Photomechanical Degradation of Thermoplastic Elastomers

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ABSTRACT: The photodegradation of thermoplastic elastomers designed for outdoor applications was studied with laboratory ultraviolet (UV) exposure in the unstrained state and under tensile strain (25 and 50%). Strained exposure caused a reduction of the strain to failure in subsequent tensile tests. For some combinations of material and exposure conditions, some recovery of extensibility occurred between 2 and 4 weeks. Microscopic examination revealed that this was probably due to embrittlement of the surface region that was sufficiently severe that surface cracks did not propagate into the interior and that the observed recovery did not correspond to repair or improvement of the material. Shielding the sample surface from UV irradiation reduced the formation of surface cracking very significantly, and it was deduced that the principal cause of degradation was photooxidation rather than ozone attack. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 150–161, 2006

Key words: degradation; elastomers; thermoplastics

INTRODUCTION

Thermoplastic elastomers (TPEs) have become well established in recent years and are used increasingly as the elastomer class of choice in a wide range of engineering applications and consumer goods.[1–4] This is mainly the result of the ease of processing (by conventional thermoplastics methods) and because the scrap material can be recycled conveniently. Many of the applications for rubber–plastic blends involve outdoor service, and it is important to know their sensitivity to weathering and to develop appropriate methods to limit degradation. This has been of considerable concern to the manufacturers of commercially available grades, and they have designed materials for use outdoors that have good lifetimes under most service conditions. They test their materials in accelerated laboratory weathering units and in selected outdoor sites with extreme climates (e.g., Florida and Arizona in the United States). They often provide data generated from such test programs to assist customers in their choice of materials and to give them some idea of the lifetime capability of the material.

Although the reliability of TPEs in outdoor service is generally acceptable, information about their behavior under tensile stress is not as readily available as it is for natural and synthetic rubbers, with which TPEs compete in some applications. Natural rubber (NR) products can degrade rapidly when exposed outdoors, particularly if loaded in tension. The cause of the degradation is often attributed to ozone attack,[5–9] but there is increasing recognition that photooxidation is often the dominant mechanism in NR and other elastomeric materials.[10–17] Studies of the ultraviolet (UV) photooxidation of thermoplastic polymers have shown that tensile stress accelerates degradation,[18–20] and the observations of elastomers follow this pattern. This has been shown most recently to apply to a family of experimental TPEs made by the blending of NR and polyethylene (PE).[14,15] The studies reported here were conducted with commercially available TPEs to determine whether tensile stress could accelerate their UV degradation and to attempt to identify the mechanisms of failure in the photodegraded materials.

EXPERIMENTAL

Materials

The materials used in this study were commercially available grades provided by Advanced Elastomer Systems NV/SA (Brussels, Belgium, and Akron, OH). Their general characteristics are given in Table I. San-

TABLE I
Material Specifications

Material	Santoprene 201-55	Santoprene 101-64	Santoprene 121-67W175	Geolast 701-70
Blend composition	EPDM/PP	EPDM/PP	EPDM/PP	NBR/PP
Specific gravity at 23°C (ASTM D 792)	0.97	0.97	0.97	1.0
Shore A hardness (ASTM D 2240)	55	64	67	70
Appearance	Natural	Black	Black	Black

EPDM: Ethylene-propylene diene methylene rubber
PP: Polypropylene
NBR: Nitrile butadiene rubber

toprene 201-55 and Geolast 701-70 were pressed at 5 MPa into sheets approximately 2 mm thick at 190°C for 2 min. The other materials were obtained from the manufacturer as sheets approximately 2 mm thick. The samples were cut into strips (100–130 mm × 12 mm) before aging. The experimental strategy and procedures were similar to those used in studies of experimental blends of NR and PE.[16,21]

UV-exposure and stress-application arrangements

The samples were exposed to UV irradiation in a constant-temperature room at 30 ± 1°C. The illumination was provided by pairs of UVA-340 fluorescent tubes (Q-Panel Co., Cleveland, OH). The intensity and spectral distribution of the tubes were checked regularly with a Bentham Instruments (Reading, United Kingdom) spectroradiometer. The spectral output of the tubes in the UV range matched the spectrum of solar radiation at Earth's surface fairly closely.[18] At higher wavelengths, the intensity was very much lower than solar radiation levels, and no heating of the samples was detected. The total intensity was about 1.8 W/m² in the wavelength range of 295–320 nm, that is, the total radiation below the wavelength of 320 nm, comparable to levels in a hot sunny climate.[22,23]

Most of the tests reported here were conducted with samples loaded in uniaxial tensile stress relaxation with simple frames that could accommodate up to 15 separate strips simultaneously. This means that the load could not be monitored on individual specimens. Stress-relaxation UV exposures were conducted at strains set at 25 and 50%. The ozone levels were checked at various sites within the room in which the UV trials were conducted, including positions close to the samples under test, and found to be below the measurement threshold for the equipment used (<0.02 ppm). In earlier studies,[15–17] when a simple shield made from aluminum foil prevented UV from reaching part of the sample surface, there was a very sharp demarcation between the degradation displayed by the exposed and unexposed zones, and such a shield is now used routinely in tests of this kind conducted in our laboratory. The shield is loosely attached so that if ozone is present in the vicinity of the sample under test, there is no impediment to it reaching the region within the shadow. Any difference in degradation on either side of the shadow boundary must then be attributed to photooxidation rather than ozone attack.

Upon the release of the samples from the stress-relaxation frames, they curved, with the exposed surface always convex. This was reported previously for experimental NR/PE TPEs.[17] More attention was paid to this phenomenon in the program of work reported here, and an attempt was made to quantify the extent of bending via the measurement of the curvature. For samples that were bent fairly modestly, this was done by the measurement of the angle between the tangents to the strip constructed at the positions of the grip jaws during UV exposure (60 mm apart; GG in Fig. 1). If the sample curved through 180° or more, the curvature was determined instead by the measurement of the diameter. The measurement was not precise because of variations in the curvature along the length and also because the samples had low stiffness and were easily deformed when handled during the measurement process. A further problem arose when samples curved through more than 360°, coiling up and causing inaccuracy due to the interference. Despite
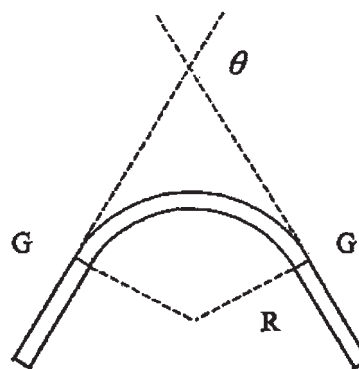

Figure 1 Schematic of a TPE sample upon its release from the grips after UV exposure under tensile strain. The portion between GG was between the grips and exposed to UV on its upper surface during the conditioning experiment.

these problems, the observed curvature was fairly reproducible in samples given the same UV-stress exposure. Furthermore, the differences between different materials and after different exposure conditions were quite large, and the measured values were recorded for comparison.

Mechanical testing

After UV exposure, the strips (100 mm × 12 mm) were tensile-tested at room temperature at a crosshead speed of 500 mm/min on an Instron 4500 (Norwood, MA) with a grip separation of 60 mm or on a Zwick UTM 1445 machine (Ulm, Germany) with a grip separation of 40 mm.

Surface degradation analysis

The samples were inspected with light optical microscopy and scanning electron microscopy (SEM) after selected periods of UV exposure and after the tensile tests. Although it is possible to view rubber samples with SEM without modification,[24] a sputtered gold coating was applied to improve the image quality.

The oxidation of rubbery samples often results in the formation of cracks or fissures on the surface, especially when tensile stress is applied during exposure. Upon the removal of the samples from the stressing jig, the cracks tended to close up and become less visible or sometimes invisible. To overcome this problem, the samples were mounted in a miniature straining device that was placed on the microscope stage; it permitted the application of a small strain during observation.[15–17] The main purpose of the straining device was to reopen cracks formed during tensile exposure, but it was also used to apply a small strain to the samples that were exposed and unstrained. With some samples, this caused a pattern of cracks to appear. It could not be determined whether these cracks were present before deformation on the microscope stage, possibly caused by mishandling, or were produced by the deformation applied for observation. Nevertheless, when three or four samples of the same type and treatment were compared, the same surface characteristics were observed. Whatever the cause of the cracks, they indicated advanced brittleness of the surface of the sample. Oblique illumination was used, and the direction of the light impinging on the specimen surface was adjusted to give greatest visibility of the cracks.

An essentially similar device was made for mounting samples for SEM observation. The conductive gold coating was applied with the sample already stretched on the jig before its insertion into the microscope. The secondary electron image was used throughout, and satisfactory images were obtained with a 15-kV accelerating potential.

RESULTS

General observations

In all cases, the region of the sample that was in the shadow formed by the aluminum foil shield showed almost no evidence of degradation. Its surface appearance was hardly distinguishable from that of an untested sample of the same material, whereas the exposed region was clearly distinguished in almost every case. A close inspection of the demarcation region at the shadow edge showed that, in nearly every case, the region that was illuminated by the UV source suffered one or more of the following: discoloration, change of gloss, and development of a pattern of cracks.

The as-pressed Santoprene 201-55 sheet was white. UV exposure caused discoloration to a pale yellow/brown color within 1 week, whether the exposure was conducted under tensile stress or in the unstressed state. The surfaces of the exposed rubber strips were examined for evidence of cracking, first without flattening of the sample, then after the flattening of any curvature that developed during UV exposure, and finally after the application of a strain (usually 25%) with the special microscope jig to maximize the visibility of any cracks that were present. The application of deformation with the straining jig might, of course, create cracking, especially if the sample had not been placed under tension previously, and the interpretation of cracks observed under such conditions must therefore be treated with caution. For the more severe conditioning trials, the surface took on a rippled appearance that was replaced by a cracking pattern when the strain was applied for microscopy. The careful manipulation of the oblique illumination was required to maximize the visibility of these effects. The observations are summarized in Table II.

Geolast 701-70 was in the form of a black sheet. It degraded less rapidly than Santoprene 201-55 (Table II). Rippling was also a feature with this material.

Less comprehensive sets of observations were made with Santoprene 101-64 and Santoprene 121-67 W175. These materials were black and became shinier upon exposure to UV; there was a clear demarcation at the shadow boundary even after just 1 week of UV exposure in the unstrained state. After an exposure of 1 week at 50% strain, the surface of Santoprene 101-64 appeared to develop very fine, shallow surface cracks, although their visibility was poor and they could not be positively identified as such.

Tensile properties

Santoprene 201-55

Engineering stress–strain curves are shown in Figure 2(a) for Santoprene 201-55 in the as-received (unaged)

TABLE II
General Observations with Samples Exposed in Stress Relaxation Rigs

Grade	UV exposure: Strain (%)/ time (days)	θ/curvature	Change in appearance of exposed surface	
			Unstrained	After application of 25% strain
Santoprene 201-55	0/7		Dulling; discoloration to pale yellow/brown	No difference
	0/28		Dulling; discoloration to pale yellow/brown	Small number of lateral cracks
	25/7		Dulling; discoloration to pale yellow/brown	No difference
	25/28		Large transverse cracks; finer longitudinal cracks	Transverse cracks open up
	50/7		Dulling; discoloration to pale yellow/brown	Faint striations
	50/28		Dulling; discoloration to pale yellow/brown; rippled, wavy	Rippling replaced by large number of transverse cracks
Geolast 701-70	0/7		None	Very faint striations
	0/28		Dulling; shadow boundary not well defined	Short, fine flaws; shadow boundary still not well defined
	25/7	5°/1.45m^{-1}	Dulling; large number of very short cracks	Cracks grow longer and thinner; rippling
	25/28	115°/33.5m^{-1}	Dulling; transverse cracking	Short wide cracks form on flattening; more form and they grow longer and thinner on straining; rippling
	50/7	15°/4.4 m^{-1}	Dulling; large number of small cracks (more than for 25/7)	Not much additional change
	50/28	180°/52.4m^{-1}	Dulling; rippling; large number of cracks, varying sizes	Visible cracks multiply on flattening; visibility reduces on straining (due to rippling); oblique illumination is required

state and for samples UV-aged for 30 days in the unstressed state and strained at 25 and 50%. UV exposure caused a significant reduction in the strain to break, with the greatest fall observed in those samples that were exposed while under tension. Exposure progressively raised the stress–strain characteristics, and this indicated that the material had become stiffer. Compared with the unaged sample, the stress measured with the sample UV-aged for 30 days at 50% strain was approximately 50% higher at low strains, becoming nearly 70% higher as the breaking point of the exposed sample was approached. This could be attributed to UV-promoted crosslinking. Figure 2(a) also shows that the application of 25% strain during UV exposure produced an intermediate level of change and that UV aging in the unstrained state produced a still smaller change. Exposure for 15 days produced fairly similar results [Fig. 2(b)]. The plot for the unaged material is again shown for comparison. The graph for 15 days of UV exposure at 50% strain superimposes almost exactly on the one obtained after

30 days of exposure at the same strain [Fig. 2(a)]. In Figure 2(b), the UV-aged samples, exposed unstressed and at 25% strain, have changed positions with respect to Figure 2(a). This acts as a reminder that although crosslinking causes stiffening, it may also lead to embrittlement and the sample may form microcracks (usually on the surface) during the tensile test, which cause a reduction in the load-bearing area and an apparent reduction in stiffness. There may therefore be competing processes operating, and simple correlations between exposure conditions and measured mechanical properties may not always occur. The cracking patterns are discussed in a later section (Surface Degradation).

Geolast 701-70

Figure 3(a) shows the engineering stress–strain behavior of Geolast 701-70 in the unaged state and after 30 days of UV exposure unstrained and at 25 and 50% strain, respectively. Again, exposure to UV caused
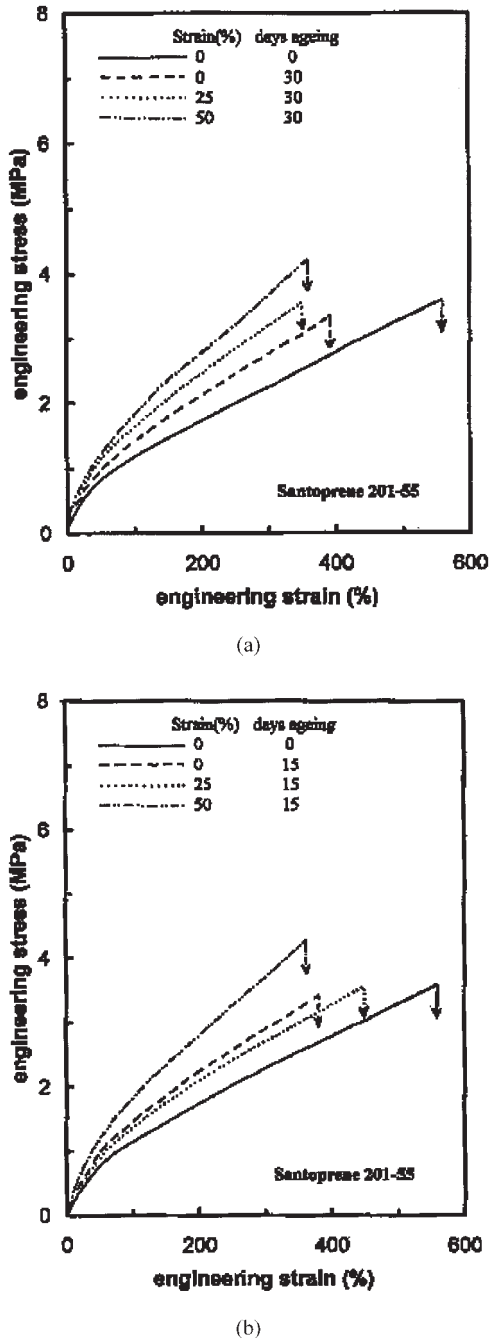
(a)

(b)

Figure 2 Tensile test results for Santoprene 201-55 samples in the unaged state and after aging under UV exposure, unstrained and strained at 25 and 50%, for (a) 30 and (b) 15 days.

significant stiffening, although the effect was much less than that with Santoprene 201-55, with the increase for 50% strain measuring approximately 20%. The change (reduction) in the breaking strain was likewise much less for Geolast 701-70 than for Santoprene 201-55. No significant fall in the breaking strain was observed in samples exposed for 15 days [Fig. 3(b)], but the stiffness enhancement was observed as before. As with Santoprene 201-55, the increase in

stiffness for Geolast 701-70 that was UV-aged at 50% strain was almost the same after 15 days as after 30 days over most of the strain range; some differences were apparent at low strains.

Santoprene 101-64

Engineering stress–strain data for Santoprene 101-64 are given in Figure 4(a–c) for exposures of 6, 17, and 26 days, respectively. The behavior in the unaged state is shown for comparison. After 6 days of UV exposure in the unstrained state, an increase in extension was recorded, to just over 125 mm [falling just outside the axis limit in Fig. 4(a)], but for strained exposure, the extension fell. In the 17- and 26-day tests, the pattern of progressive reduction in extensibility seen with Santoprene 201-55 was repeated; that is, the observed extension fell in the following order: unaged > unstrained UV exposure > 25% strain UV exposure > 50% strain UV exposure [Fig. 4(b,c)]. The segregation of the stress–strain curves for this material was not as clear-cut as that observed with Santoprene 201-55 and Geolast 701-70, but again most of the UV-exposed samples showed greater stiffness than the material aged at the same strain but in the dark. The apparent reduction in stiffness after long exposures [e.g., see the results for samples aged at 50% extension in Fig. 4(c)] was probably the result of surface cracking, leading to a reduced load-bearing area (as discussed later).

Santoprene 121-67 W175

The extension obtained with this material was generally not as great as that observed with Santoprene 101-64 (Fig. 5; cf. Fig. 4). For each of the exposure times (6, 17, and 26 days), the smallest observed extension was obtained for samples exposed to UV at 50% strain. No pattern emerged for the samples exposed with smaller strains, and in two cases, extensions greater than that obtained with the unaged material were recorded. A possible explanation for this is that beneficial UV-promoted crosslinking may occur at relatively modest exposures, and the properties are much more dependent on adventitious flaws in the test piece than on the chemical modifications produced by the photomechanical conditioning. As with the other materials, the UV-exposed samples were usually stiffer than those aged at the same strain in the dark.

Santoprene 121-67 W175 is designed for outdoor use, and the aforementioned behavior is superior to that of Santoprene 101-64. The difference in performance is fairly modest, however, perhaps because the method of testing used in this work may probe different aspects of TPE performance than those used conventionally to judge weatherability.
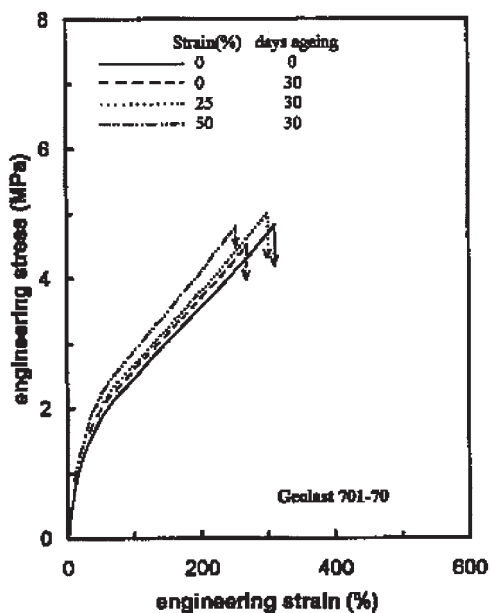
(a)
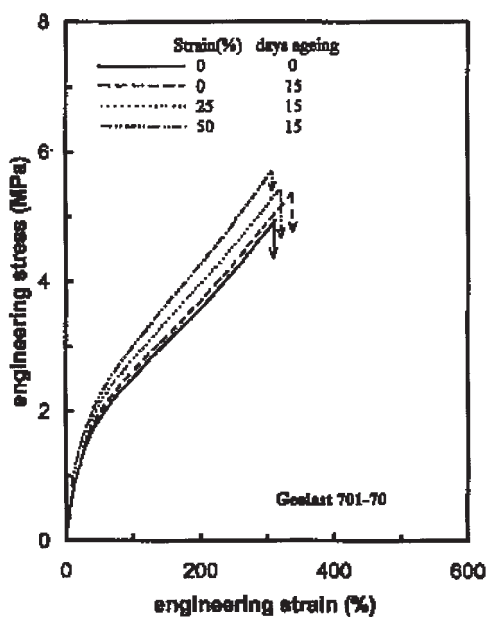
(b)

Figure 3 Tensile test results for Geolast 701-70 samples in the unaged state and after aging under UV exposure, unstrained and strained at 25 and 50%, for (a) 30 and (b) 15 days.

Comparison of sensitivities to UV degradation

The effect of UV irradiation was assessed in a semiquantitative way by the calculation of the ratio (r) of the extension at break of the UV-exposed samples to the extension at break of the unconditioned sample made from the same material (i.e., unexposed and not subjected to straining). The results for Santoprene 101-64 and Santoprene 121-67W are plotted in Figure 6. This

confirms that, in some cases, the conditioned sample extended more than the unconditioned sample ($r > 1$). The most striking feature of Figure 6 is that for several combinations of material and strain conditions during UV exposure, the extension observed after approximately 2 weeks was less than that after 1 week and after approximately 4 weeks, giving a U-shaped plot.

No results were recorded for exposures of 1 week for Santoprene 201-55 and Geolast 701-70, but the results obtained after 15 and 30 days, respectively, show that there was no corresponding minimum in extensibility for these materials at 2 weeks of exposure under the conditions applied here (Table III). This does not mean that a minimum would not be observed under any conditions: it was simply fortuitous that the conditions applied in this study gave rise to the observation of a minimum for Santoprene 101-64 and Geolast 701-70. Further discussion of this can be found in the Recovery section.

Effect of aging extended samples in the dark

Figure 7 shows similar data for samples that were conditioned by the application of a tensile strain (25 or 50%) with no UV exposure for comparison with Figure 6. Minima are again visible after approximately 2 weeks of conditioning at 50% strain, but they are less pronounced than the minima in Figure 6. Santoprene 101-64 conditioned at 25% strain showed the least change in extensibility both under UV exposure and in the dark.

Surface degradation

Santoprene 201-55

The surface of this material was featureless under the light microscope for all combinations of UV-exposure time and strain during exposure until a deformation was applied during microscopic observation. For samples exposed for 1 or 2 weeks, the surface remained featureless even when they were deformed on the microscope stage. After 4 weeks of exposure, degradation became evident when the samples were deformed for microscopy. For the exposed and unstrained sample, the application of 25% strain on the microscope jig produced a cracking pattern similar to that obtained with an NR–PE blend exposed for 14 days at 25% strain (Fig. 5 in ref. 16). After 4 weeks of UV exposure at 25% strain, a network of fine cracks was visible when the sample was flattened for observation under the microscope, although the surface appeared featureless as long as it maintained the curvature that developed as a result of the exposure. This pattern deformed in an affine manner and increased visibility when a strain was applied on the microscope stage (Fig. 8). No
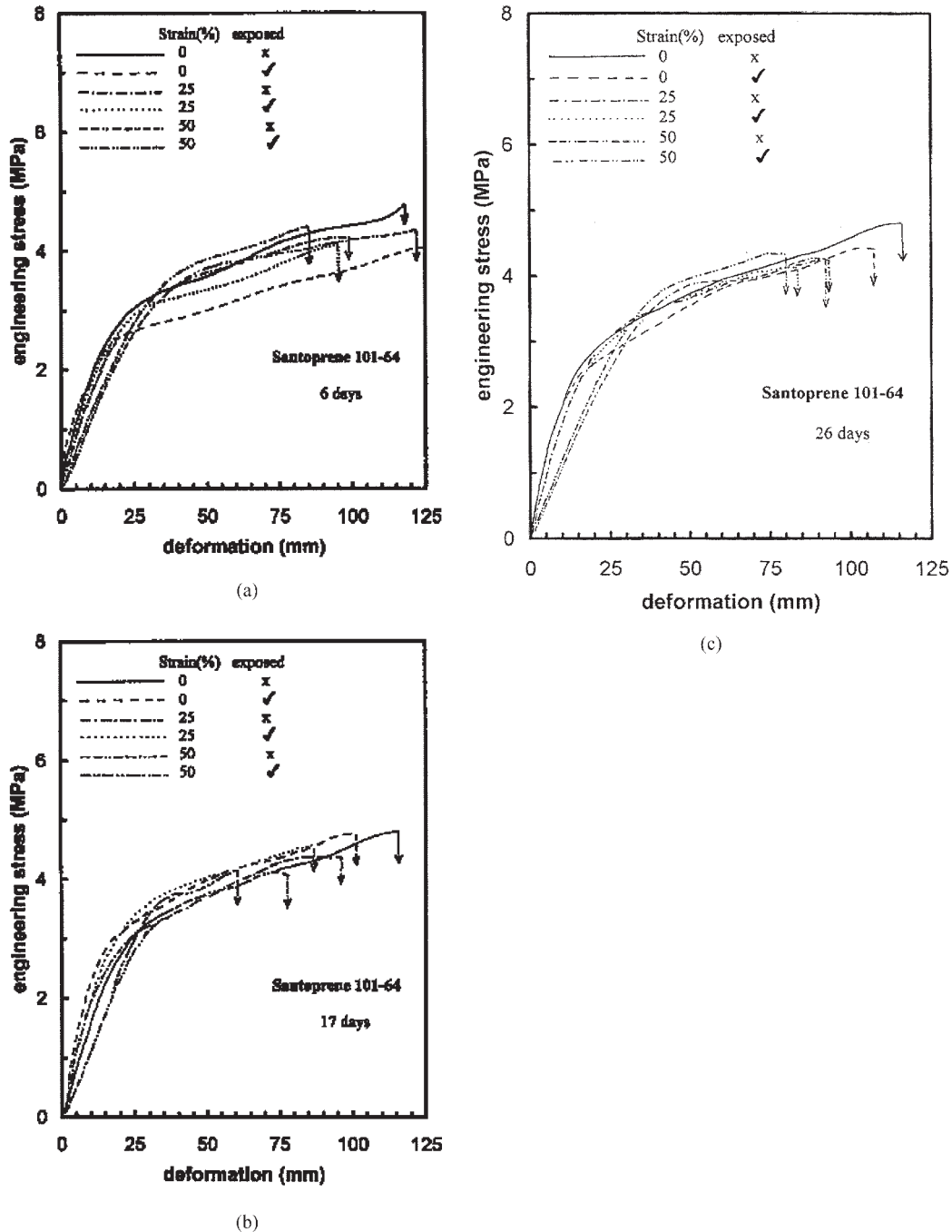
(a)

(b)

(c)

Figure 4 Tensile test results for Santoprene 101-64 samples in the unaged state and after aging under UV exposure, unstrained and strained at 25 and 50%, and in the dark at 25 and 50% strain for (a) 6, (b) 17, and (c) 26 days. The unstrained sample exposed for 6 days failed in the tensile test after just over 125 mm of extension, just outside the limit of the axis.

significantly different features were apparent after 4 weeks of UV exposure at 50% strain.

When we inspected the samples with SEM, fine features, invisible under the light microscope, were found. Figure 9 shows a fine crack on the surface of a sample that was exposed to UV for 2 weeks unstrained. Such flaws were well separated on the surface. They would likely be sites for further crack growth if the sample were to be further extended.

Geolast 701-70

The exposed and unstrained samples showed progressive degradation with the exposure time. After 1 week, the surface was fairly featureless even when strained on the microscope stage. After 2 weeks, striations were visible on straining on the microscope, and after 4 weeks of exposure, the striations were more pronounced and opened up with the application
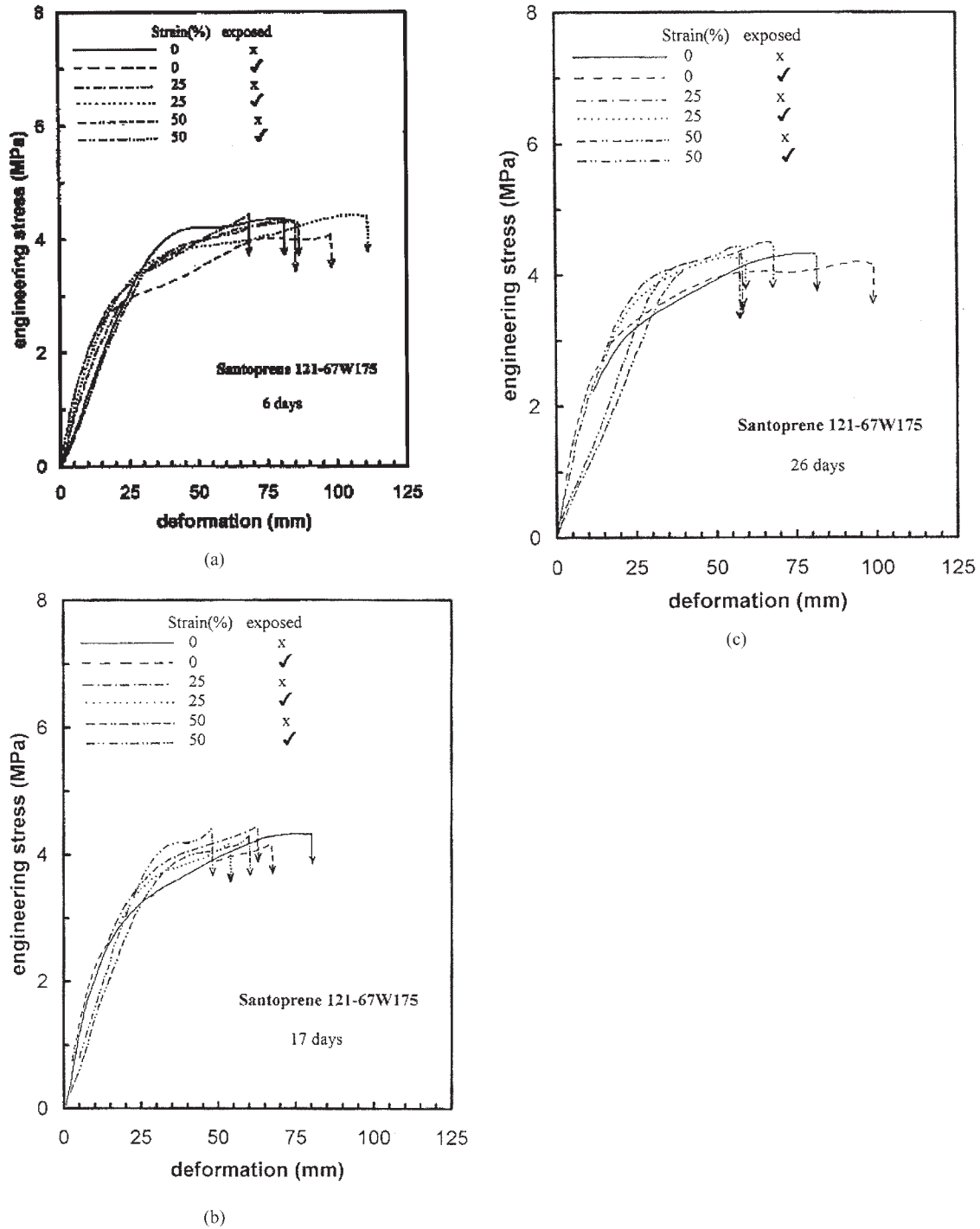
Figure 5 Tensile test results for Santoprene 121-67W175 samples in the unaged state and after aging under UV exposure, unstrained and strained at 25 and 50%, and in the dark at 25 and 50% strain for (a) 6, (b) 17, and (c) 26 days.

of strain on the microscope stage, as might be expected if they were shallow cracks (Fig. 10). The samples that were exposed under tensile strain were curved when removed from the exposure frame. The exposed (convex) surface contained a dense pattern of fine cracks after an exposure of only 1 week at 25% strain. Longer exposure times and/or exposure at 50% strain caused more severe cracking (Fig. 11). Flatten-

ing the samples for microscopy caused the cracks to close up partially, sometimes sufficiently to reduce their visibility.

Santoprene 101-64

After exposure for 1 or 2 weeks, Santoprene 101-64 showed a slightly roughened appearance upon obser-
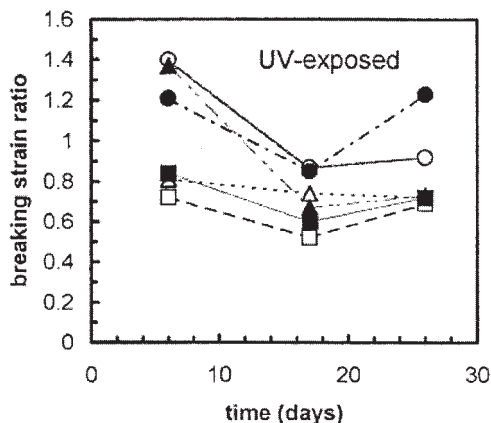
Figure 6 Breaking strain ratios after different times of UV exposure for (○) unstrained, (△) 25% strained, and (□) 50% strained Santoprene 101-64 and for (●) unstrained, (▲) 25% strained, and (■) 50% strained Santoprene 121-67W.
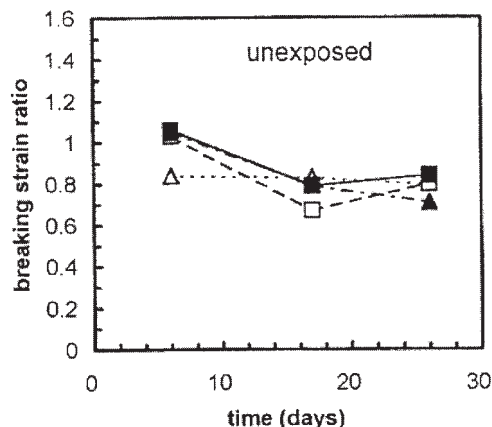

Figure 7 Breaking strain ratios after different times of aging in the dark for (△) 25% strained and (□) 50% strained Santoprene 101-64 and for (▲) 25% strained and (■) 50% strained Santoprene 121-67W.

vation under the microscope. After 26 days of exposure at 50% strain, extensive cracking was visible when the samples were strained on the microscope (Fig. 12). Figure 12 shows clearly the shadow demarcation line.

Santoprene 121-67W175

The surface of Santoprene 121-67W175 was degraded slightly more than that of Santoprene 101-64 after 2 weeks of exposure (all strain conditions). There was a hint of striations (possibly diffuse cracking) upon the flattening or stretching of the samples on the microscope stage. After 4 weeks of exposure at 50% strain, a well-developed crack pattern was obtained (Fig. 13).

DISCUSSION

Degradation mechanisms and cracking patterns

The ranges of exposure times and strains used in the experimental program were too small to permit a comprehensive assessment of the effect of the application of strain during UV exposure, but some gen-

eral points have emerged. For at least some polymers, photooxidation is accelerated by the application of tensile stress.[15,18–20,25–29] If this is the case with the TPEs studied here, both scission and crosslinking are expected to increase when tensile strain is applied during UV exposure. If crosslinking dominates, this will be expected to cause an increase in stiffness. Both scission and crosslinking will cause embrittlement of the surface (where the reaction rate is highest), and if fissures are formed in the embrittled layer (either during exposure or during the subsequent tensile test), this will reduce the load-bearing area and cause a decrease in the measured stiffness. The development of curvature in samples that were exposed to UV irradiation while under tensile strain imitates that observed with ex-

TABLE III
Ratios of Strain at Break of Samples After Strain and/or UV Conditioning to Strain of Unconditioned Sample at Break

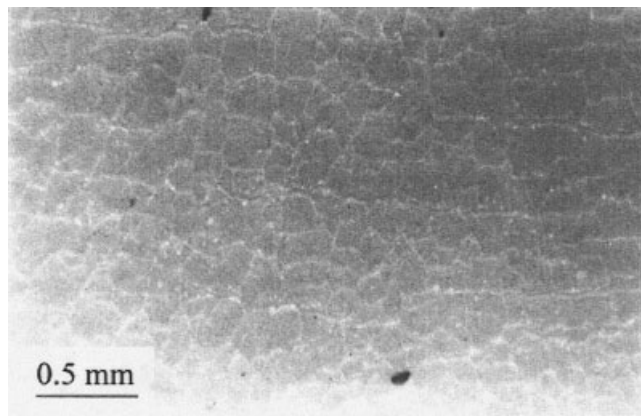|	Strain during UV exposure (%)	15 days	30 days
Santoprene 201-55	0	0.69	0.70
	25	0.80	0.63
	50	0.64	0.64
Geolast 701-70	0	1.09	0.86
	25	1.03	0.97
	50	1.01	0.81

0.5 mm

Figure 8 Light microscopy image of the surface of Santoprene 201-55 after 4 weeks of UV exposure at 25% strain, showing a network of fine cracks. The tensile axis during both UV exposure and microscopy was vertical; note the cracks running both perpendicularly and parallel to this direction.
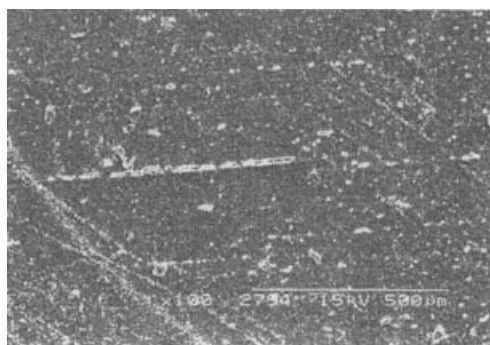
(a)
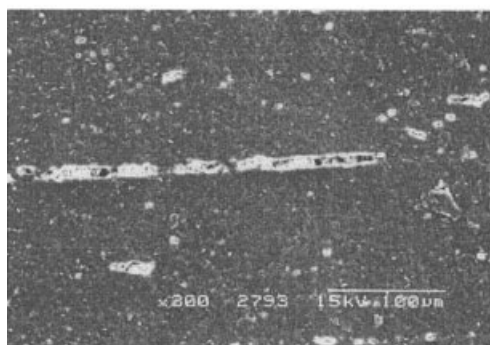
(b)

Figure 9 SEM images of the surface of unstrained Santoprene 201-55 after 2 weeks of UV exposure: (a) an isolated fine crack and (b) the same crack at a higher magnification.

Figure 10 Light microscopy image of the surface of unstrained Geolast 701-70 after 4 weeks of UV exposure (25% strain was applied to take the micrograph).

Chemical mechanism of degradation

The use of a shield showed very clearly that direct UV exposure was required to produce the surface crack-

(a)

(b)

Figure 11 Light microscopy images of the surface of Geolast 701-70 after 4 weeks of UV exposure at 50% strain: (a) low-magnification image showing the full width of the sample (~12 mm) and (b) higher magnification image of part of the surface. The strain axis was vertical.

perimental TPE blends of NR and PE, as reported previously,[17] and the explanation for their formation follows that offered before. The broken fragments of molecules that suffer photooxidative scission will not contract as much as an unbroken molecule when the stress is removed, so when a sample is removed from the straining rig, the exposed surface contracts less than the unexposed surface, which suffers less molecular damage and retains more of its rubbery properties. The differential contraction causes curvature in the sense observed. If cracking occurs in the strained state, this will lead the way to even greater irreversible deformation because creep extension will take place at the crack roots. When the sample is released from the straining rig and contraction of the rubbery material near the unexposed face occurs, the cracks are not able to close completely because of the deformation at the roots. This incomplete crack closing may contribute to the rippling effect observed in some samples. The axial contraction that occurs when samples are released from the stress-relaxation frames is accompanied by (Poisson) expansion in transverse directions, and this probably causes the cracking parallel to the stress axis seen in some samples (e.g., Fig. 8).
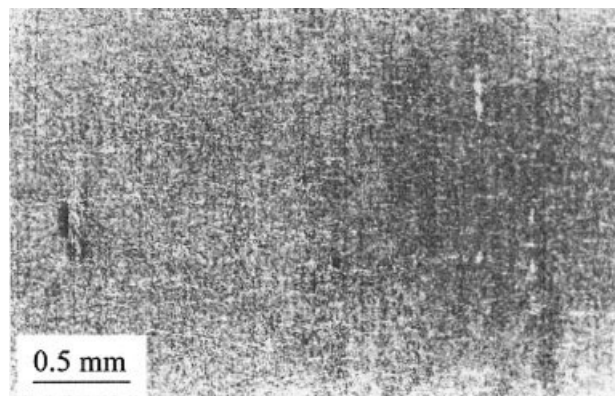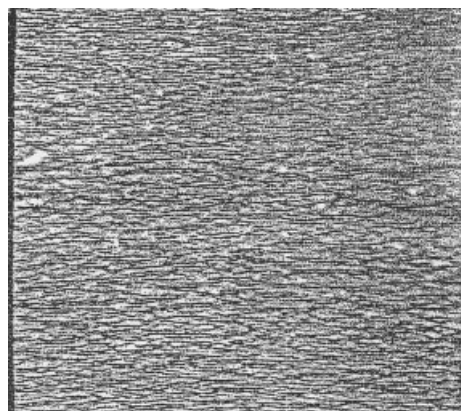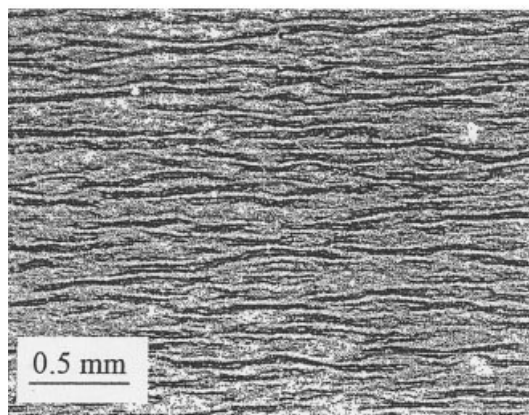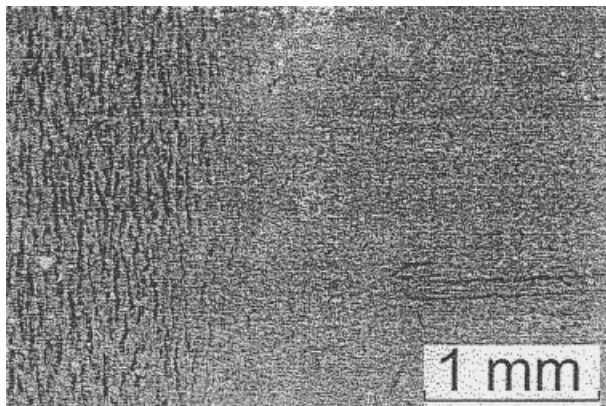
Figure 12 Light microscopy image of the surface of Santoprene 101-64 after 4 weeks UV exposure at 50% strain The strain axis was horizontal. The shadow edge of the shield is clearly visible.

ing patterns observed in these tests (e.g., see Fig. 12). Although UV is known to produce ozone from atmospheric oxygen, it is almost inconceivable that the ozone level just inside the shadow is very different from that in the exposed region. Therefore, although a contribution to degradation from ozone attack cannot be ruled out, it is evident that the major contribution is due to photooxidation.

Photochemical degradation is currently under study in our laboratory. The weathering of a few polymers was treated by Davis and Sims.[5] UV light initiates free-radical oxidation at the exposed surface of the product to generate a layer of oxidized rubber. Moisture and heat can then initiate crazing of the surface. The degradation of unsaturated elastomers is an autocatalytic, free-radical chain reaction. Once oxidation starts, it sets off a circular chain reaction that accelerates degradation unless stabilizers are used to interrupt the oxidation cycle.

UV irradiation of unsaturated rubbers results in the following changes:[5] the appearance of absorption bands at 1725 cm^{-1} attributed to the stretching vibration of the C=O carbonyl groups, at 3440 cm^{-1} due to the stretching vibration of the —OH hydroxyl group, and at 1160 cm^{-1} due to the C—O group. These chemical changes are indicative of oxidative degradation and the accompanying chain scission. The growth of carbonyl groups is a recognized means of following the photooxidation of polypropylene, which is a constituent of Santoprene materials. Oxidative breakdown is thus facilitated by the presence of hydrogen atoms attached to tertiary carbon atoms. However, the oxidation rate in polypropylene is reported to be not as fast as the number of tertiary hydrogen atoms because of crystallinity and other reasons.

Recovery

The extension to break was greater after 4 weeks of exposure than after 2 weeks for many of the material-

conditioning combinations tested in this study. This seems to indicate some recovery of the property. It is clear that this does not coincide with the repair of damage or a beneficial modification of the state of the material, however, because the surface cracking patterns develop significantly between 2 and 4 weeks (Table II). It is speculated that the reason for the recovery in this property (extension) is that the surface region becomes extremely brittle under prolonged conditioning, especially when this includes UV exposure, and that it breaks easily, allowing the formation of the cracking patterns (e.g., Figures 11–13). The surface layer is so fragile that more cracks form in it when further extension is applied during the tensile test. This partially unloads the neighboring cracks and postpones the formation of a dominant crack that is able to propagate into the relatively undamaged material underneath. The extension is then controlled by the material that is located in the interior, and extensibility is therefore (partially) restored. This is analogous to the phenomenon of recovery that has been observed during photodegradation studies of polypropylene and that has also been dismissed as of no practical value.[30–34] The phenomenon is nevertheless of importance because it can give the illusion of material improvement when tests are performed. Of special concern, in a test program that is based on fairly long intervals between property measurements, it would be easy to miss the condition under which a sample has a property minimum, and a falsely favorable result would be recorded. To avoid falling into this trap, it is advised that property interrogation should be conducted at fairly short intervals and that material quality should not be judged with a single property or characteristic.
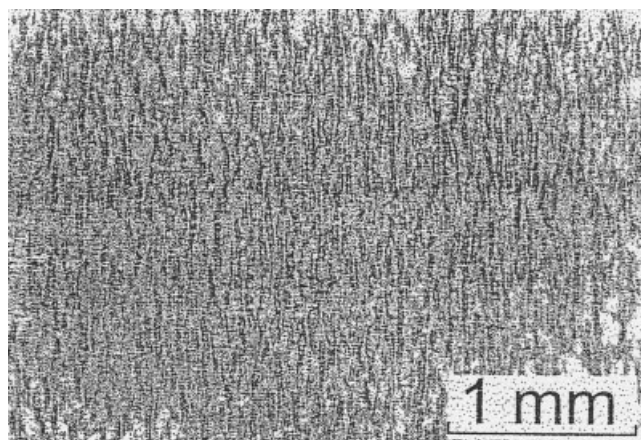

Figure 13 Light microscopy image of the surface of Santoprene 121-67W after 26 days at 50% strain. The strain axis was horizontal.

Comparison with other TPEs

The conditions applied in these tests are very severe. The most resistant of the NR–PE blends studied previously under similar conditions was the one stabilized by isopropyl paraphenylene diamine (IPPD).[16] Some samples of this material were tested during this program for comparison and failed before completion of 4 weeks of exposure at 50% strain, whereas the commercial grades survived this treatment. In the previous study, the blend containing IPPD was far superior to the same blend with no UV stabilizer, and it is deduced that the commercial materials studied here have a level of UV protection that is probably adequate for a wide range of applications. Nevertheless, they showed progressive deterioration reminiscent of that observed with the experimental materials, although it developed more slowly. It is evident that further improvements in UV stabilization would be beneficial in some applications.

CONCLUSIONS

Commercially available TPEs have been shown to be sensitive to UV exposure, and the combination of UV exposure and tensile deformation is particularly potent. Photooxidation, rather than ozone attack, is the principal cause of property deterioration. With the test procedures applied in the research reported here, the grades specifically developed for outdoor applications did not display particularly superior performance. The materials were, however, significantly more resistant to UV degradation than TPEs compounded without UV protection. Photooxidation, rather than ozone attack, was identified as the principal cause of degradation during UV exposure.

Some recovery of extensibility was observed during the 2–4-week exposure interval, but on closer analysis, it was deduced that no material repair or improvement had taken place and that this apparently beneficial change was not reflected in other properties. Care must be taken when test programs are planned and the results are interpreted to ensure that a condition under which a material possesses an apparent property minimum is not missed as the result of interrogation intervals that are too long or as the result of using too few material characterization parameters.

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