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SURFACE MICROCRACKING INDUCED BY WEATHERING OF POLYCARBONATE SHEET

ANALYZED

by A. Blaga and R.S. Yamasaki

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SOMMAIRE

Une étude a été entreprise à la DRB/CNR de l'effet de trois facteurs du milieu - la température, l'humidité et le rayonnement - sur la durabilité de plaques commerciales exposées aux intempéries. Les résultats de l'étude sont décrits dans cette communication et un mécanisme est proposé pour la formation des microfissures en surface des plaques en polycarbonate dans des conditions d'exposition extérieure.

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Surface microcracking induced by weathering of polycarbonate sheet

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Polycarbonate sheet subjected to outdoor weathering for relatively short periods develops a network of surface microcracks on the side exposed to solar radiation. Artificial weathering and SEM microscopy were used to illustrate the process of microcrack formation. Microcracking occurs under the influence of light radiation in conjunction with cycling of either temperature and moisture or temperature alone. The use of radiation by itself, or even relatively severe cycling of temperature and humidity without radiation, does not induce microcracking. According to the proposed mechanism, the resin of the exposed surface undergoes, with weathering, a gradual reduction in strength owing to a lowering of its molecular weight as a result of photochemical degradation. Cyclic variation of temperature and humidity in natural and artificial weathering imposes on the surface material a type of stress fatigue. Such stress fatigue is caused by the non-uniform dimensional changes that result from thermal and moisture content gradients between the surface and the bulk of the resin and from inhomogeneities and defects. When the fatigue limit of the surface material at a microsite becomes lower than the physically induced stresses, the resin cracks.

1. Introduction

Polycarbonate sheeting is used increasingly as shatter-proof glazing material in public and industrial buildings because of its very high impact resistance and excellent transparency. As it is becoming economically more attractive, polycarbonate is also entering other fields of materials application where it will be exposed to various interior and exterior environments. It is, therefore, essential that its performance in these environments be understood, in particular, its resistance to outdoor weathering.

A relatively new commercial plastic material, polycarbonate, has undergone very few weathering studies [1, 2]. Those that have been done have been concerned only with the photochemical processes of degradation by solar radiation. A number of studies have been carried out that demonstrate the reaction mechanism of photochemical degradation of the polycarbonate polymer by subjecting it to accelerated weathering [3] or to irradiation with longwave ultraviolet light approximating that of natural sunlight [1, 4, 5]. This work on the degradation of polycarbonate in both outdoor and artificial environments has generally been carried out on film material and has covered relatively short periods of time. In all these studies the physical effects of temperature and humidity, two important factors of most environments, have been neglected.

A study has, therefore, been undertaken at DBR/NRC of the effect of three environmental factors – temperature, humidity, and radiation – on the durability of commercial polycarbonate sheeting exposed in an outdoor environment. Scanning electron microscopy (SEM) was used to assess changes in surface structure, and examination of the exposed side revealed the formation of a network of surface microcracks after 30 to 32 months. Samples of polycarbonate sheet were then subjected to various artificial weathering treatments in an attempt to reproduce this type of

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TABLE I Methods of environmental ageing of polycarbonate sheets

Method	Ageing conditions General	Details
1	Outdoor weathering at Ottawa (temperate northern climate)	Samples exposed at 45° facing south, with no backing, in accordance with ASTM D1435.
2	Cyclic variation of temperature, humidity and radiation (Atlas Xenon Arc Weather-Ometer)	4 h at 100% r.h. and 12° C†, water spray on, no radiation; 4 h at 50% r.h. and 55° C, radiation on, water spray off; 3 cycles per day.
3	Continuous radiation at constant temperature and humidity (Atlas Xenon Arc Weather-Ometer)	R.h. at 50% and panel temperature of 55° C at all times
4	Cyclic variation of temperature between − 18 and 25° C	10 min cooling to − 18° C and 10 min warm-up to 25° C
5	Cyclic variation of temperature and humidity (Aminco Climate Lab)*	7 h at 100% r.h. and 56° C; 5 h at 25 to 100% r.h. and 11 to 56° C; 2 cycles per day

*More details are given in [6] Figs. 1 and 2; deionized water at 9° C is sprayed on the exposed side of the panel.

†The temperatures are those of the samples.

TABLE II Data on the formation of surface microcracks in polycarbonate sheet

Exposure method	Side examined	Time to first occurrence of single cracks*	Time to formation of network of cracks*	Total exposure period	Conclusions
1	back	no cracks	no cracks	82 m	Environmentally induced stress fatigue does not produce surface microcracks on the back (unexposed side) because of absence of radiation.
1	front	20 – 23 m	30 – 32 m	82 m	Shows that radiation is necessary to induce formation of microcracks.
2	front	370–375 cy	440 cy	750 cy (6015 h)	Confirms results observed for exposure 1, front.
2	back	no cracks	no cracks	750 cy (6015 h)	As no cracks were detected at the end of treatment, this observation confirms results of exposure 1, back.
3	front	no cracks	no cracks	4200 h	Radiation in the absence of stress does not produce microcracks even after a relatively long period of treatment.
3 + 4†	front	2100 h + 1200 cy	2100 h + 1800 cy	2100 h + 1800 cy	Shows that microcracking can be produced even when radiation of surface is carried out prior to temperature cycling.
3 + 4†	front	4200 h + 845 cy	4200 h + 1450 cy	4200 h + 1450 cy	Shows that when the surface is pre-irradiated for a longer period, shorter temperature cycling is required to induce formation of microcracks.
3 + 4	back	no cracks	no cracks	4200 h + 1450 cy	The back (non-irradiated side) does not develop surface microcracks when subjected to thermally induced stress fatigue, thus confirming results of exposure 1, back and exposure 2, back.
5‡	–	no cracks	no cracks	2100 cy	Relatively severe, environmentally induced stress fatigue does not induce surface microcracks in the absence of radiation.

*Time of occurrence of surface microcracks is given in months (m), cycles (cy) or hours (h).

†These samples were subjected to continuous radiation for 2100 and 4200 h, respectively, prior to subjecting them to temperature cycling.

‡In this method both sides are subjected to the same exposure.

failure and thus gain insight into the process of surface deterioration.

In this paper the results of the study are described and a mechanism proposed for the formation of surface microcracks in polycarbonate sheeting under the conditions of the outdoor exposure. An understanding of the process of surface deterioration and the role of the environmental factors involved should permit development of more adequate methods of assessing the durability of polycarbonate and possibly other thermoplastic materials.

2. Experimental

2.1. Materials and methods of ageing

Commercial glazing sheet (3.0 mm thick) of bisphenol A polycarbonate was used in this study. Although most of the samples were of stabilized polycarbonate, unstabilized sheet was also used for comparison in the outdoor weathering. Initially, sheets of polycarbonate were exposed outdoors at a weathering site at Ottawa, but samples were subsequently exposed to various accelerated weathering treatments. Details of both outdoor exposure and methods of accelerated ageing are given in Table I.

2.2. Examination of surface microcracking by scanning electron microscopy

The formation of surface microcracks was followed by a Stereoscan scanning electron microscope operated at 20 kV and a tilt angle of 45°. Specimens were coated first with carbon and then with gold to prevent surface charging.

3. Discussion of results

The formation of surface microcracks in polycarbonate sheets and their characteristic features at various stages of environmental ageing treatments are illustrated by SEM micrographs in Figs. 1 to 14. Unless otherwise specified, the SEM micrographs refer to stabilized polycarbonate samples. Table II summarizes the results and conclusions of the study.

3.1. Surface microcracking during outdoor weathering

Polycarbonate sheets weathered outdoors at Ottawa (Table I, method 1) developed surface microcracks on the side exposed to solar radiation. Figs. 2 and 3 illustrate the incipient stage of surface microcracking that occurred after 20 to 23 months of exposure. The very narrow (0.1 to 0.2 μm in width), randomly-oriented initial cracks propagate slowly with ageing and intersect to form a network. This network of relatively shallow cracks divides the surface of the sheet into predominantly triangular and four-sided polygons (Figs. 4, 6 and 7).

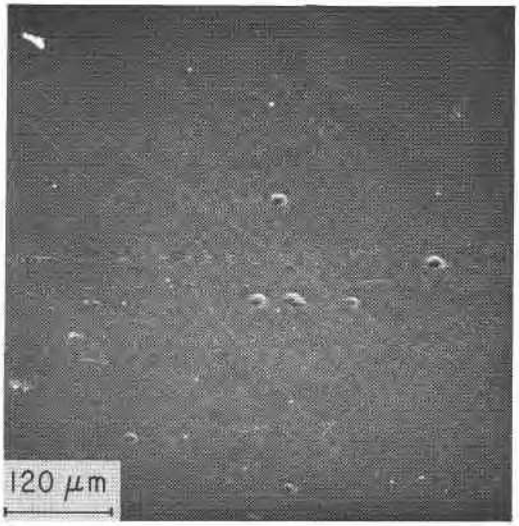

Figure 1 Polycarbonate sheet. Control.

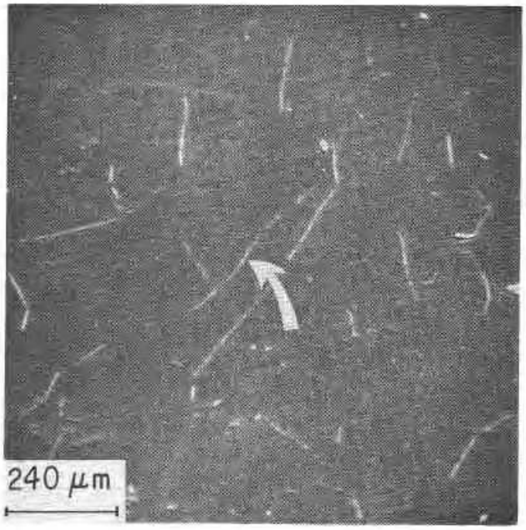

Figure 2 Polycarbonate sheet weathered outdoors for 23 months.

At relatively low magnification the cracks appear as bright lines because of electrical charging (Figs. 2 and 4). At higher magnification, however, they display the usual characteristics of cracks (Figs. 3 and 5) and show none of the features of crazes as this term is currently understood [7].

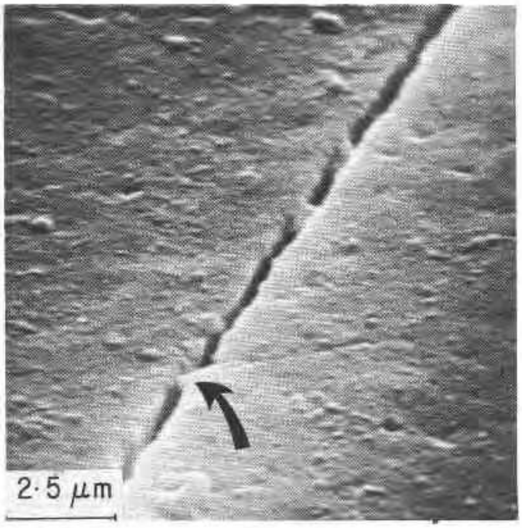

Figure 3 Polycarbonate sheet weathered outdoors for 23 months.

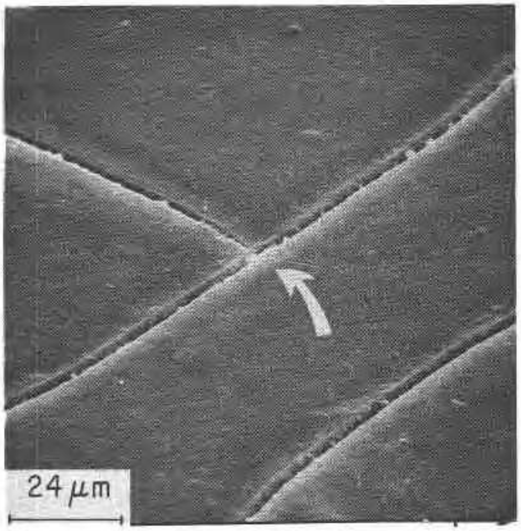

Figure 5 Polycarbonate sheet weathered outdoors for 55 months.

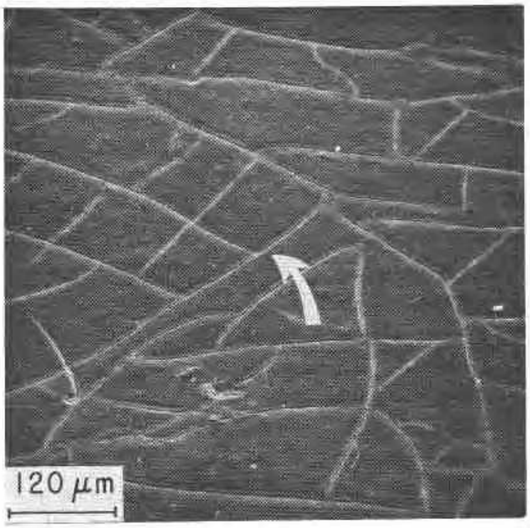

Figure 4 Polycarbonate sheet weathered outdoors for 55 months.

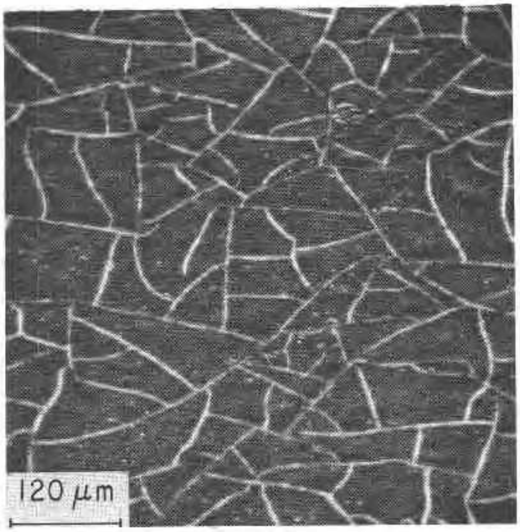

Figure 6 Polycarbonate sheet weathered outdoors for 82 months.

The areas confined between the intersecting cracks decrease with weathering because the surface resin layers continue to fracture, forming new cracks. Figs. 6 and 7 show the surface of the exposed side of stabilized and unstabilized sheets weathered outdoors for 82 months. As expected, the surface microcracks of the unstabilized sheet are deeper and wider than those of the sheet made from stabilized material; their number per unit area of surface (density of cracks) is also greater, as evidenced by the smaller area of the polygons formed by the cracks.

The back of the polycarbonate sheet, which is exposed to essentially the same environmental conditions except for the action of radiation, did not show any evidence of surface microcracks (Fig. 8), indicating that radiation is necessary for their formation.

3.2. Accelerated weathering with cycling of radiation, humidity and temperature

Exposure of polycarbonate sheets to alternate cycles of radiation and water spray in the Xenon

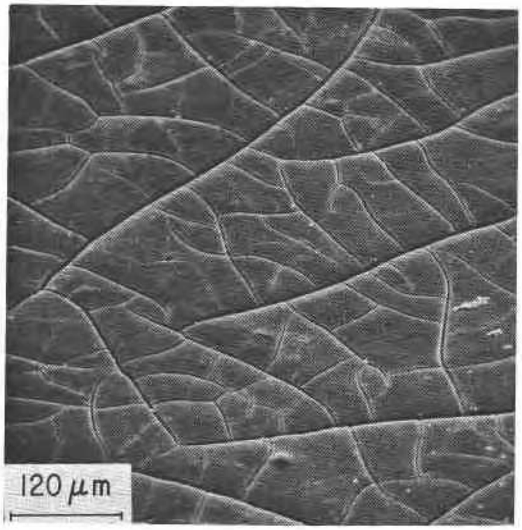

Figure 7 Unstabilized polycarbonate sheet weathered outdoors for 82 months.

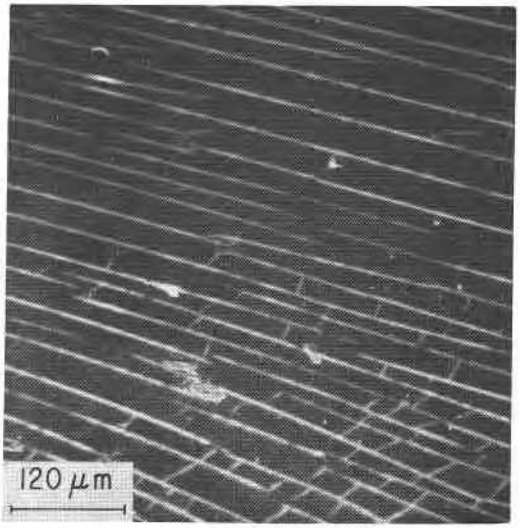

Figure 9 Polycarbonate sheet aged in the Weather-Ometer for 375 cycles.

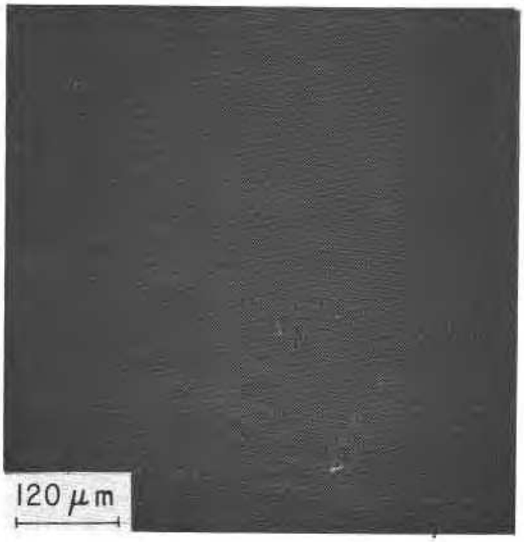

Figure 8 Polycarbonate sheet (back side) weathered outdoors for 82 months.

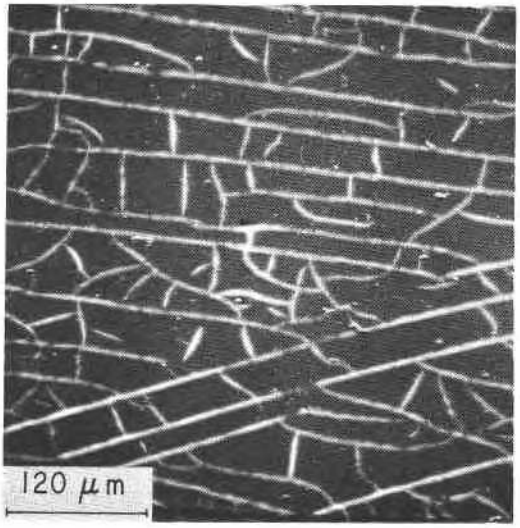

Figure 10 Polycarbonate sheet aged in the Weather-Ometer for 440 cycles.

Arc Weather-Ometer* (Table I, method 2) resulted in the formation of surface microcracks in the exposed (front) side of the samples. The initial cracks were usually parallel (Fig. 9), unidirectional and occurred after 370 to 375 cycles (each lasting 8 h). Secondary, mostly parallel, cracks subsequently formed, intersecting the initial cracks (Figs. 9 to 11) to produce a network.

The polygons formed by microcracks induced by Weather-Ometer ageing were generally fairly regular in shape (usually rectangular), perhaps because of the good reproducibility of cycles and relatively uniform change in the environmental conditions at the sample during any given cycle. This is in contrast to the irregular polygons formed during outdoor weathering, where the environmental conditions are quite variable during a cycle and from one cycle to another.

As for outdoor weathering, the density of the cracks increased with ageing and the back (unexposed) of the sheet did not undergo surface microcracking.

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*Trade Mark.

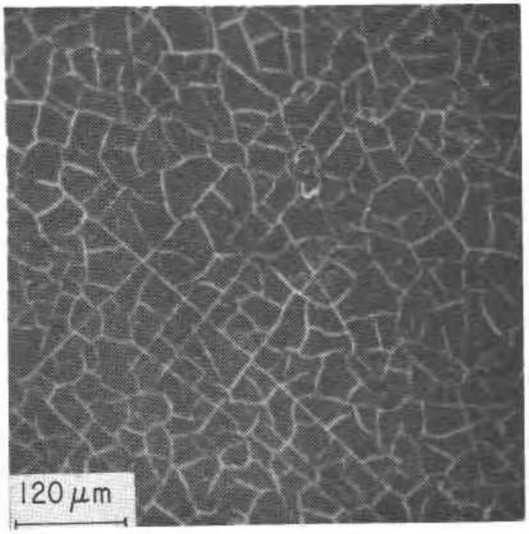

Figure 11 Polycarbonate sheet aged in the Weather-Ometer for 750 cycles.

3.3. Accelerated weathering with continuous radiation and constant temperature and humidity

Continuous radiation at 55°C (sample temperature) and 50% r.h. (Table I, method 3) did not produce surface microcracking in polycarbonate sheet even after 4200 h (Table II, method 3), a period equivalent to 8400 h of intermittent radiation with temperature and humidity cycling (Table I, method 2).

3.4. Thermal cycling of pre-irradiated polycarbonate sheet

When polycarbonate sheet, pre-irradiated as described in the previous section (Table I, method 3) was subjected to temperature cycling between -18 and 25°C (Table I, method 4) surface microcracks were produced on the pre-irradiated side only (Table II, methods 3 and 4). They were much finer than those produced in either outdoor weathering or Weather-Ometer ageing. Thermal cycling did not induce microcracking in the non-irradiated (control) sheet.

The sheet pre-irradiated for 2100 h developed incipient microcracks after about 1200 temperature cycles and a network of very fine cracks after about 1800 cycles (Figs. 12 and 13). The density of the cracks was very high, as shown in these micrographs of relatively high magnification. The polycarbonate sheet pre-irradiated for 4200 h required only 845 temperature cycles to develop incipient microcracks. A full network of surface microcracks formed after about 1450 cycles.

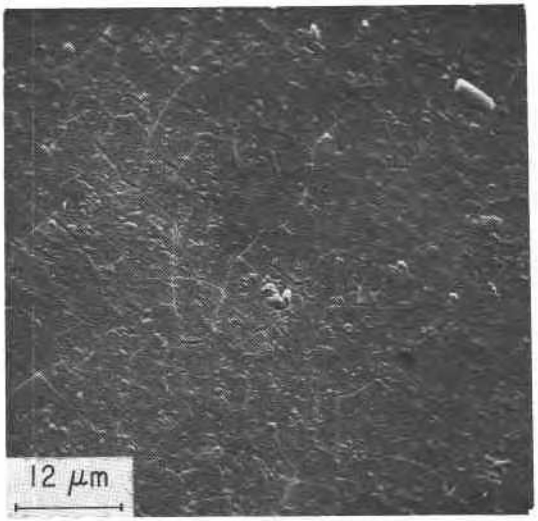

Figure 12 Polycarbonate sheet subjected to 2100 h continuous radiation in the Weather-Ometer and subsequently to 1800 temperature cycles.

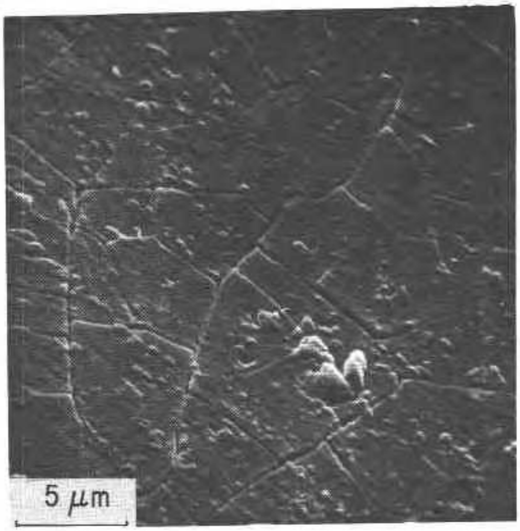

Figure 13 Polycarbonate sheet subjected to 2100 h continuous radiation in the Weather-Ometer and subsequently to 1800 temperature cycles.

3.5. Exposure to variable temperature and humidity without radiation

Polycarbonate sheet subjected to cycles of humidity and temperature (Table I, method 5) did not develop surface microcracks (Table II, method 5) even after 2100 cycles (approximately 3 yr). Cycling of temperature and humidity induces localized, alternating microstresses between the surface resin layer and the bulk of the material, and at flaws and inhomogeneous points in the surface, causing a type of stress fatigue. These observations corroborate those presented earlier and demonstrate that surface microcracks in a sheet of polycarbonate are not caused by environmentally induced stresses alone even if they are relatively severe; the degradative action of radiation is also required.

4. Mechanism of surface microcracking

In outdoor weathering and in most of the ageing treatments described, the polymeric material in the surface region of the sheet undergoes dimensional changes as a result of cyclic variations in temperature and humidity. Cyclic changes of temperature result in alternating volume expansions and contractions of the material; cyclic variations of humidity cause absorption and desorption of moisture, and this in turn results in alternating swelling and shrinking. Dimensional changes induced by both temperature and moisture may be in the same or in opposite directions, depending upon the exposure conditions to which the material has been subjected.

For example, during very hot, humid summer days, plastic sheets exposed outdoors undergo thermal expansion at the same time as swelling caused by water absorption. During hot, dry periods they undergo thermal expansion, but moisture-induced volume change may be in the opposite direction because of water desorption. Similar volume change relations can occur during artificial exposure (Table I, methods 2 and 4).

The average magnitude and rate of volume change could be relatively large and variable, depending on the state of the plastic and the conditions imposed. For artificial weathering exposure, thermally induced volume change was estimated to be 0.86% for a temperature change of 43° C and cubic thermal coefficient of expansion of $20 \times 10^{-5}\,^\circ\mathrm{C}^{-1}$. The rates of volume change were uniform for a given imposed cycle, but varied with conditions of exposure. In outdoor weathering, thermally induced volume changes can be irregular with respect to both value and rate because of fluctuations in the weather.

Although the equilibrium amount of water absorbed is relatively low (0.45%, McBain quartz balance, 100% r.h., 23° C), the volume changes induced by moisture may be significant, especially when these volume changes are in the same direction as those induced thermally. In both artificial and outdoor weathering the amount and rate of water absorption will change with time as a result of surface cracking, formation of hydrophilic groups by hydrolysis, and reduction in molecular weight. In particular, gradual reduction in molecular weight will result in an increasing number of chain ends that will augment the number of submicroscopic voids. An increased number of voids will cause absorption of larger amounts of water, probably at higher rates of absorption.

Owing to gradients in temperature and moisture content in the plastic and to the presence of inhomogeneities and flaws [7], the cyclic dimensional changes that occur are not uniform with depth nor are they uniform at the same depth beneath the surface. They cause a variable, nonuniform stress that exerts a type of stress fatigue on the material. Thermally or moisture-induced stresses can be relatively large, depending on conditions. For example, shortly after the change from radiation to water spray (Weather-Ometer exposure, Table I, method 2) the topmost layer will be at approximately 9° C, the temperature of the water spray; at the same time, because of the low thermal conductivity of the material, the layer at 10 to 20 μm depth will still be at 55° C (panel temperature during radiation). Consequently, the resin in the top layer tends to contract, but it is restrained by the underlying layers, which are still in the expanded state. This produces tensile stresses in the top layers. If, for simplicity, uniform temperature and stress in the surface plane are assumed, the difference in thermal stresses, $\Delta\sigma$, between the top layer and the layer at 10 to 20 μm depth can be estimated using the following equation:

$$\Delta\sigma = E\alpha\Delta T,$$

where E is the modulus of elasticity, α the coefficient of thermal expansion, and ΔT the difference in temperature. The estimated difference in thermal stress was 7.3×10^6 Pa (1060 psi), using 2.41×10^9 Pa, $6.6 \times 10^{-5}\,^\circ\mathrm{C}^{-1}$ and 46° C for E, α and ΔT, respectively.

Initially, the polymeric material in the surface has a stress-fatigue limit (maximum stress below which fracture by fatigue never occurs) higher than the environmentally induced stresses and thus undergoes repeated reversible deformation without fracture. Owing to the action of the ultraviolet portion of solar radiation, the material of the exposed surface layers undergoes a gradual decrease in molecular weight [8] by a process of photo-oxidative chain scission [9]. This decrease, which does not occur in the bulk material nor in the surface layers of the side not exposed to solar radiation, is in proportion to the amount of irradiation by ultraviolet light.

A decrease in molecular weight causes a lowering of the total attractive forces between adjacent polymer chains, and this, in turn, lowers the resistance of the resin to fracture. When the fatigue limit at a given site becomes lower than the environmentally induced differential stresses, fracture of the surface resin occurs, producing microcracks. Because of gradients in the stresses involved, the cracks grow from the surface inwards and are V-shaped, with the median plane approximately perpendicular to the sheet; the cracks are limited to the exposed surface region (Fig. 14).

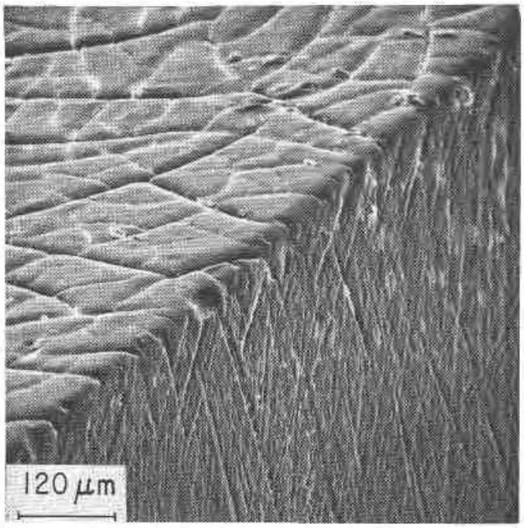

Figure 14 Cross-section of polycarbonate (unstabilized) sheet weathered outdoors for 77 months.

5. Conclusions

Polycarbonate sheet subjected to outdoor weathering for a relatively short period (30 to 32 months) develops a network of surface microcracks on the side exposed to solar radiation. Artificial weathering studies show that microcracks are formed under the influence of light radiation and cycling of either temperature and moisture or temperature alone. The use of radiation by itself, or even severe cycling of temperature and humidity without radiation, does not produce microcracking.

It is believed that cyclic variation of temperature and humidity in natural and artificial weathering imposes a type of stress fatigue on the material. This physically induced stress fatigue is caused by the non-uniform dimensional changes that result from thermal and moisture content gradients between the surface and the bulk resin and from inhomogeneities and defects inherent in the material. With weathering, the resin of the exposed surface undergoes gradual photochemical degradation that reduces its strength. When the fatigue limit at a microsite becomes lower than the physically induced stresses, the resin undergoes fracture to produce microcracks.

The cracks grow from the surface inward and are V-shaped, indicating that the stresses involved have a gradient. Although the ultraviolet-stabilized polycarbonate sheet showed considerably less severe degradation than the unstabilized sheet, results described here demonstrate that protection against the effects of radiation is still not adequate.

Acknowledgements

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