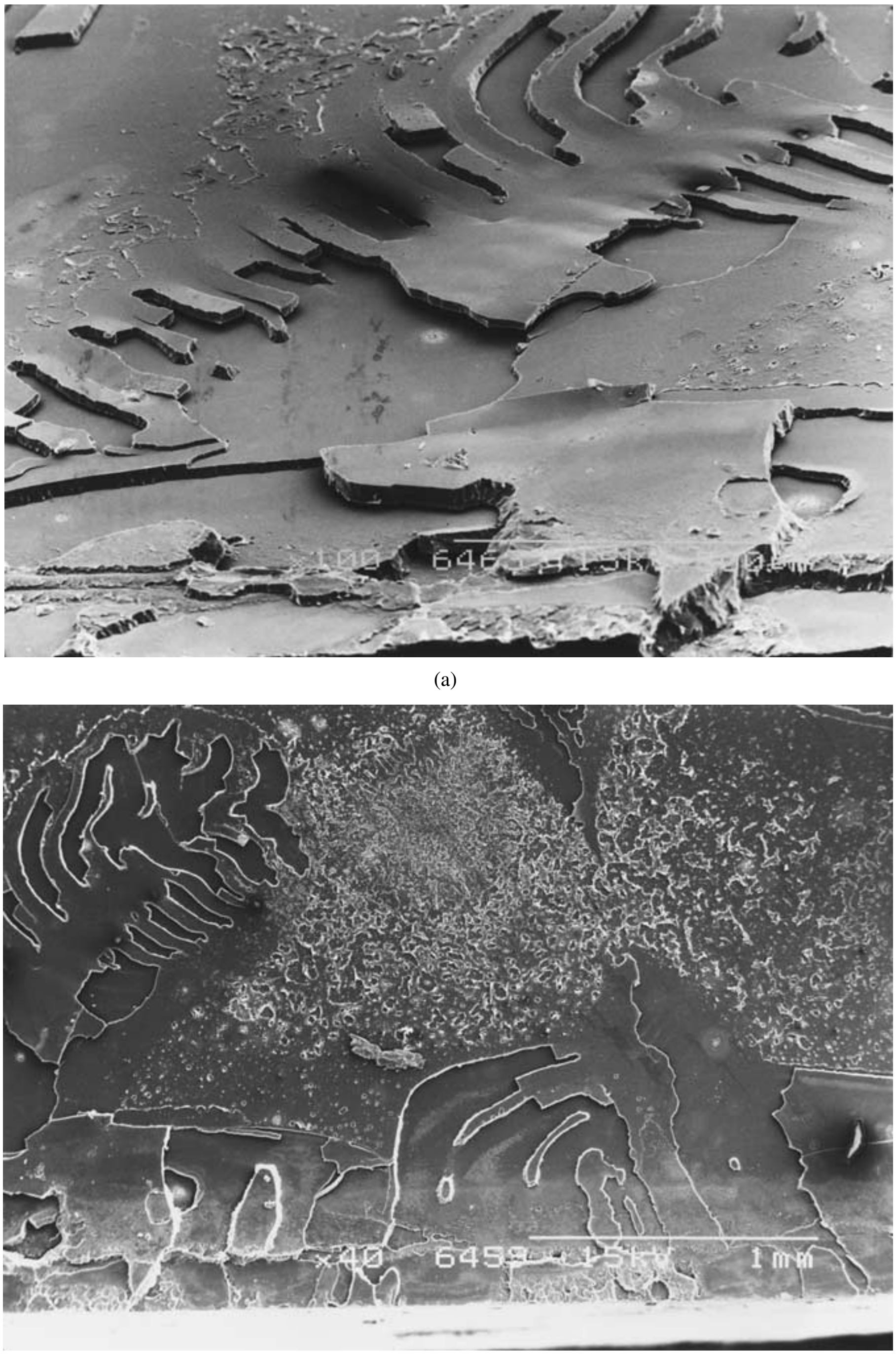
Figure 6 Craze ranking for different PS blends versus exposure time.

quite sudden for most blends. Samples which showed the greatest scatter in properties also showed scattered craze rankings or less well-defined crazing patterns. It should be noted that most blends progressed from rank 3 or rank 4 to rank 5 directly and that rank 4 seems to be an alternative to rank 3 rather than a step in a progressive series of changes. Rank 3 crazing corresponded to samples with poorer properties than rank 4 (recall that the "craze ranking" was chosen according to the visual appearance of the craze).

3.2. Scanning electron microscopy

Tensile fracture surfaces of the various blends when tested after three weeks exposure are compared here.

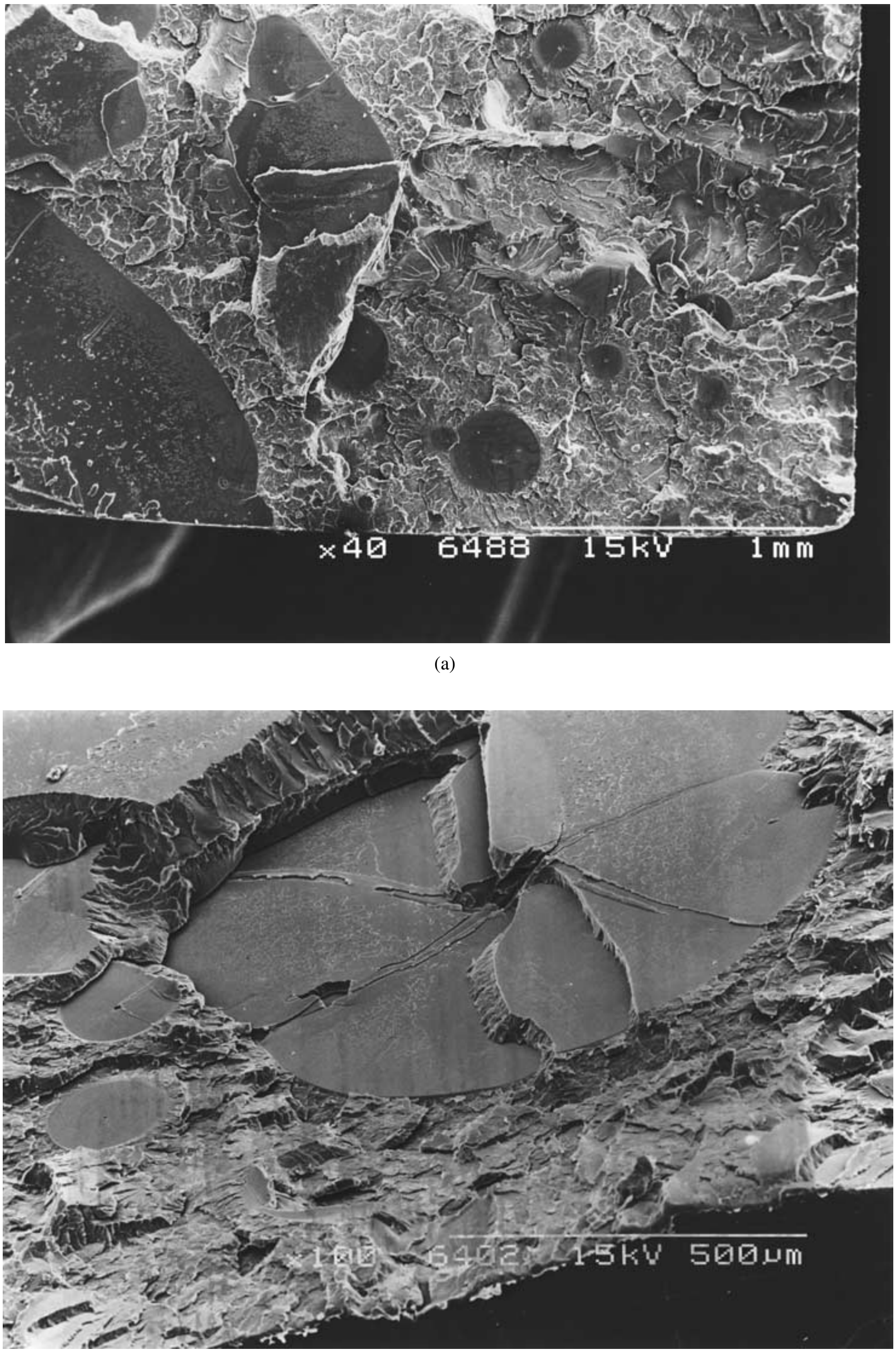
Fig. 7 shows the fracture surface of PS-V. The appearance is similar to that commonly found for general



(a)

(b)

Figure 7 Part of the fracture surface of PS-V formed during a tensile test conducted after 3 weeks UV exposure. (b) general view; (a) magnified image of the region in the top left hand corner of (b) after tilting.



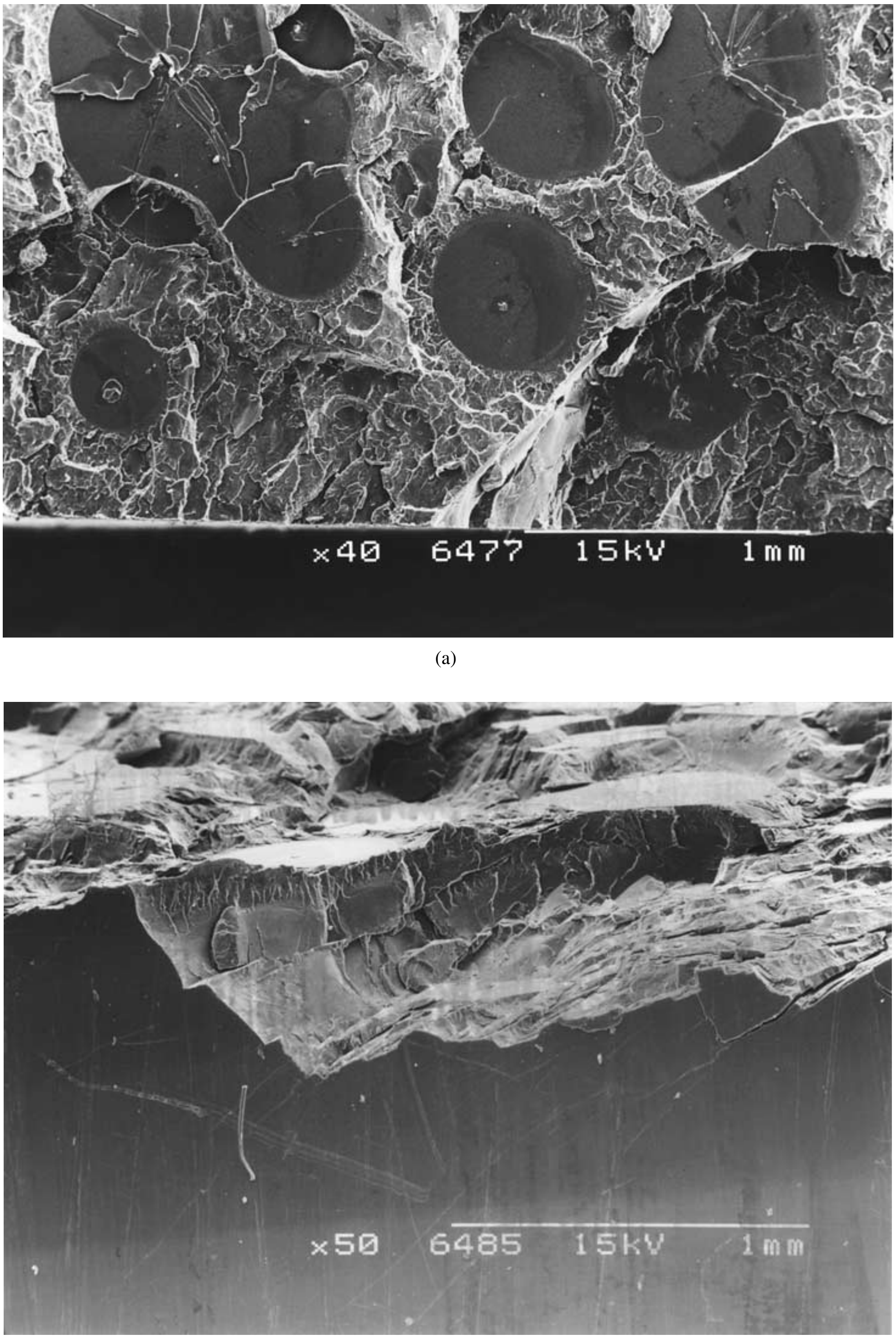
(a)

(b)

Figure 8 Part of the fracture surface of PS-V + U formed during a tensile test conducted after 3 weeks UV exposure. (a) low magnification; (b) tilted view showing that the discs are not co-planar.

purpose polystyrene tested without UV exposure (e.g. see references [38–40]). The fracture surfaces of both PS-V + U and PS-C both contain disc-shaped features (Figs 8 and 9). Presumably these formed and coalesced quickly, before significant development of similar features through the rest of the samples since very few discs were visible in the broken fragments. Fracture occurred by a crack running through such features and jumping from one plane to another by steep paths leaving characteristic markings on the fracture surface (Figs 8 and 9). When PS-U was tensile tested after three weeks exposure, no discs were visible in the broken fragments nor on the fracture surfaces, which reflected the fine crazing that appeared to be present when viewed by eye (Fig. 10).

The fracture surface of a bar containing material photo-degraded before the three week exposure applied here is shown in Fig. 11. The craze that covers the surface appears to be rather fragile and has a dense population of ring-shaped markings, mostly in the range



(a)

(b)

Figure 9 Part of the fracture surface of PS-C formed during a tensile test conducted after three weeks UV exposure. (a) low magnification; (b) tilted view showing that the discs are not co-planar.

1–4 microns in diameter. Similar features were seen in some locations on the fracture surface of PS-V + U (Fig. 12).

4. Discussion

It is evident that the mechanical test results for PS-V + P are inferior to those for PS-V + C at all exposure times, showing that the inclusion of photo-degraded material has caused extra property deterioration. In fact the PS-V + P measurements follow those for PS-V + U fairly closely though this must be regarded as accidental because of the unknown nature of the recycled component in PS-V + U. The fracture surfaces produced with samples of PS-V + P and PS-V + U after three weeks UV exposure show similar characteristics, implying, perhaps that pro-degradant behaviour of some of the "uncontrolled" recyclate was similar to that of the recyclate from photo-degraded bars. Surprisingly the PS-C samples appear to be superior to those made from 80% virgin PS plus 20% recycled material (PS-V + C) at low exposure times but properties fall off rapidly after 3 weeks

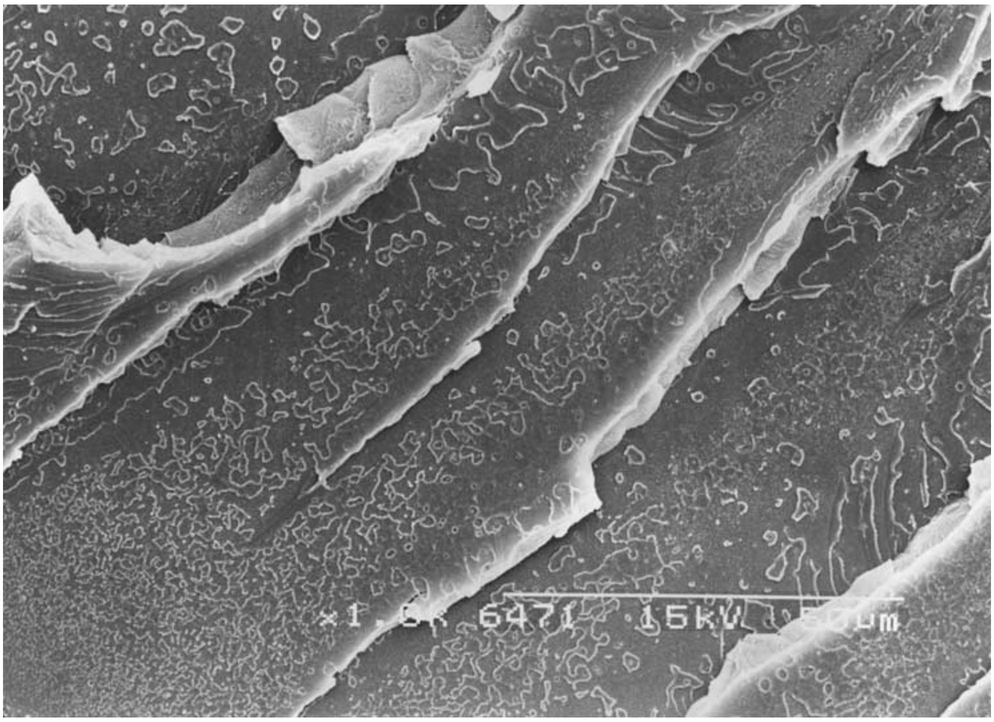


Figure 10 Part of the fracture surface of PS-U formed during a tensile test conducted after 3 weeks UV exposure.

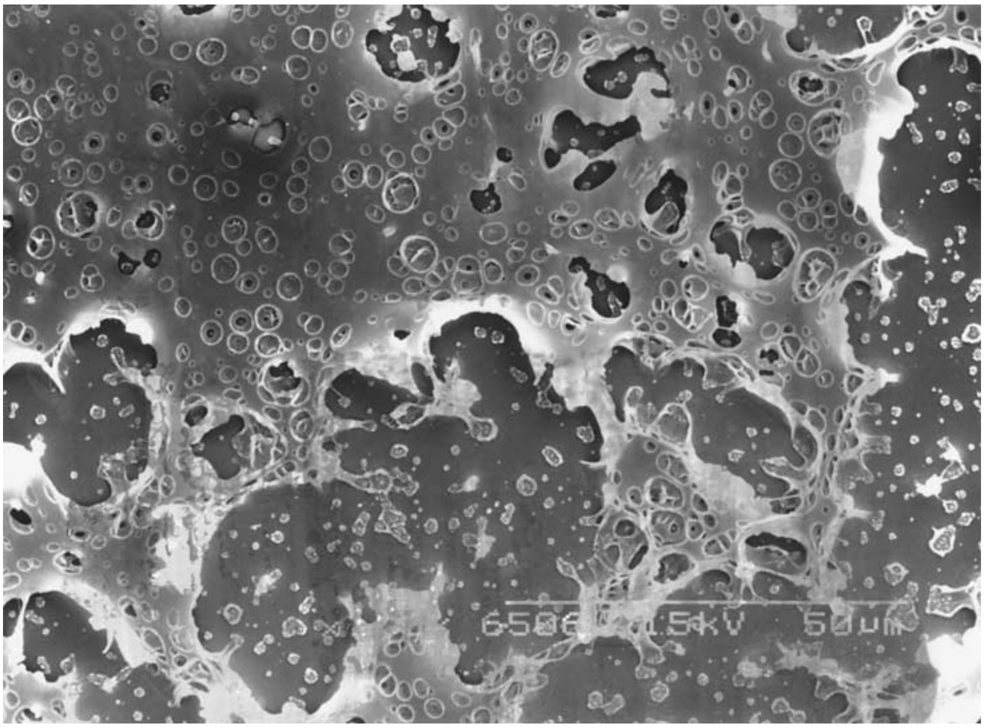


Figure 11 Part of the fracture surface of PS-V + P formed during a tensile test conducted after 3 weeks UV exposure.

exposure and are no better than those for the other compounds by 8 weeks exposure. The PS-C bars gave results superior to those for PS-U at most exposure times.

Different blends of polystyrene showed different crazing characteristics in the as-moulded state, and all blends containing recycled material changed the crazing characteristic (or "rank") after applying UV exposure. All blends containing recycled material became very brittle within 6 weeks UV exposure and did not show any extensive crazing at break, though fine craze remnants covered the fracture surfaces. Some of the blends developed disc-shaped crazes during tensile tests performed after intermediate UV exposures. It is speculated that these nucleate at flaws present in the recycled component. The blend containing recyclate from deliberately photodegraded samples was the first to show a change in the crazing rank when exposed to UV irradiation.

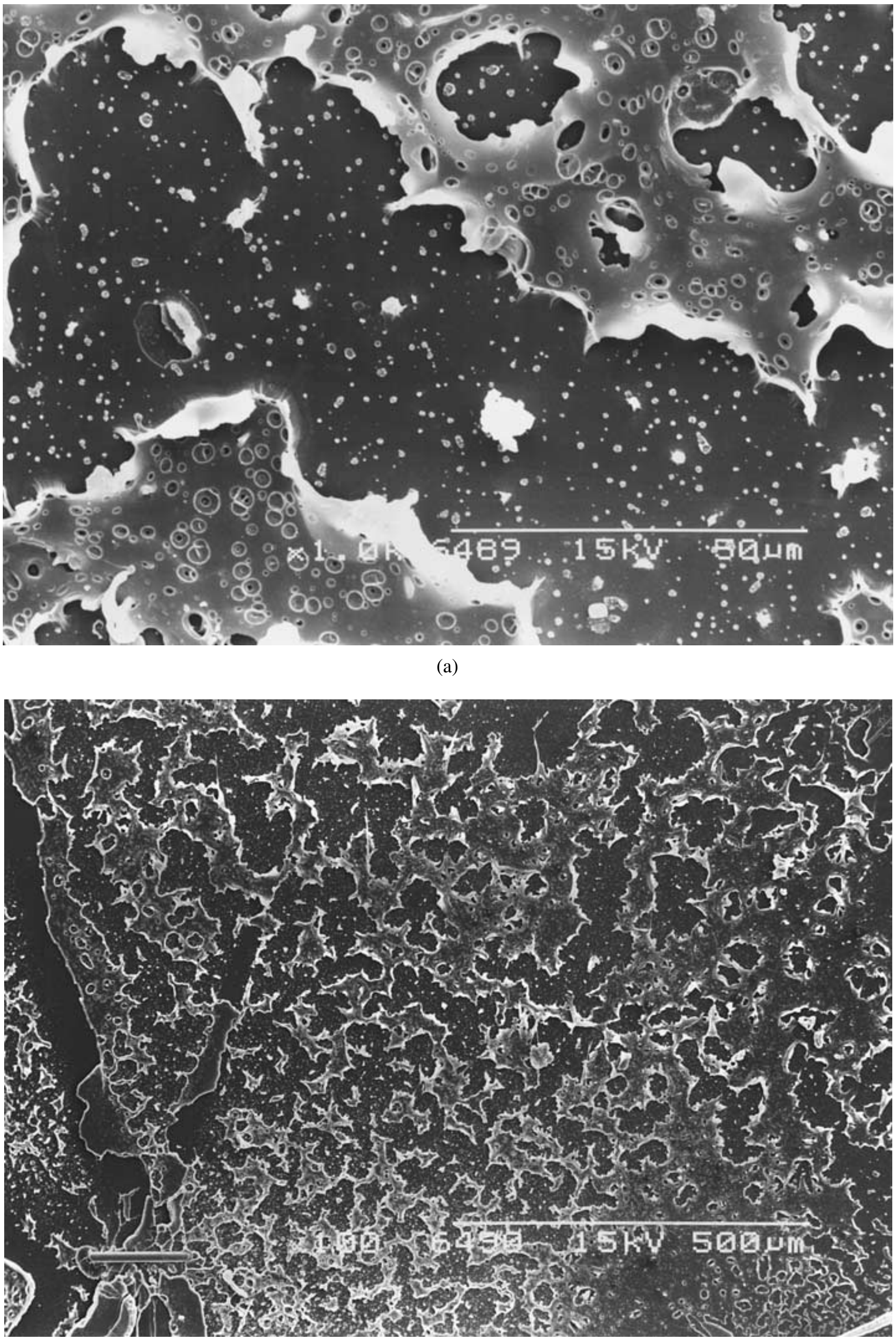


Figure 12 (a) High magnification view of part of the fracture surface of PS-V + U formed during a tensile test conducted after 3 weeks UV exposure; (b) intermediate magnification with region shown in (a) at the centre.

5. Conclusions

- Inclusion of recyclate lowered strength.
- Prior to UV exposure, a mixture containing photodegraded recyclate gave similar properties to mixtures containing recyclate that had not been photodegraded.
- When exposed to UV, a mixture containing photodegraded recyclate degraded more rapidly than mixture containing "clean" recyclate that had not been photodegraded.
- When exposed to UV, a mixture containing "uncontrolled" recyclate degraded more rapidly than mixture containing "clean" recyclate; this deterioration was similar to that observed with the mixture containing photodegraded recyclate.
- Bars made from mixtures of virgin polymer with recyclate deteriorated less rapidly than those made from 100% recyclate.

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Received 1 May
and accepted 2 November 2001