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Effects of Long-Term Weathering and Angle of Exposure on the Deterioration of Polycarbonate

by A. Blaga and R.S. Yamasaki

ANALYZED

Reprinted from
Durability of Building Materials
Vol. 3, No. 4, July 1986
p. 327-341
(IRC Paper No. 1413)

Price $2.00

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RÉSUMÉ

Des feuilles de polycarbonate à fini superficiel standard et à surface protégée par une pellicule ont été exposées aux intempéries, en positions horizontale (0°) et verticale (90°), pendant des périodes atteignant dix ans. Ce document porte sur la dégradation, sous l'effet des intempéries, des caractéristiques de ces deux types de feuille telles que la résistance à la microfissuration superficielle, le facteur de transmission solaire, la résistance à la traction, l'allongement et le module d'élasticité. Pour ces deux types de polycarbonate, un réseau de microfissures superficielles s'est formé sur l'un des côtés de la feuille, c.-à-d. sur le dessus (face exposée) en position horizontale et sur la face sud en exposition à 90°. Le taux de microfissuration superficielle était beaucoup plus élevé sur la face exposée des deux types de feuille de polycarbonate en exposition à 0° que sur la face sud en exposition à 90°, car les surfaces sont soumises à un plus fort rayonnement ultraviolet en position horizontale qu'en position verticale.

Le vieillissement n'a qu'un léger effet sur la résistance à la
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Durability of Building Materials, 3 (1986) 327—341
Elsevier Science Publishers B.V. Amsterdam — Printed in The Netherlands

EFFECTS OF LONG-TERM WEATHERING AND ANGLE OF EXPOSURE ON THE DETERIORATION OF POLYCARBONATE

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(Received September 10, 1985; accepted November 26, 1985)

Keywords

Windows	Plastics	Properties	Mechanical Physical
		Mechanisms/Causes of failure	Weathering Photodegradation Cracking

ABSTRACT

Blaga, A. and Yamasaki, R.S., 1986. Effects of long-term weathering and angle of exposure on the deterioration of polycarbonate. *Durability of Building Materials*, 3: 327—341.

Polycarbonate sheets with a standard surface finish and with a film-protected surface were weathered outdoors at both a horizontal (0°) and a vertical (90°) angle of exposure for periods of up to ten years. The weathering-induced deterioration in the properties of these two types of sheet, such as resistance to surface microcracking, solar transmittance, tensile strength, elongation, and modulus of elasticity, is discussed. Both types of polycarbonate developed a network of surface microcracks on one of the sides, i.e. on the upper (exposed) side in the 0° angle exposure, and on the south side (S-side) in the 90° exposure. The rate of surface microcrack formation was much higher on the exposed side of both types of polycarbonate at the 0° exposure than on the S-side at the 90° exposure because surfaces receive more ultraviolet radiation at a horizontal angle than at a vertical angle.

Weathering has only a slight effect on tensile strength at yield and elongation at yield, but induces a relatively large deterioration in tensile strength at break and elongation at break. The angle of exposure did not have a significant effect on tensile strength or on elongation. The modulus of elasticity of both types of polycarbonate, weathered at either 0° or 90°, increased at a relatively fast rate in the early years of exposure, reached a maximum, then decreased. At the end of ten years of weathering, the modulus of elasticity of the polycarbonate sheet was either higher or moderately lower.

1. INTRODUCTION

A combination of outstanding properties, including rigidity, toughness, transparency, and heat resistance, makes bisphenol A polycarbonate an attractive plastic for a variety of uses in building, construction and engineering. For example, because of its very high initial impact resistance and excellent transparency, polycarbonate sheeting is used increasingly as shatterproof glazing and in composite security glazing. As production costs continue to decrease, polycarbonate is increasingly being used for new applications; for example, solar collectors, automotive parts, street lighting, traffic light, aircraft, optics, and sports and leisure articles.

The performance of polycarbonate under various conditions needs, therefore, to be well understood — in particular, its resistance to the effects of one of the most common and harmful environments, the outdoors. This environment (determined by the natural weather) includes most of the factors involved in the deterioration of plastic-based materials: humidity (water), sunlight, temperature (level and variations) and oxygen. The ultraviolet portion of the sunlight is the most potent single factor of deterioration, although when combined with infrared light and/or oxygen it is even more severe. Stresses resulting from fluctuations in humidity and temperature and from the heterogeneous nature of the material also play an important role in the deterioration process (Blaga and Yamasaki, 1972), 1973a, 1976).

The research described in this paper is part of a study of environmentally-induced deterioration in the properties of polycarbonate sheeting materials. Previous papers described the results of work on the mechanism of surface microcracking of polycarbonate (Blaga and Yamasaki, 1976), the effect of outdoor weathering on the molecular weight and tensile properties of polycarbonate (Yamasaki and Blaga, 1977), and weathering-induced changes in the tensile impact strength of polycarbonate exposed at different angles (Yamasaki and Blaga, 1982). The results either described deterioration in individual properties or covered the effect of a relatively short exposure. This paper reports a systematic study on weathering-induced deterioration of several properties over a relatively long-term exposure (up to ten years) both of polycarbonate with a standard surface and of polycarbonate with a film-protected surface. The deterioration in such properties as resistance to surface microcracking, solar transmission, tensile strength, elongation and modulus of elasticity is discussed.

2. EXPERIMENTAL

2.1 Materials

The samples used in the outdoor exposure were cut from commercial UV-stabilized glazing sheeting of (bisphenol A) polycarbonate. Two types of sheet were used: sheet with a standard surface (PC-S) and sheet protected with a surfacing film (PC-P). Commencing in February, 1973, a set of ten panels ($165 \times 305 \times 3.2$ mm) of each type of sheeting was subjected to outdoor weathering at Ottawa (humid, continental, northern climate) in accordance with ASTM Method D 1435, and at each of two angles: at 0° (horizontal), and facing south at 90° (vertical). A test panel was removed annually from each set for examination.

2.2 *Apparatus and methods*

The changes in surface properties as a function of weathering time were followed by a Stereoscan scanning microscope (SEM). The instrument was operated at 20 kV using a tilt angle of 45°. The specimens were coated first with carbon and then with gold to prevent surface charging.

The tensile properties were measured at 22°C in accordance with ASTM Method D 638M, using an Instron Model 1122 Universal Testing Machine at a crosshead speed of 5 mm/min and a chart speed of 50 mm/min. An optical microscope was also used to supplement the SEM surface examination.

Solar energy transmittance measurements were performed with a Beckman UV, Visible and Near IR Spectrophotometer Model 5270, using ASTM E424 Method A.

3. DISCUSSION OF RESULTS

Visual and microscopic (SEM and optical microscope) observations, as well as solar transmittance measurements, indicated that, depending on the length of exposure, weathering induces considerable deterioration in the surface quality of both PC-S and PC-P sheet, in the form of surface microcracking, yellowing, haziness, and a decrease in solar energy transmittance.

3.1 *Surface microcracking*

3.1.1 *Exposure at a 0° angle*

The nature of surface microcracks induced by weathering in PC-S and PC-P exposed at 0° and 90° to the horizontal for periods of up to ten years is illustrated in the SEM photomicrographs (Figs. 1—7).

SEM observations indicated that in the early stages of weathering

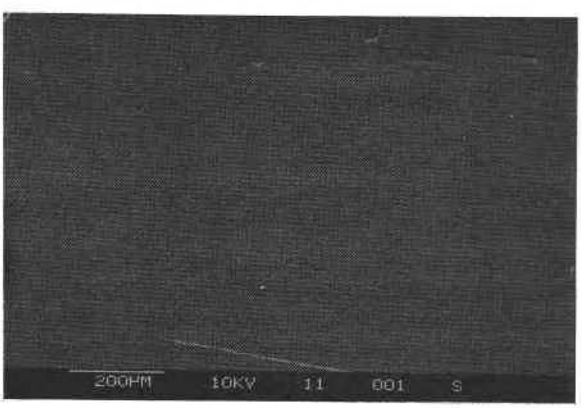


Fig. 1. Control (unexposed) polycarbonate sheet with a standard surface finish (PC-S).

Fig. 2. Upper (exposed) surface of PC-S sheet weathered at a 0° angle for 3 years.

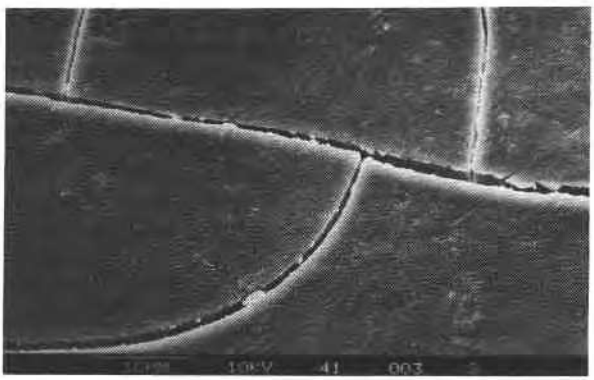


Fig. 3. Exposed surface of PC-S sheet weathered at 0° for 3 years.

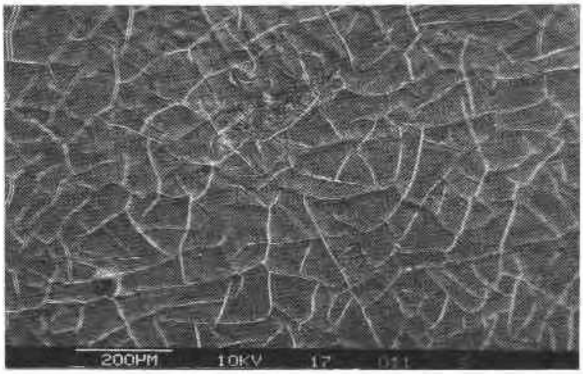


Fig. 4. Exposed surface of PC-S sheet weathered at 0° for 10 years.

Fig. 5. Exposed surface of polycarbonate sheet protected with a surfacing film (PC-P) weathered at 0° for 10 years.

Fig. 6. South-facing surface of PC-S sheet weathered at 90° for 5 years.

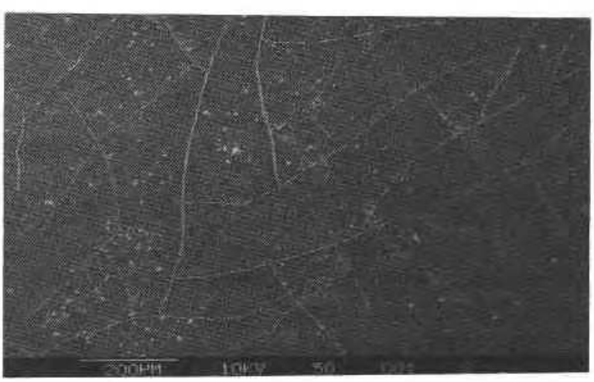


Fig. 7. North-facing surface of PC-S sheet weathered at 90° for 10 years.

exposure at 0°, the upper (exposed) side of PC-P sheet had higher resistance to surface microcracking than the upper side of PC-S sheet. In PC-P sheet, incipient microcracks occurred after 48—50 months of weathering, whereas in PC-S sheet initial microcracks were observed after only 20—24 months of outdoor exposure.

The initially narrow, randomly-oriented cracks grow in width and depth and propagate slowly with weathering, then intersect and form a network of cracks (Figs. 2, 3 and 6). The areas confined between the intersecting cracks, predominantly triangles or four-sided polygons, decrease with weathering as the surface material continues to fracture, resulting in higher crack density, i.e. number of cracks per unit area (Figs. 4 and 5).

Although PC-P exhibits better microcracking resistance than PC-S in the early stages of weathering, its cracking resistance becomes comparable to that of PC-S with a longer exposure, as it develops a similar network of microcracks (Fig. 5). After about one year of outdoor exposure at an angle of 0°, the surfacing film of PC-P sheet undergoes gradual delamination, forming flakes adhering at some sites of the surface. The flakes are visible to the naked eye, but could not be adequately illustrated photographically. Thus, the surfacing film provides only limited protection against the harmful effects of weathering.

SEM observations did not reveal the presence of any surface microcracks on the lower (unexposed) side of either PC-S or PC-P panels exposed at a 0° angle, even at the end of ten years of weathering. Such a result is explained by the fact that harmful ultraviolet (UV) radiation is almost entirely absorbed by the exposed surface layers of polymer (Yamasaki and Blaga, 1977), and therefore could not affect the unexposed side. This result confirms the results of earlier experiments indicating that UV radiation is necessary for the formation of surface microcracks (Blaga and Yamasaki, 1973b, 1976). As previously reported, surface microcracking is produced by a mechanism in which UV radiation acts in conjunction with stress-fatigue induced by fluctuations in moisture and/or temperature (Blaga and Yamasaki, 1973b, 1976). Stress-fatigue without UV radiation or UV radiation without stress-fatigue does not induce surface microcracking.

3.1.2 Exposure at a 90° angle

Exposure to weathering at a 90° angle resulted in a much lower rate of microcrack formation than exposure at 0° in both PC-S and PC-P sheet. The initial surface microcracks occurred on the south-facing side (S-side) after approximately four years of outdoor exposure. After five years of weathering at 90°, the S-side of both PC-S and PC-P developed a network of microcracks comparable to that on the upper surface of sheet weathered at 0° for only three years (Fig. 6). The surfaces of both types of polycarbonate sheet had similar networks of microcracks at the end of ten years of weathering. The lower rates of formation of surface microcracks on the S-side of sheet weathered at 90° are attributed to the lower total amount of UV light radiation impinging on that side compared with the upper side of sheet exposed at 0° (Yamasaki, 1983).

The north-facing side (N-side) of both PC-S and PC-P is more resistant to surface microcracking than the S-side, the initial microcracks being detected only after nine years of exposure. The microcrack network of relatively low (crack) density, formed on the N-side of the PC-S panel weathered at 90° for ten years, is illustrated in Fig. 7. The areas of the polygons confined by the cracks are still fairly large and the crack depth is relatively low, an indication that surface microcracking is still in the early stages.

The greater resistance to surface microcracking of the N-side of the panels is due to less UV radiation being received compared with the S-side.

The presence of cracks has a marked influence on most properties of plastic-based materials. Although surface microcracking affects only a thin layer (5—10 nm) of the exposed side of plastic sheet, it causes a disproportionate decrease in strength properties (Yamasaki and Blaga, 1977). Also, surface microcracks in combination with other weather-induced surface flaws result in a decrease in transparency by scattering the incident light instead of transmitting it.

3.2 Solar energy transmittance

The changes in solar energy transmittance resulting from weathering exposure of PC-S and PC-P are presented in Fig. 8 and listed in Tables 1 and

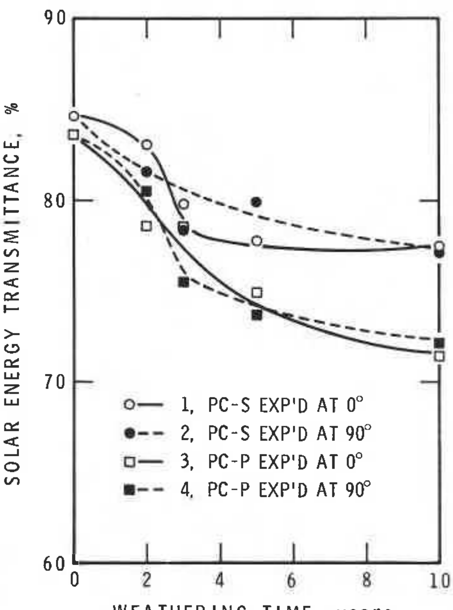


Fig. 8. Solar energy transmittance versus weathering time of PC-S and PC-P.

TABLE 1

Weathering-induced changes in properties[a] of polycarbonate sheet[b] with standard surface finish (PC-S)

Weathering time (y)	Exposure angle	Solar transmittance[c] (Δ%)	Tensile strength at yield (at break) (Δ%)	Elongation at yield (at break) (Δ%)	Modulus of elasticity (Δ%)
2	0°	−3.7	−4 (−26)	+2 (−88)	+5
5	0°	−5.4	−4 (−26)	−3 (−86)	+10
10	0°	−8.9	−4 (−25)	+2 (−84)	+8
2	90°	−1.8	−4 (−25)	+2 (−75)	+8
5	90°	−6.9	−4 (−27)	−8 (−86)	+23
10	90°	−8.5	−5 (−26)	−8 (−88)	+21

[a]Actual values of properties given in Figs. 8, 10, 12 and 14.
[b]3.2 mm thick.
[c]Single measurements.

TABLE 2

Weathering-induced changes in properties[a] of polycarbonate sheet[b] with surface protected by laminated film (PC-P)

Weathering time (y)	Exposure angle	Solar transmittance[c] (Δ%)	Tensile strength at yield (at break) (Δ%)	Elongation at yield (at break) (Δ%)	Modulus of elasticity (Δ%)
2	0°	−3.8	<−1 (−27)	−8 (−92)	+9
5	0°	−10.5	<−1 (−26)	−8 (−85)	+3
10	0°	−13.9	<−1 (−26)	−8 (−89)	+1
2	90°	−1.3	−1.6 (−25)	−15 (−)	+23
5	90°	−11.9	−2.6 (−28)	0 (−90)	+5
10	90°	−14.7	−2.6 (−27)	0 (−91)	−3

[a]Actual values of properties given in Figs. 8, 11, 13 and 14.
[b]3.2 mm thick.
[c]Single measurements.

2. The solar energy transmission spectrum (in the wavelength range of 290 to 2600 nm) of PC-S sheet weathered for two, five and ten years is compared with that of the control in Fig. 9. The results show that PC-S sheet retained approximately 91% of its initial solar transmittance after ten years of weathering at either 0° or 90° (Table 1).

Weathering induces a much larger reduction of solar transmittance in PC-P than in PC-S. At the end of ten years of outdoor exposure, the transmittance of PC-P sheet was only 85—86% of that of the control. Most of the decrease in transmittance of both PC-S and PC-P occurred in the first three years of outdoor exposure (Fig. 8). The rate of decrease in transmittance was generally faster in panels exposed at 0° than in those exposed at 90°, but after ten years the transmittance was about the same for both angles.

The spectrum curve of PC-S (Fig. 9) indicates that weathering causes a relatively large decrease in the spectral transmittance at wavelengths between 380 and 550 nm, which are part of the near-ultraviolet and visible regions, but induces only a moderate reduction in transmittance in the visible region between 550 and 750 nm; it does not affect the transmittance in the near-infrared range of the spectrum. The decrease in the transmittance of PC-P sheet follows a pattern similar to that observed for PC-S sheet. The angle of exposure had some effect on the lowering of transmittance of PC-S and PC-P in the first two years of weathering, but did not affect the pattern of transmittance change with respect to wavelength.

Thus, weathering affects mostly the visible light transmittance, which is an

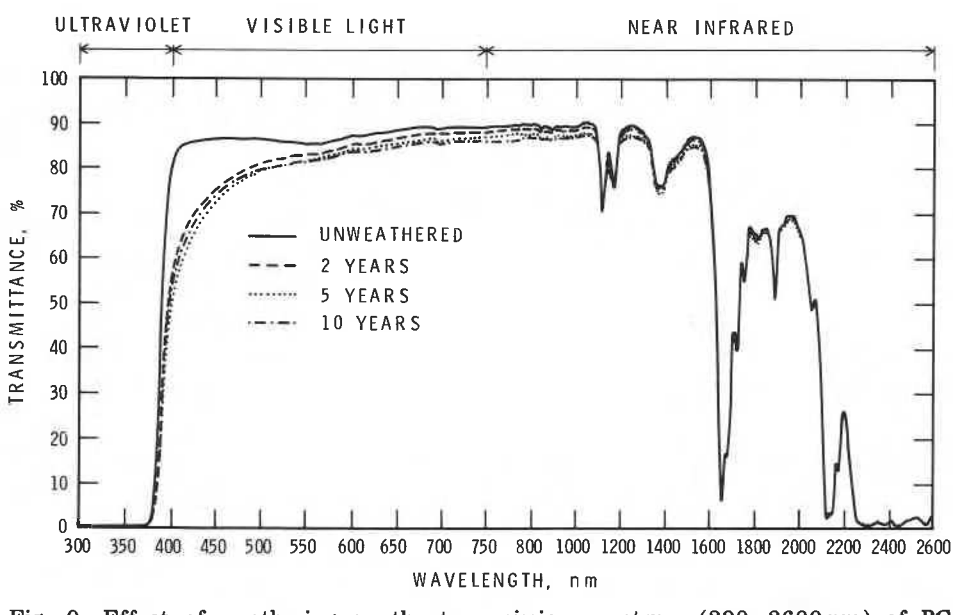


Fig. 9. Effect of weathering on the transmission spectrum (290—2600 nm) of PC-S exposed at 0°.

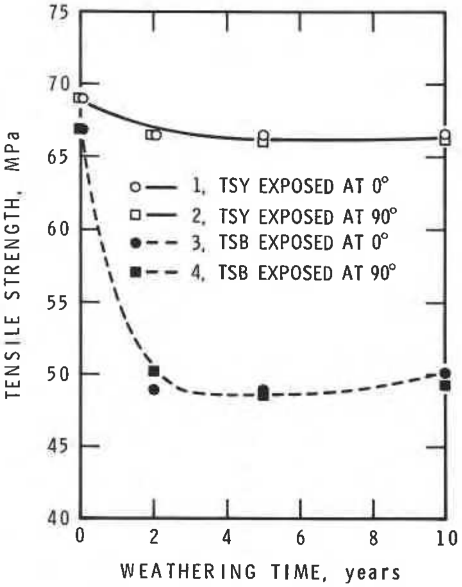
important property for transparent plastics used in glazing and light-transmitting applications. A decrease in light transmission results from the loss of surface quality of the sheet and discoloration of the basic polymer, caused by photodegradation. The surface quality of plastic sheet is lowered by surface microcracks, surface erosion, pitting, scratching and other damage caused by exposure to the service environment.

3.3 Effect of weathering on tensile properties

In Figs. 10 to 14 are presented plots of the tensile properties of PC-S and PC-P sheet as a function of weathering time for periods of up to ten years. Results of mechanical testing are summarized in Tables 1 and 2.

3.3.1 Tensile strength and elongation

Weathering affects tensile strength and elongation at yield only slightly, but induces relatively large decreases in tensile strength and elongation at break (Figs. 10—13). After ten years of weathering, the tensile strength at yield (TSY) of PC-S and PC-P panels was lowered by only 4—5% and 1—3%, respectively. The tensile strength at break (TSB), on the other hand, of both PC-S and PC-P panels weathered for the same length of time decreased by as



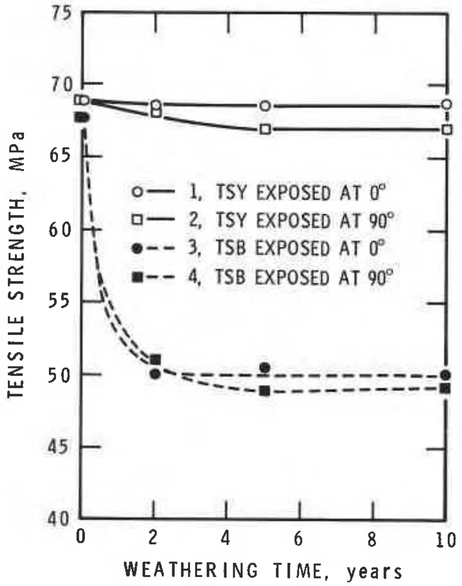
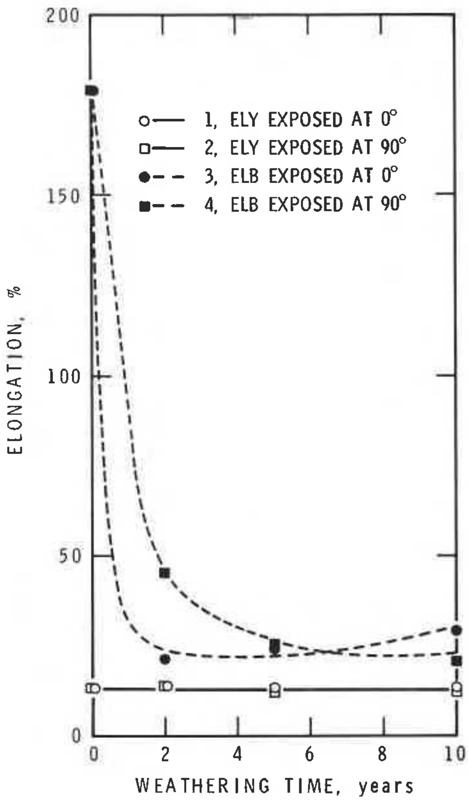


Fig. 10. Effect of weathering on tensile strength at yield (TSY) and tensile strength at break (TSB) of PC-S.

Fig. 11. Effect of weathering on tensile strength at yield (TSY) and tensile strength at break (TSB) of PC-P.



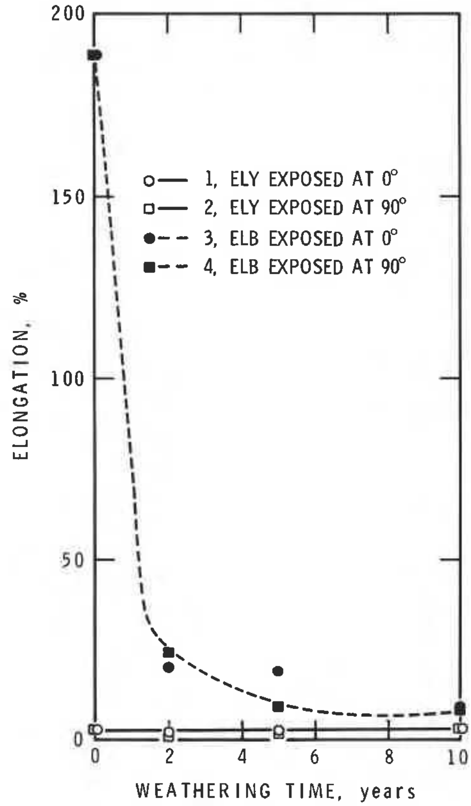


Fig. 12. Effect of weathering on elongation at yield (ELY) and elongation at break (ELB) of PC-S.

Fig. 13. Effect of weathering on elongation at yield (ELY) and elongation at break (ELB) of PC-P.

much as 25—27% (Tables 1 and 2). Most of the deterioration in TSY and TSB of both PC-S and PC-P occurred in the initial two years of exposure to weathering (Figs. 10 and 11). The angle of exposure did not have a significant effect on the weather-induced deterioration of TSY or TSB.

The effect of weathering on elongation is similar to that observed for tensile strength, that is, the elongation at yield (ELY) was either not affected or decreased only slightly (PC-P), whereas elongation at break (ELB) was sharply reduced (Figs. 12 and 13). After ten years of weathering, the ELB of PC-S and PC-P decreased by 84—88% and 89—91%, respectively. As was observed for tensile strength, most of the decrease in elongation in both PC-S and PC-P occurred in the first two years of weathering. The angle of exposure had only a slight or moderate influence on elongation.

The relatively small decrease in TSY and ELY induced by weathering polycarbonate-based sheet is explained as follows. The stress-strain behaviour

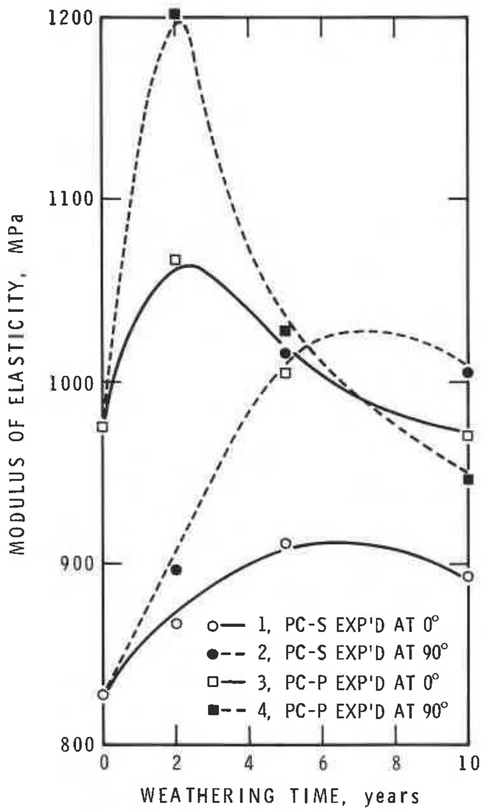


Fig. 14. Effect of weathering on modulus of elasticity (ME) of PC-S and PC-P.

up to the yield point is determined partly by valence bond deformation (bond bending and bond stretching) and the change in the distances between neighbouring molecules, which are reversible phenomena constituting the elastic component of the strains involved, and partly by irreversible viscous flow. The reversible process is not dependent on the molecular weight, whereas the viscous flow is molecular-weight-dependent. The small decrease in the TSY and ELY of the exposed sheet indicates that viscous flow plays only a small role, and that the elastic process is a predominant factor in determining the level of tensile properties at yield. The small decrease in TSY may be attributed to some viscous flow caused by the application of stress.

The TSB and ELB of polymeric materials are generally determined by the intermolecular forces (attractive forces between adjacent molecules and molecular chain entanglements) that increase with the molecular weight up to a certain value, characteristic of each polymer (Deanin, 1972). ELB is a measure of the extent to which polymer molecules slide past each other (by viscous flow) before separating completely at failure. The decrease in molecular weight, which occurs in the weathering of plastics (Yamasaki and

Blaga, 1977), results in a reduction of the intermolecular forces. Therefore, failure in the weathered polycarbonate occurs at a lower strain than in the control because of easier plastic flow and thus faster separation of molecules; this results in a lower ELB. In addition, failure strength and strain at failure can decrease as a result of increased surface damage, such as surface cracks, which serve as initiators for crack propagation and failure.

3.3.2 Modulus of elasticity

The modulus of elasticity (ME) of PC-S increased in the first six to seven years of outdoor exposure, reached a maximum, and then decreased (Fig. 14, curves 1 and 2). After ten years of weathering, it was still 8% and 21% higher, at 0° and 90° to the horizontal, respectively, than the ME of the control (Table 1). Similarly, the modulus of elasticity of PC-P increased at both 0° and 90° during the initial exposure, reached a maximum at 2—2½ years of weathering, then decreased sharply (Fig. 14, curves 3 and 4). After ten years, the ME of PC-P is either not affected (at 0°) or slightly lower (at 90°) than the ME of the control (Table 2). During most of the outdoor exposure, the weathering-induced changes in ME are generally greater for panels exposed at 90° than for those weathered at 0°, the only exception being the PC-P panel exposed at 90°. The ME of this panel is consistently slightly lower for weathering times longer than seven years.

Thus, weathering did not generally cause a reduction in the final ME of polycarbonate panels, although it induced relatively severe deterioration in other properties investigated in this and previous studies (Blaga and Yamasaki, 1976; Yamasaki and Blaga, 1977). Neither the presence of surface microcracks nor the reduction in molecular weight resulted in a lower ME. The ME is generally not dependent on the molecular weight (Deanin, 1972), because the elastic response of a polymer depends on reversible valence bond deformation (e.g. bond bending and stretching) and reversible changes in the distances between neighbouring molecular chains; intermolecular attractive forces, which are molecular-weight-dependent, are not involved.

4. CONCLUSIONS

Outdoor weathering for periods of up to ten years induces a marked deterioration in the properties of polycarbonate sheet with both a standard surface and a protected surface exposed at 0° and 90° to the horizontal. Weathering results in surface microcracking, a decrease in solar energy transmittance and deterioration of tensile strength.

Both types of polycarbonate sheet, weathered for a relatively short time at either 0° or 90°, developed a network of surface microcracks on the side receiving the greatest amount of radiation, i.e. on the upper (exposed) side in the 0° angle exposure, and on the south side (S-side) in the 90° exposure. The rate of surface microcrack formation is much higher on the upper side of both types of polycarbonate at the 0° exposure than on the S-side at the

90° exposure, because surfaces receive more ultraviolet radiation at a horizontal angle than at a vertical angle.

The lower side of plastic sheet weathered at a 0° angle does not develop microcracks because the harmful UV radiation is almost entirely absorbed by the bulk polymer of the sample. The N-sides of both types of sheet exposed at 90° are about equal in resistance to surface microcracking; the crack resistance is considerably higher than that of the S-side because the N-side receives much less UV radiation.

Weathering has only a slight effect on the tensile strength at yield and elongation at yield, but induces a relatively large deterioration in the tensile strength at break and elongation at break. Most of the deterioration in tensile strength at break and elongation at break occurred in the first two years of exposure. The angle of exposure does not significantly affect either tensile strength or elongation. The modulus of elasticity of both types of polycarbonate weathered at 0° and 90° increases at a relatively fast rate in the early years of exposure, reaches a maximum, then decreases. At the end of ten years of weathering, the ME of PC-S was 8% and 21% higher, at 0° and 90° respectively, compared with that of the control. The ME of PC-P was either slightly higher (in the 0° exposure) or moderately lower (in the 90° exposure) at the end of ten years of weathering.

ACKNOWLEDGEMENT

The authors wish to thank R. Lacroix and E.G. Quinn for performing the experimental part of this study. This paper is a contribution from the Division of Building Research, National Research Council Canada, Ottawa, Canada.

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