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**EFFECT OF THE ENVIRONMENT ON THE DURABILITY OF
PLASTIC-BASED MATERIALS**

by A. Blaga

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Effect of the environment on the durability of plastic-based materials

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Plastics in use are exposed to diverse environments, some of which exert a detrimental effect, resulting in overall deterioration. Studies carried out at the Division of Building Research, National Research Council Canada, on the effect of natural and artificial environments for several plastic materials have established the types of change in their properties and the mechanisms involved. Detrimental changes resulting from environmentally-induced deterioration include chemical degradation, discoloration, surface cracking, crazing, loss of compounding ingredients (e. g., exudation, leaching), fibre release (in glass-reinforced plastic), impairment of mechanical and electrical properties, loss of gloss, reduction of light transmission, opacification and pitting and scratching.

1. INTRODUCTION

Because plastics come in many types and shapes, they are increasingly used in a wide variety of building applications; for example, inner partitions, cladding and siding for exterior walls, insulation, glazing, window and door frames, luminous ceilings, roofing, vapour barriers, and piping materials. Consequently, plastic-based materials are exposed to diverse environments that can affect them within a relatively short time and cause an overall deterioration of their useful properties. A marked change in properties can impair or even render the plastic component unsuitable for service. There is, therefore, a great need to understand their performance and durability. Studies performed at the Division of Building Research, National Research Council Canada (DBR/NRCC), on the effect of natural and artificial environments for several plastic materials have established some of the types of detrimental change in properties and the mechanisms involved ([1]-[7]).

The information acquired in these studies has been successfully used to develop an accelerated test for assessing the relative resistance to deterioration of various types of glass-fibre-reinforced polyester composite ([8], [9]). Knowing the effect of environmental factors and the processes involved should help to develop plastic materials with improved durability characteristics. In this review, common deterioration-induced failures and the processes leading to them are described

very briefly, using results generated for the most part in the DBR/NRCC laboratory, but information reported by others is also included.

2. EFFECT OF SERVICE ENVIRONMENT

Like most materials, plastics are affected by certain conditions (factors) of the service environment. They generally undergo permanent, irreversible changes in their properties, which is detrimental to performance. Such changes may be either chemical or physical but are usually of both types. Detrimental change in the chemical structure of plastic is sometimes termed degradation, whereas impairment of physical properties is called deterioration. However, deterioration may also refer to the overall impairment of the material characteristics, i. e., both chemical and physical properties. The resistance of a plastic part or structure to deterioration depends to a great extent on compositional factors such as the chemical nature of the basic resin, the type of additive used in the formulation, the nature and amount of reinforcement (in composites), and the type of surface finish.

Detrimental changes (flaws or failures) in properties may be detected either visually or with the aid of various instruments: optical or scanning electron microscope (SEM) to detect cracks; infrared (IR) spectrophotometer and thermal analysis instruments; and mechanical testing instruments to assess changes in mechanical properties.

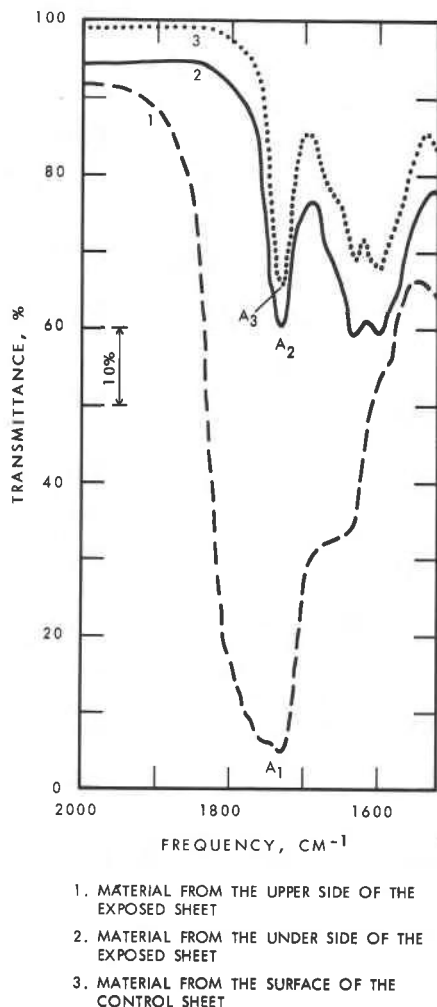


Fig. 1. — Infrared spectra of PVC plastic (KBr technique).

One of the most harmful environments is the outdoors (natural weathering). It includes most of the variables that induce deterioration in plastics: sunlight, humidity (water), temperature changes and oxygen. Stresses resulting from the fluctuation of humidity and temperature and the heterogeneous nature of the material play an important role in the deterioration process ([1]-[6]). To study deterioration, the natural environment is often simulated. Plastics are exposed to specific environments in which selected factors suspected of inducing deterioration are used in isolation or in combination with one or more other factors.

2. 1. Manifestations of deterioration

Detrimental changes resulting from environmentally-induced deterioration include chemical degradation, discoloration, surface cracking, crazing, loss of compounding ingredients (e. g., exudation, leaching), fibre release (in glass-reinforced plastic), impairment of mechanical properties, loss of gloss, reduction of light transmission, opacification, pitting and scratching, and impairment in electrical properties.

2. 2. Chemical changes

Although some slight changes in the chemical nature of plastics may take place during processing, the most significant degradation occurs during exposure to the service environment. Conditions during processing are relatively severe (e. g., excessive heat, molecular shearing), but exposure to them is of short duration. Chemical changes, which may occur in a small fraction of the polymer molecules during fabrication, result in formation of sensitizing groups. These undesirable chemical structures, inherent impurities, and some of the added ingredients can initiate or often accelerate deterioration during use.

Temperature changes, humidity and mechanical stresses are usually lower in the service environment than during fabrication, but the time of exposure is considerably longer. In addition, natural conditions normally fluctuate, in contrast with the more constant conditions of fabrication.

Chemical changes induced by weathering in plastic materials are generally the result of a complex set of processes in which the combined action of ultraviolet (UV) light and oxygen are predominant ([10]-[13]). The overall process, usually initiated by the UV portion of sunlight in the presence of oxygen (in the air), is referred to as oxidative photodegradation or photo-oxidation. To undergo photo-oxidation, a plastic must absorb light energy, more specifically, UV light (wavelengths of 290⁽¹⁾ to 400 nm have energies of the same magnitude as the bond strength in most polymers) [12]. The absorbed UV light energy causes dissociation (breaking) of the chemical bonds (mostly C—C and C—H) in the molecule of one or more constituents of a polymeric material. This dissociation, with or without participation of oxygen, can lead subsequently to one or more of the following chemical changes: cleavage into smaller molecules (chain scission), cross-linking, elimination of small molecules (e. g., hydrogen chloride, carbon dioxide, carbon monoxide, water), formation of double bonds in the main chain (e. g., in PVC as a result of dehydrochlorination) [10] and light-induced hydrolysis. The most frequent light-induced chemical degradation processes in polymeric materials are chain scission and cross-linking, accompanied by concomitant formation of functional groups such as carbonyl (C=O), carboxyl (—COOH), hydroxyl (—OH), and peroxides (—O—O—). It is generally believed that the —CO-group, inherently present in the polymer molecule or formed during processing, is the major cause of chain scission, leading to a decrease in the molecular weight ([11]-[13]). This makes the polymer less resistant to fracture [14] and affects physical properties in general. Such chemical changes can be detected by various techniques, including solubility testing (e. g., to detect cross-linking), thermal analysis, spectrophotometry ([10], [13]) and gel permeation chromatography (GPC) [14].

⁽¹⁾ Only radiation greater than 290 nm in wavelength normally reaches the earth's surface, radiation of shorter wavelengths being absorbed by the atmosphere.

Figure 1 illustrates a significant change in a portion of the IR spectrum (between 1550 and 1900 cm^{-1}) for rigid poly(vinyl chloride) (PVC) sheet weathered for 5 years in Ottawa [15]. The broad, intense band in the (A_1) specimen, with a maximum at about 1730 cm^{-1} (5.8 μm), is attributed to absorption of light energy by the $-\text{CO}$ -group in a variety of oxygen-containing structures such as aldehydes, ketones, carboxylic acids and β -chloro carbonyl compounds [16]. Similar bands in the spectra of the underside (A_2) and the control (A_3) are relatively weak and sharp; they are due to absorption by the $-\text{CO}$ -group inherent in the small amounts of plasticizer molecule present in the PVC resin formulation. The increase in band size on the upper surface is the result of oxidative photodegradation caused by weathering. The intensity of the IR band is proportional to the concentration of the $-\text{CO}$ -group and is, therefore, a good measure of the extent of photo-oxidation ([10], [13], [17]). The IR spectra of PVC material from the exposed surface at depths greater than 5 to 6 μm were not significantly different from those of the control, demonstrating that light-induced degradation is confined to a thin layer at the surface of material receiving direct sunlight radiation ([3]-[5]) (as is the case for most other flaws induced by exposure to the outdoor environment). Such degradation at the surface of a plastic part can affect mechanical properties out of all proportion to the actual damage; the resulting flaws and discontinuities in the resin can initiate fracture at stress levels much lower than those for unweathered material ([7], [14]).

2.3. Discoloration

Colour change is the most common, and usually the first, visible change in plastics. It is usually due to a change in the chemical structure of the basic resin. The extent to which plastics discolour with exposure depends on the chemical nature and purity of the resin, the kind and amount of protective additive (usually a UV absorber) and the technique used to produce the plastic part. Resistance of plastics to discoloration ranges from very good (no significant colour change in 10 or more years of outdoor exposure) to very low (significant changes after a few hours or days of exposure to sunlight). Poly(methyl methacrylate) (PMMA) is known to be very resistant to discoloration, whereas unpigmented and/or inadequately stabilized PVC is one of the least resistant ([10], [12], [13]).

2.4. Surface cracking

Surface cracks, the most common type of surface deterioration induced by the service environment, often occur on a microscopic scale. Surface microcracks affect most of the useful physical properties of plastic materials [14]. Although cracking and fracture behaviour of virgin plastics has been extensively studied ([18], [19]), the information available on surface cracks induced by deterioration is scarce and mainly descriptive. Considerable research has been carried out at DBR/NRCC on the role of environmental and material factors involved in surface deterioration leading to

crack formation. As a result, a mechanism was postulated for the overall surface deterioration of plastic-based sheets ([1]-[4]). According to this mechanism, surface microcracks are produced by environmentally-induced stresses in conjunction with resin degradation. The stresses are caused by differential dimensional changes (strains) induced by humidity and temperature ([2], [3], [20]) as a result of the inherent micro- and macroheterogeneity of plastic-based materials ([21]-[23]). Since these stresses are mainly due to cyclic fluctuations, they exert a type of stress-fatigue on the material. In the early stages of aging, the polymeric material in the upper surface layers directly exposed to the environment has a stress-fatigue limit (maximum stress below which fracture never occurs) higher than the stresses induced by humidity and/or temperature changes; it thus undergoes repeated reversible deformations without fracture. As weathering continues, however, the exposed surface material undergoes gradual degradation, which lowers its resistance to fracture. When the fatigue limit at a given site becomes lower than the environmentally-induced stresses, fracture of the resin occurs and cracks develop.

SEM photomicrographs (figs. 2 to 6) illustrate some of the features of surface microcracks induced by weathering in sheets of bisphenol A polycarbonate and conventional glass-fibre-reinforced polyester (GRP). Generally, the cracks are confined to the surface of the plastic structure where most of the degradation is taking place and where the stress-fatigue is intense. Initially short and narrow (figs. 2 and 3), the randomly-oriented surface cracks propagate slowly, growing wider and deeper with exposure time, and intersecting to form a network. As a result, the surface of the plastic becomes divided into predominantly triangular or four-sided polygons (figs. 4 and 5). Because of the gradients in the stresses, the cracks grow from the surface inward and are V-shaped (fig. 6). Although the surface microcracks induced by weathering are relatively shallow, about 5 to 10 μm deep (fig. 6), and occur only on the surface directly exposed to sunlight, they

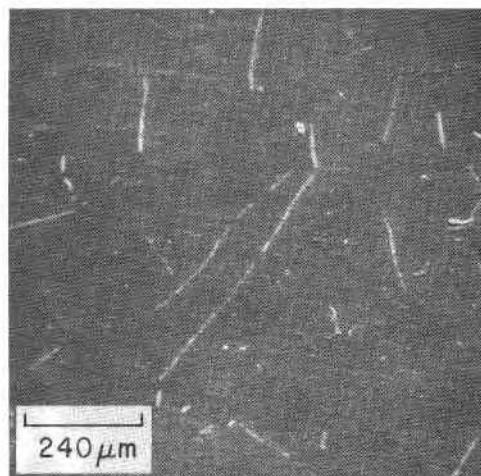


Fig. 2. — Upper (exposed) side of polycarbonate sheet weathered for 23 months (SEM photomicrograph).

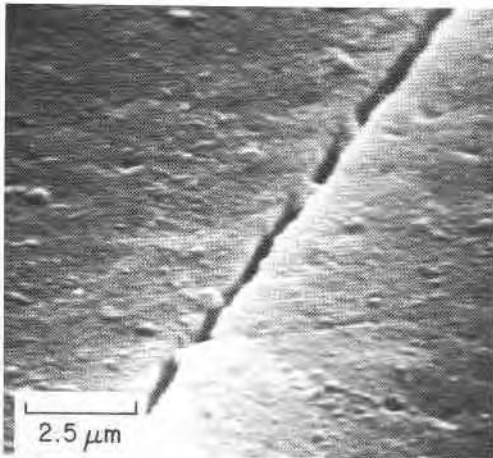


Fig. 3. — Polycarbonate sheet weathered for 23 months (SEM).

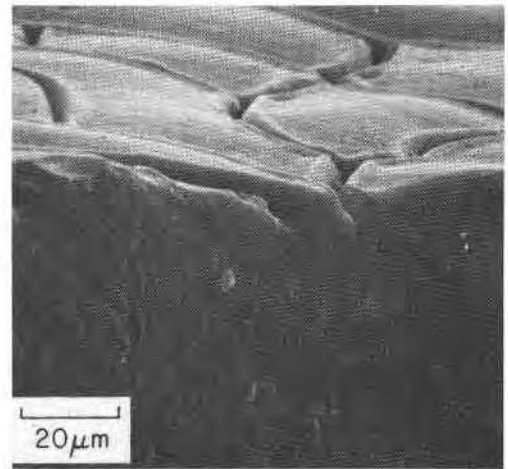


Fig. 6. — Cross-section of GRP sheet weathered outdoors for 80 months (SEM).

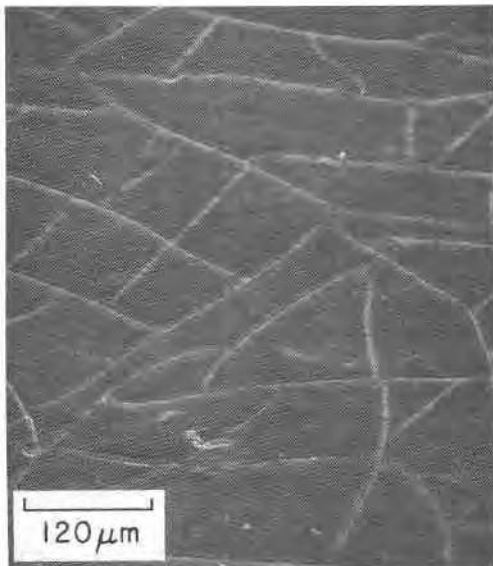


Fig. 4. — Polycarbonate sheet weathered outdoors for 55 months (SEM).

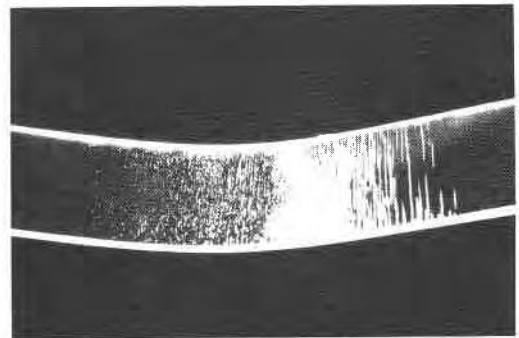


Fig. 7. — Photograph of crazed region of polycarbonate produced by subjecting the surface layer to stress (by bending a 3-mm thick sheet) in the presence of methanol.

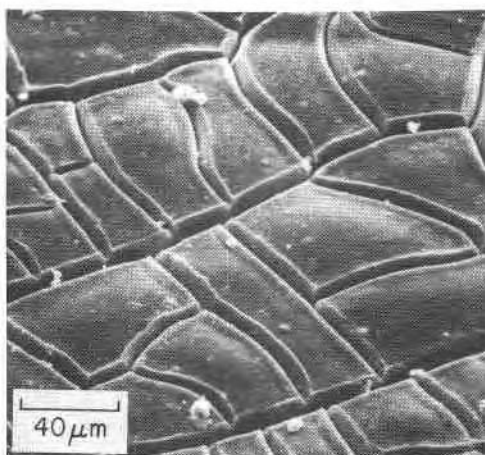


Fig. 5. — GRP sheet weathered outdoors for 80 months (SEM).

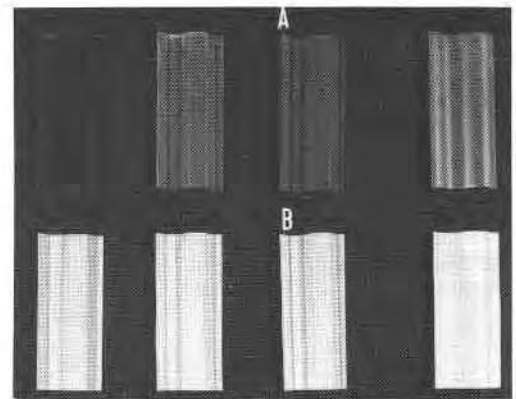


Fig. 8. — Photograph of PVC sheet of various colours (from left to right: coral, green, yellow, light green). A, Control; B, Weathered (5 years).

usually have a marked effect on the strength of plastic materials [14].

2.5. Crazes

These flaws usually appear just below the surface of plastic materials so that they reflect light and give the affected site a milky appearance. These apparent cracks occur in polymeric materials in sharply confined regions of oriented material mechanically continuous with the surrounding bulk polymer. The crazed regions consist of polymeric material lower in density than the

surrounding matrix, having a void content of 40 to 60% [24].

Crazes may form under tensile stress, but in active environments (notably organic liquids) they can develop under very low stress levels and initiate catastrophic fracture. Like cracks, crazes in isotropic materials grow at right angles to the major principal tensile stress. They may be healed by heating, which permits retraction and disorientation. Figure 7 shows a crazed region in a sheet of polycarbonate (PC), which appeared 10 to 15 seconds after the sheet was bent and subsequently dipped in methanol. Crazes develop easily in thermoplastics such as poly (methyl methacrylate), polycarbonate and polystyrene and may be detected both visually and microscopically.

2.6. Loss of compounding ingredients

2.6.1. Exudation

The loss of a compounding ingredient from the plastic occurs when a constituent migrates to the surface, forming a thin layer of deposit (exudate). For example, weathering of PVC resulted in the formation of an exudate consisting of a plasticizer derivative [5]. The PVC formulation contained epoxidized soya-bean-oil plasticizer, which underwent hydrolysis and thus became incompatible with the plastic material system. The more hydrophilic substance resulting from hydrolysis of the plasticizer, was forced to the surface by repeated diffusion of water from the plastic in conjunction with repeated contraction caused by moisture and temperature fluctuations in the outdoor environment. Because of the lower temperature and less available water, the exudate on the underside was thinner. Loss of plasticizer from the plastic may contribute to lowering the elongation. The presence of exudate on the surface will also reduce the light transmission of the translucent PVC sheet and impair the aesthetic appearance of coloured plastic parts. This is illustrated in figure 8, in which samples of four PVC sheets initially translucent and of different colours (from left to right: coral, green, yellow, light green) are compared. As their surfaces became covered with a layer of solid deposit (exudate) over 5 years, they assumed a greyish-white, opaque appearance regardless of their initial colour,

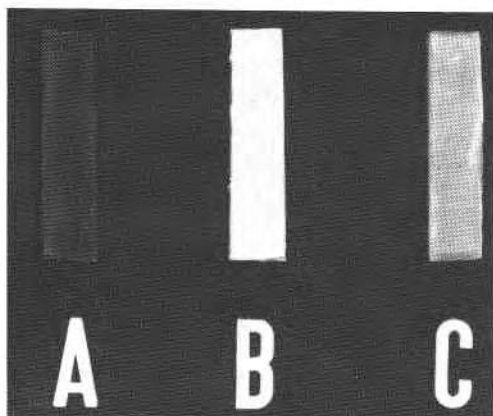


Fig. 9. — Photograph of green PVC sheet. A, Control; B, Weathered (5 years); C, Aged in humidity-temperature cycling cabinet for 175 days (350 cycles).

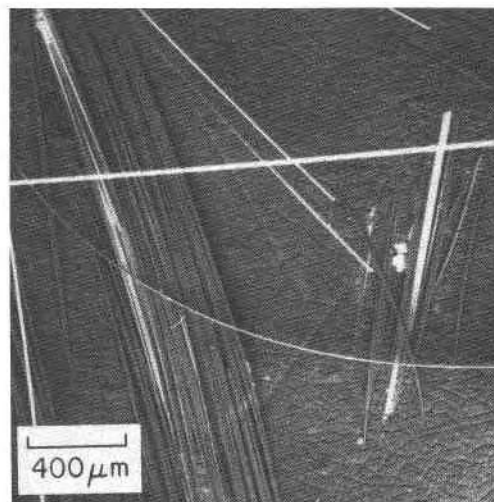


Fig. 10. — GRP sheet weathered for 5 years (SEM).

the greyish tint probably due to the accumulation of dirt. In figure 9, the surface of a green sheet of PVC weathered outdoors for 5 years (B) and aged in the humidity-temperature cycling cabinet (C), respectively, is compared with that of the control (A). Aging under humidity-temperature cycling conditions caused a white exudate to form, similar to that occurring in outdoor weathering. Laboratory results have also demonstrated that hydrolysis of the epoxy plasticizer yields a complex mixture of products bearing predominantly hydroxyl groups. The modified plasticizer is less compatible with the polymer system and will gradually migrate out by a mechanism in which water plays an important role. Exudation may also produce changes in the mechanical properties of the plastic materials [5].

2.6.2. Brittleness

The term "brittle" implies that there is no detectable plastic deformation in a material prior to failure when it is subjected to a mechanical load. In plastics that are tough and deformable before use, aging may cause a lowering of the strain to failure, that is, it may cause a gradual embrittlement. Embrittlement may be induced by a variety of factors. During environmental aging, the two major types of degradation, cross-linking and molecular chain scission, are the principal causes of embrittlement. Studies show that weathering makes polycarbonate sheet extremely brittle, as evidenced by a marked reduction in elongation to failure and strength [14]. They also show that the material in the exposed surface undergoes a drastic decrease in molecular weight after a short period of weathering [14] as a result of photo-oxidative molecular chain scission [25].

2.7. Fibre release in glass-fibre reinforced plastics

The advanced stage of this type of deterioration, commonly referred to as "fibre pop-out", is characterized by the presence of numerous fibres lying free on the surface except for those ends or points along their length that are still embedded in the matrix (fig. 10).

Figure 11 compares the surface of the control sheet and the upper (exposed) side of glass-fibre reinforced polyester (GRP) sheet weathered outdoors for 5 years. Weathering has caused considerable breakdown in the interface of the exposed side, resulting in a surface covered extensively with denuded fibres. The scattered fibres and voids formed in the interface breakdown diffuse the light instead of transmitting or reflecting it, giving an opaque appearance to the originally translucent sheet. Extensive breakdown at the interface makes the GRP sheet unsightly and, if it is severe, will also have a detrimental effect on mechanical properties. The extent of deterioration on the underside is considerably less, indicating that weather conditions prevailing there are less severe than those acting on the upper (exposed) side.

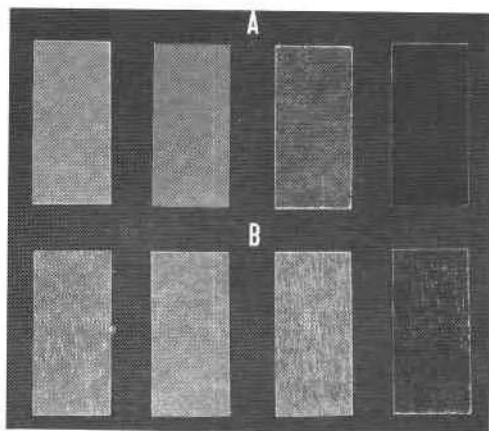


Fig. 11. — Photograph of different coloured flat sheets (aquamarine, yellow, colourless, green). A, Control; B, Upper side (exposed) weathered for 5 years.

The mechanism leading to fibre release is very similar to that for surface microcracking ([1]-[3]). Stress fatigue and matrix deterioration of GRP composites cause the glass-resin interface of the outermost layers of material to break down, resulting in fibre release by the surface matrix. The effect of stress fatigue is, however, considerably greater on the interface than on the matrix, owing to larger dissimilarities in properties of the two main components (the glass reinforcement and the resin). Therefore, breakdown at the interface generally occurs at a faster rate than deterioration of the matrix not associated with the glass reinforcement.

Resistance to weather-induced surface deterioration of GRP composites leading to fibre release depends largely on the type and proportions of acids, glycols and cross-linking monomers used to produce the polyester, since they influence the photochemical stability, cross-link density and water sorption characteristics of the matrix [26]. Resins made with isophthalic acid, it has been shown, are much more resistant to deterioration than resins made with orthophthalic acid (conventional resin), with equivalent UV stabilization ([26]-[29]). Fire-resistant resins, such as those made with chlorinated acids or anhydrides, have very low resistance to weathering ([26], [30]). For example, in GRP sheets made from tetrachlorophthalic acid-based

polyester resin, the rate of fibre release was 2.5 to 3 times faster than in conventional sheet [30]. Using neopentyl glycol instead of the usual propylene glycol in producing polyesters increases the durability of GRP composite ([26], [29], [31]). General weathering properties improve markedly when mixed monomer systems are used as cross-linking agents. For example, replacing part of the styrene monomer with methyl methacrylate leads to less fibre release, better resistance to cracking, and improved gloss and clarity retention ([26], [32]).

The overall durability of GRP sheets can also be improved by modifying the structure of the surface material, e.g., using gel coats, surface finishes and protective films with good weather resistance ([26], [30], [33]). These measures not only protect against the harmful effects of UV light, but also reduce greatly the physically-induced stress fatigue at the interface and decrease the rate of breakdown by keeping fibres away from the surface.

2.8. Impairment of mechanical properties

In general, weathering gradually impairs most mechanical properties of plastics. The initial composition, the morphology, the presence and type of reinforcement, and the nature of the service environment determine which mechanical properties will be affected ([5], [6], [14]).

For example, the net ultimate tensile strength and elongation of UV-stabilized polycarbonate sheet exposed outdoors for 46 months were only 70 and 10%, respectively, of their initial values [14]. The tensile impact strength was reduced to 30% of its original level after only 2 years of outdoor exposure [7]. Deterioration of mechanical properties in polycarbonate is believed to be caused by photo-oxidative degradation, which decreases the molecular weight of the resin and results in surface microcracking ([4], [14]).

Lightly plasticized PVC sheets similar in composition but different in colour, when weathered for 5 years, underwent a reduction in tensile strength by various degrees, to a maximum of 16% (orange) [5]. Moderate increases of approximately 6 to 7% in modulus of elasticity were observed in all but one sample, which showed no change (white). A loss in tensile strength indicates that outdoor weathering caused chemical degradation. An increase in the modulus resulting from the loss of plasticizer ([34], [35]) was also found by the author [5]. The mechanical property of thermoplastics most subject to deterioration is the elongation at break, which is considered the most meaningful index of weatherability ([35], [36]). It reflects, to some extent, changes in both plasticizer content and chemical decomposition of the resin. The retention of percent elongation in the PVC sheets (weathered for 5 years) ranged from about 17% (coral) to about 30% (yellow).

The angle at which a plastic material is used in the outdoor environment strongly affects the rate of deterioration of its mechanical properties. Study has indicated that loss of tensile impact strength is considerably greater in plastic sheets weathered at 45 deg

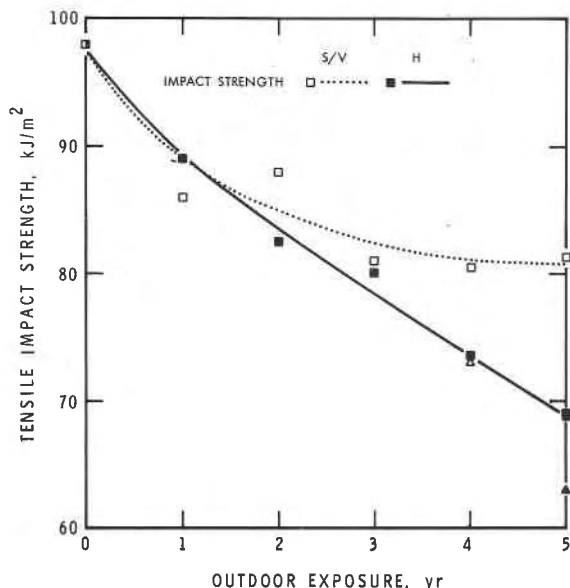


Fig. 12. — Effect of weathering at 90 deg (S/V) and 0 deg (H) exposure angles on tensile impact properties of PMMA sheet.

(angle with the horizon) ⁽¹⁾ or in the horizontal position (angle of 0 deg) than in those exposed vertically ⁽¹⁾ (angle of 90 deg) [7]. For example, the tensile impact of poly (methyl methacrylate) was reduced by 30% from its initial value (98 kJ/m²) in samples weathered for 5 years in a horizontal position, but by only 20% in samples exposed vertically for the same period (fig. 12). Similar results were found for various other plastics used in the weathering study. The faster rate of loss in tensile impact in sheets mounted (on racks) horizontally or at 45 deg is caused by the greater amount of UV light received by the samples for these angles of exposure [37].

⁽¹⁾ Facing south.

2.9. Other environmentally-induced failures

Reduction or loss of gloss, reduction in light transmission, opacification, pitting and scratching, and impairment in electrical properties are other changes induced by exposure to the service environment.

Gloss, the attribute of surfaces that causes them to have a shiny or lustrous appearance, is generally the result of specular reflection of light by the surface of a sheet or object. It is thus a measure of this reflective ability, which usually varies with the surface smoothness and flatness. A roughening of the surface material caused by overall breakdown during exposure results in greater diffuse reflection of the impinging light and, consequently, in a loss of gloss.

Depending on the type of plastic and service exposure, light transmission, which can be important in certain applications, may be affected in different ways [38]; in extreme cases it may be completely obstructed. Light transmission may be reduced by loss of surface quality and/or by changes in the bulk of the plastic material. Loss of surface quality can be caused by scratching, abrasion and/or, more often, by surface deterioration from exposure to the environment; e.g., surface exudate, cracking, crazing and fibre release (in GRP). The surface flaws cause the incident light to scatter, decreasing the portion of light being transmitted. Light transmission may also be reduced by changes in the bulk of the plastic such as discoloration of the resin and colour change in the pigments or dyes.

The effect of outdoor weathering on the light transmission of three common plastics used in glazing and lighting applications has been studied at DBR/NRCC [38], and the result is shown in figure 13. The visible light transmission of poly (methyl methacrylate) used as glazing in the outer pane of an exterior window facing south was only slightly affected by weathering after 11 years and half of service. This is understandable, as PMMA is known to be one of the most

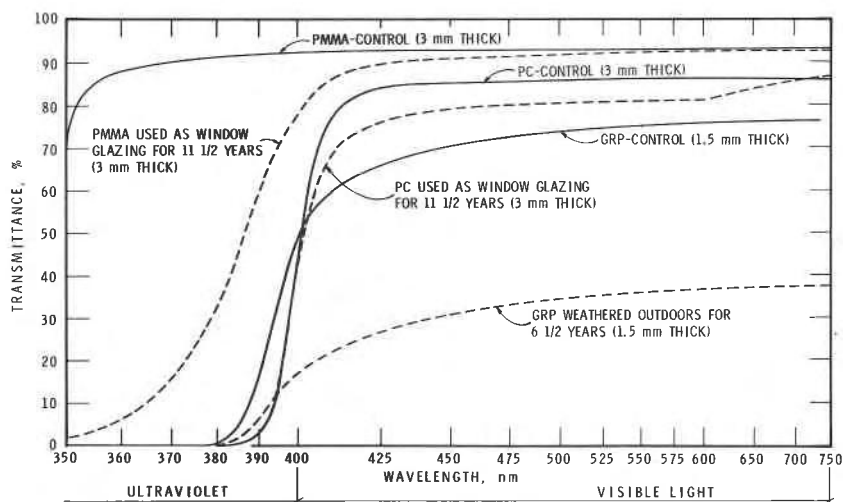


Fig. 13. — Effect of weathering on light transmission of glazing plastics used in windows (PMMA and PC sheet) of DBR/NRCC building or exposed (GRP), on racks at 45 deg, facing south at the Ottawa site.

weather-resistant plastics ([39], [40]). Conventional polycarbonate glazing, under similar conditions and for the same duration, underwent a moderate reduction in visible light transmission. The light transmission of GRP sheet, the least weather-resistant of the three plastic-based glazing materials, exposed outdoors (45 deg, facing south) for 6 years and half, was considerably reduced.

Pitting and scratching are caused by the contact or impact of sharp and hard objects; these flaws may also be caused by airborne particles. Pitting and scratching, if extensive, may not only impair the appearance and light transmission of the plastic part, but may also affect the mechanical properties by acting as stress concentrators.

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RÉSUMÉ

Effet du milieu sur la durabilité de matériaux composés de matières plastiques. — Mis en œuvre les matériaux composés de matières plastiques sont exposés à des milieux divers dont certains ont un effet nocif qui amène une détérioration générale. Une modification notable des propriétés du matériau peut altérer le composant plastique ou même le rendre impropre au service. Performance et durabilité doivent donc être clairement établies. Les études réalisées à la Division de Recherche du Bâtiment du Centre National de Recherche du Canada (DRB/CNRC) sur les effets des milieux naturels et artificiels sur divers matériaux ont dégagé quelques types d'altération des propriétés et leurs mécanismes.

Les altérations que provoquent les détériorations causées par le milieu comprennent modifications chimiques, décoloration, perte de brillant, fissuration superficielle, faïençage, perte de matière (par exemple exsudation, lessivage), relâchement de fibres (dans les plastiques renforcés de fibres de verre), diminution des propriétés méca-

niques et électriques, opacification, etc. Les défauts ou défaillances peuvent être détectés soit à vue, soit au moyen d'instruments : microscope optique ou électronique (par exemple pour détecter les fissures), spectrophotomètres infrarouges (par exemple pour détecter les altérations chimiques) et machines d'essai mécaniques (pour évaluer les modifications des propriétés mécaniques).

Les facteurs les plus communs de détérioration des matières plastiques : énergie solaire, humidité, température et oxygène agissent dans le milieu naturel. Les contraintes causées par les variations de température et d'humidité jouent un rôle important dans la détérioration des matières plastiques. C'est après avoir compris les mécanismes de détérioration que l'on pourra améliorer la résistance aux actions climatiques des matières plastiques et concevoir des méthodes d'essai pour apprécier leur durabilité. On examine ici brièvement les défaillances les plus communes causées par détérioration et les mécanismes qui les ont déterminées. Les résultats d'essai ont été produits par le Laboratoire du DRB/CNRC mais s'y ajoutent des données fournies par d'autres sources.