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Publisher's version / Version de l'éditeur:

Matériaux et constructions. Materials and Structures, 18, 107, pp. 337-343, 1985-09

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Effect of Weathering on the Water Sorption of GRP Sheet Material

by A. Blaga

ANALYZED

Reprinted from
Matériaux et Constructions
Vol. 18, N° 107, Septembre-Octobre 1985
p. 337-343
(IRC Paper No. 1378)

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Effect of weathering on the water sorption of GRP sheet material

A. Blaga

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Water sorption-desorption isotherms of glass-reinforced polyester (GRP) surface material, unweathered and weathered for periods of up to 6 1/2 years, have been determined over the entire relative vapour pressure range. The equilibrium sorbed water content of the weathered surface material is higher than that of the sheet exposed outdoors for the same length of time, by a factor of up to two. Also, the equilibrium sorbed water content of the degraded surface material increases with weathering time much faster than that of the GRP sheet.

Isotherms of GRP sheet indicate that the equilibrium content of sorbed water is consistently higher in weathered samples than in unweathered sheet and is an increasing function of weathering time for periods of outdoor exposure of up to 7 1/2 years. The rates of water sorption and desorption of weathered GRP sheet, as assessed by the combined mean coefficient of diffusion $[1/2 (\bar{D}_s + \bar{D}_d)]$ increase markedly with weathering time.

INTRODUCTION

Water, in the form of vapour, liquid or ice, affects most of the useful properties of exposed glass-reinforced polyester (GRP) composites. Sorbed water can induce physical and chemical changes by itself or in conjunction with other environmental agents, such as heat, ultraviolet light or oxygen ([1]-[4]).

Sorption and desorption of water by GRP results in swelling and shrinkage. Because of fluctuations of humidity in the environment, these alternating dimensional changes are cyclical. The combined effects of the cyclical dimensional changes induced by moisture and temperature produce stress fatigue in the GRP composite, resulting in surface deterioration ([1], [2]). Furthermore, water sorbed in voids or cavities may cause cracking as a result of the freeze-thaw phenomenon.

Sorbed water may also react with the ester linkages ($-\text{CO}-\text{O}-$) of the polymer molecular chain, producing chain scissions. In conjunction with ultraviolet light and oxygen, water may take part in photo-oxidative reactions. Both of these processes change the chemical nature of the matrix polymer, usually resulting in detrimental changes in the properties of the GRP composite.

Water, therefore, plays a significant role in the long-term performance of GRP composite material, particularly in outdoor applications. Most of the studies reported on the water sorption of plastic-based materials deal with the effect of sorbed water on the mechanical properties of special purpose composites reinforced

with high modulus fibers ([5]-[7]). These studies do not deal with the effect of weathering on the water sorption characteristics. A more systematic study has been carried out, therefore, on the water sorption properties and sorbed water-induced dimensional changes of unweathered and weathered GRP composite. Previous papers reported the water sorption characteristics and dimensional changes of unweathered and weathered GRP exposed outdoors for 3 years ([8], [9]). This work has now been extended to cover weathering periods of up to 7 1/2 years. This paper also describes the water sorption-desorption isotherms of thin specimens of GRP material taken from the top layers of the sheet surface, unweathered, and weathered for periods of up to 6 1/2 years.

EXPERIMENTAL PROCEDURES

Materials

Commercial samples of GRP composite (0.8-mm thick sheet, produced by a continuous process) used in this study consisted of approximately 25% weight of silane-treated glass fiber (E-glass) in the form of chopped strand mat and 75% weight of a general purpose resin. The acrylic modified resin, thermosetting and UV-stabilized, was produced by cross-linking 60 parts (by weight) of unsaturated polyester with 40 parts of a 3:1 mixture of styrene and methyl methacrylate at 110-140°C, using a peroxide catalyst. The weathering of GRP sheet was carried out on horizontal racks in

Ottawa, in accordance with ASTM D 1435. Thin specimens of surface material (0.08-mm thick) were prepared by wearing off material from one side (the back of the sheet, for weathered specimens) with a grinding wheel fitted with carborundum paper of increasing degree of fineness, using water cooling.

Water Sorption Apparatus

A series of six glass tubes, each containing one calibrated spring balance (McBain-Bakr type) sensitive to weight changes of 1.2×10^{-5} g, were connected by a suitable valving system and through a manifold to a vacuum line, a micrometer, a vacustat (mercury manometer) and a thermostated water source (reservoir). The lower part of each tube was placed in a thermostated water bath controlled at $23 \pm 0.2^\circ\text{C}$ and immersed so that the water level was about 8 cm above the upper ends of the specimen.

The range of constant water vapour pressures was obtained by adjusting (increasing or lowering) the temperature of the water reservoir. The relative pressures were determined by calculating the ratio of the absolute pressure (p) at the temperature of the water reservoir

Fig. 1. — Effect of weathering on the equilibrium water sorption isotherm of GRP composite mat. I, —●— sheet (unweathered); II, —○— thin specimen of unweathered sheet surface material; III, —□— thin specimen of sheet surface material weathered for 3 years; IV, —△— thin specimen of sheet surface material weathered for 6 1/2 years.

to that (p_0) at the temperature of the thermostated water bath.

Procedures

The isotherm were determined by increasing the vapour pressure in steps in the evacuated system (essentially air-free) at constant temperature, and obtaining equilibrium values at each step (fig. 1 and 2).

Sorption- and desorption-time experiments were carried out with the equipment described previously [8]. At zero time, the relative vapour pressure was suddenly increased (in sorption) or decreased (in desorption) from the initial to the final value and the weight changes were determined as a function of time. The experiments were of the integral type [6], i. e., zero vapour pressure was used as initial pressure in sorption and as final pressure in desorption. A relative vapour pressure of 0.975 was used as the final pressure for sorption and as initial pressure for desorption (fig. 3).

Results and discussion

Weathering affects only a thin layer of surface material (at most 8 μm) of the exposed side of GRP sheet, about 1% of the total thickness ([1], [11]). Thus, use of the whole sample for assessing weather-induced changes in properties, although practical, is not characteristic of the affected material. Therefore, to obtain a better understanding of the effect of weathering on water sorption and desorption, thin specimens were used without introducing any errors resulting from excessive surface areas, voids, microcracks, etc. The specimens used in this study were 0.08-mm thick, obtained from surface material of the unweathered (control) and weathered sheet (exposed surface).

The water sorption-desorption isotherms of thin specimens of surface material (control, weathered for 3 years, and weathered for 6 1/2 years) are shown in figure 1. Sorption-desorption data are presented in table I.

Water sorption-desorption isotherms and rates of sorption and desorption were also determined for GRP sheets weathered for 7 1/2 years. The water sorption-desorption data of the weathered sheets and the control are presented in tables I and II; the sorption-desorption isotherms are shown in figure 2 and the curves of rates of sorption and desorption, in figure 3.

Water Sorption and Desorption in Thin Specimens of Surface Material

The isotherm of thin specimens of surface material exhibits hysteresis and is very similar in shape to that of GRP sheet (fig. 1). At relative pressures (p/p_0) lower than 0.60, the equilibrium sorbed water content during sorption in the unweathered thin specimen material does not differ significantly from that of the whole sheet. However, at p/p_0 higher than 0.60, the equilibrium sorbed water content (designated M_∞) of the thin specimen is increasingly higher than that of the GRP sheet (table I, fig. 1). At or near the saturation

Fig. 2. — Effect of weathering on the equilibrium water sorption isotherms of GRP sheet (sealed edges). I, —●— control sheet; II, —○— sheet weathered for 3 years; III, —□— sheet weathered for 7 1/2 years.

vapour pressure ($p/p_0 = 0.90 - 1.00$), the M_∞ in the thin specimen reaches a value 41 to 50% higher than that of the whole GRP sheet. Similarly, during desorption, the increase in M_∞ of thin specimen material at a given p/p_0 is also markedly larger than that of the GRP sheet over the entire p/p_0 range. The increase ranges

from about 30% (at $p/p_0 = 0.60$) to 60% (at $p/p_0 = 0.90$). The greater amounts of M_∞ occurring in a thin specimen of surface material, in comparison with those in the GRP sheet, cannot be attributed solely to larger relative outer surface areas (¹) (table I). Larger relative outer surfaces would cause the water sorption phenomenon to be more reversible in the thin specimen than in the GRP sheet, resulting in a reduced area of the hysteresis loop rather than in a larger area. Therefore, the greater amount of M_∞ in the thin specimen than in the GRP sheet may be due mainly to a factor or factors other than increased amount of outer surfaces, e.g., formation of additional polar hydrophilic groups as a result of mechanochemical degradation during the preparation of the test specimen. During the preparation of thin specimens of surface material by grinding, the mechanical forces can cause breaking of molecular chains of the polymer matrix. The resulting molecular fragments possess reactive sites, which may react with water (used for cooling) or oxygen to produce polar hydrophilic groups, e. g., $-\text{COOH}$ and $-\text{OH}$. Such mechanochemically-induced degradative reactions occur in polymeric substances [10]. In solid polymer-based materials these reactions are practically irreversible.

The thin specimens used in the sorption-desorption experiments, with a thickness of 0.08 mm represent at most 10% of the total thickness of a GRP sheet. As weathering affects only a thin layer of surface material, the thin specimens, although rich in deteriorated material, are still diluted with non-degraded material by a factor of up to 10.

The equilibrium amount of sorbed water in thin specimens increased very strongly with weathering time (table I, fig. 1). The greatest increase occurred at p/p_0

(¹) Surface specimens had the same mass as those of whole sheet, but consisted of several rectangular layers of surface material.

Fig. 3. — Effect of weathering on the rate of sorption and desorption of GRP sheet at $23 \pm 0.2^\circ\text{C}$ and $p/p_0 = 97.5$. I, —○— control sheet; II, —□— sheet weathered for 3 years; III, —▽— sheet weathered for 7 1/2 years.

between 0.40 and 0.60. The M_{∞} of the thin specimen material weathered for three years is 90 ($p/p_0 = 0.60$) higher than that of the control (unweathered, thin specimen material), while material weathered for 6 1/2 years is 175% higher than the control. Similar trends in the change of M_{∞} with weathering time were observed during desorption (table I and fig. 1). The extent of mechanochemical degradation in the weathered thin specimen material should be comparable to that of the control, because the grinding during preparation of the specimen is carried out from the unexposed side (involving unaffected material). Therefore, the change in sorptive capacity of the thin specimen material exposed outdoors is due mainly to weathering. Also, the hysteresis loop of the thin specimen material weathered for three years was generally much larger than for the control (unweathered, thin specimen surface material).

Effect of Weathering on Water Sorption-Desorption Properties of GRP Sheet

In figure 2, the equilibrium sorption-desorption isotherms of GRP sheet weathered for 3 years and for 7 1/2 years are compared with those of the control. All three isotherms are similar and are of Type III BET. The sorption branches of the isotherms are nearly linear for p/p_0 lower than 0.75. At p/p_0 greater than 0.75, the sorption curves assume a sharply increasing curvature, becoming concave towards the sorbed water axis. Generally, a Type III isotherm in solid polymer-water systems indicates that the water-water (penetrant-penetrant) interaction is stronger than the water-polymer interactions. The linear portion of the isotherm indicates a mode of sorption in which the sorbed water molecules are randomly distributed in the bulk structure of the polymer matrix, so that a mixture similar to a true solid solution is produced. Thus, at p/p_0 between 0 and 0.75, the sorption obeys Henry's law of ideal solution. The sharp increase in the equilibrium amount of sorbed water at p/p_0 greater than 0.75 may

be due to the relatively strong tendency of water molecules to associate through hydrogen bonding, forming clusters inside the polymer matrix. This obviously induces an increase in the equilibrium sorptive capacity of the GRP with increasing p/p_0 . Hysteresis was observed in the sorption isotherms of all GRP samples over the entire p/p_0 range. Also, the content of sorbed water is consistently higher in weathered samples and is an increasing function of time of exposure to weathering. For example, in the relative pressure range of 0.60 to 0.90, the sorbed water content of GRP sheet weathered for three years is about 43 to 16% higher than in the unweathered (control) sheet, while for sheet weathered for 7 1/2 years, it is 60 to 37% higher than in the control. Similar trends in the change induced by weathering in the equilibrium water content of GRP sheet were observed for other values of p/p_0 (table I and fig. 2).

Thus, weathering causes a marked increase in the sorptive affinity of GRP composite material towards water. This increased affinity for water may be attributed to the formation of additional hydrophilic polar groups in the polymer matrix, resulting from the degradation reactions (e. g., hydrolytic and photo-oxidative) induced by outdoor weathering ([1], [12]). The concentration of polar groups (e. g., $-\text{OH}$, $-\text{COOH}$, $-\text{OOH}$, $-\text{CO}-$) increases with the extent of deterioration and thus with the exposure time [4]. Therefore, longer outdoor weathering of GRP composite should result in higher amounts of sorbed water, mainly as a result of hydrogen bonding and the creation of voids. Also, weathered thin specimens of the exposed surface material, which have a higher proportion of degraded material than the bulk of the sheet, will have greater equilibrium amounts of sorbed water than the GRP sheet weathered for the same length of time. For example, the M_{∞} of thin specimen material weathered for 3 years is greater than that of the GRP sheet exposed outdoors for the same duration by a factor that increases from 1.6 to 1.9 when the p/p_0 varies from 0.40 to 0.80 during sorption (table I).

TABLE I
EFFECT OF WEATHERING ON THE EQUILIBRIUM WATER SORPTION
OF GRP COMPOSITE MATERIAL AT $23 \pm 0.2^\circ\text{C}$ ⁽¹⁾

Sample Description	Equilibrium Sorbed Water			
	p/p_0 0.40	p/p_0 0.60	p/p_0 0.80	p/p_0 1.00
Control sheet ⁽²⁾	0.38 (0.54)	0.56 (0.75)	0.80 (0.99)	1.35
Sheet weathered for 3 years ⁽²⁾	0.46 (0.60)	0.70 (0.84)	0.97 (1.10)	1.55
Sheet weathered for 7 1/2 years ⁽²⁾	0.54 (0.62)	0.78 (0.90)	1.12 (1.21)	1.75
Thin specimens of surface material (control) ⁽³⁾	0.38 (0.72)	0.63 (0.98)	1.05 (1.30)	2.02
Thin specimens of surface material weathered for 3 years ⁽³⁾	0.72 (1.26)	1.20 (1.68)	1.80 (2.23)	3.28
Thin specimens of surface material weathered for 6 1/2 years ⁽³⁾	1.33 (1.56)	1.74 (2.08)	2.60 (2.71)	4.00

⁽¹⁾ Data taken from isotherms of figures 1 and 2; numbers in parentheses are equilibrium water content during desorption.

⁽²⁾ Flat, colorless sheets, smooth surfaced, made by a continuous process; specimens were rectangular ($38 \times 12 \times 0.80$ mm), approx. 0.6 g edges sealed with paraffin wax.

⁽³⁾ Specimens consisted of several rectangular (0.08 mm thick) layers of surface material, approx. 0.6 g.

TABLE II

RATE OF WATER SORPTION AND DESORPTION IN GRP SHEET AT $23 \pm 0.2^\circ\text{C}$ AND $p/p_0 = 0.975$ ⁽¹⁾

Sample Description ⁽²⁾	Equilibrium amount of sorbed water M_∞ (%)	Time of half-concentration (50%) change ($t_{1/2}$, h)		$\bar{D}_s$ ($10^9 \text{cm}^2 \text{s}^{-1}$)	$\bar{D}_d$ ($10^9 \text{cm}^2 \text{s}^{-1}$)	Combined Mean ⁽³⁾ $\bar{D} = 1/2 (\bar{D}_s + \bar{D}_d)$
		Sorption	Desorption			
Unweathered sheet (control)	1.22	59.29	51.12	1.47	1.70	1.58
Sheet weathered for 3 years	1.38	39.18	35.40	2.22	2.46	2.34
Sheet weathered for 7 1/2 years	3.70	28.09	30.58	3.10	2.84	2.97

⁽¹⁾ Data taken from figure 3.
⁽²⁾ Detailed description of GRP samples given in table I.
⁽³⁾ $\bar{D}_s$ and $\bar{D}_d$, mean coefficients for sorption and desorption, were calculated by the formula $\bar{D} = 0.049 (l^2/t_{1/2})$.

Effects of Weathering on the Rate of Water Sorption and Desorption

In figure 3 are presented the relative amounts of sorbed and desorbed water (Mt/M_∞) ⁽¹⁾ at p/p_0 of 0.975 of GRP sheets (weathered and non-weathered) as a function of the square root of time. As the shape of the sorption curves indicates, the sorption process is Fickian in nature. The sorption and desorption curves have no inflexion points and are approximately linear for relative amounts of water sorbed or desorbed up to 60-70% of the equilibrium amounts. For Mt/M_∞ above the linear point, both the sorption and desorption curves are concave with respect to the time axis.

The specimens used in the experiments are plane sheets with edge surfaces sealed (with paraffin wax). Therefore, the sorption and desorption of water occurs through the two surfaces, and the process is a one-dimensional diffusion in and out of the sheet. The rates at which water diffuses into and out of the GRP sheet are usually expressed in terms of diffusion coefficient. For specimens of GRP sheet exposed to a water-vapour environment under the conditions used in this study, a good approximation of the diffusion coefficient is the combined mean $[1/2 (\bar{D}_s + \bar{D}_d)]$ of the values of the mean coefficients of sorption ($\bar{D}_s$) and desorption ($\bar{D}_d$) ([13], [14]). Therefore, the combined mean coefficient will be used to assess the changes induced by outdoor weathering in the rate of sorption and desorption of the GRP sheet. The mean diffusion coefficients can be calculated from sorption-desorption data (table II and fig. 3) by the simple formula, $\bar{D} = 0.049 (l^2/t_{1/2})$, where l is the thickness of the sheet specimen and $t_{1/2}$ is the time at half-saturation (when $Mt/M_\infty = 1/2$) ([8], [13]).

As figure 3 indicates, the rate of sorption and desorption of GRP sheet at p/p_0 of 0.975 increases with weathering time. This is also confirmed by a marked increase in the combined mean coefficient of diffusion. For example, the combined mean coefficient of diffusion of GRP sheet weathered for 3 years is 50% higher than that of the control, and for sheet weathered for 7 1/2 years, it is 90% higher than the control (table II). Results also indicate that in the GRP sheet weathered

for 3 years and in controls, desorption of (sorbed) water occurs at a higher rate than sorption. For example, the diffusion coefficient for desorption ($\bar{D}_d$) of the weathered sheet is 10% higher than the corresponding diffusion coefficient for sorption, and for the control, $\bar{D}_d$ is 20% higher (table II). In contrast, weathering of the GRP sheet for 7 1/2 years results in lower rates for desorption than for sorption; the value of $\bar{D}_d$ is only approximately 90% of that of $\bar{D}_s$.

Thus, results indicate that weathering markedly influences the rates of movement of water vapour in and out of GRP sheet materials. High rates of sorption and desorption are due to chemical and physical changes resulting from the weather-induced deterioration of the GRP sheet. In fact, visual examination of the GRP samples revealed that weathering caused discoloration, a manifestation of photo-oxidative degradation. The discoloration is due to the UV light-induced formation of carbonyl groups ($-\text{CO}-$) in conjugation with double bonds. In the end, this reaction and other degradation processes result principally in polymer-chain scissions and cross-linking ([1], [8]). The scission reactions produce molecular chain ends, an accumulation of which at certain sites may result in the formation of submicroscopic voids. A gradual increase in the number of such voids, which are usually concentrated in the surface layers of the GRP sheet, may result in increasing sorption rates. Observations by the scanning electron microscope did not reveal any significant surface deterioration of the GRP sheet weathered for 3 years, but indicated the occurrence of surface microcracks in sheets weathered for seven and one-half years. The surface microcracks as well as the increased number of submicroscopic voids may account for the much higher sorption and desorption relative rates for the GRP sheets weathered for 7 1/2 years, in comparison with those of sheets weathered for 3 years and the control.

Effects of Deterioration on Hysteresis

The occurrence of hysteresis in the isotherms in which the desorption curve is above the sorption curve indicates that there are more active sites available or accessible for association with water molecules during desorption. The increased number of active sites may have been produced by hydrolytic reactions during the

⁽¹⁾ Mt and M_∞ are the cumulative mass of water sorbed at time t and at equilibrium ($t = \infty$), respectively.

overall sorptive process. Another factor that probably contributed to higher equilibrium sorbed water in desorption is the presence in the polymer matrix of different molecular arrangements (e. g., of polymer chains and segments of chains) that render the sorptive sites more accessible to water molecules. The different molecular arrangements result from irreversible swelling strains induced by water during sorption [12].

The hysteresis loop of unweathered (control) thin specimen material is markedly larger than that of the control sheet (fig. 1). This may be due to greater accessibility of water to active (sorptive) sites in thin specimens than in sheet specimens, resulting from a higher proportion of new molecular arrangements induced by larger swelling strains during the sorption process. Larger strains are the result of matrix deterioration during the preparation of the thin specimens by grinding. Sorbed water is shown to induce greater swelling in deteriorated plastic materials than in controls [9]. Although weathering resulted in a considerably higher hysteresis loop in the sorption-desorption isotherms of thin specimens weathered for 3 years than in the control, it induced a sharply smaller loop in those of thin specimens weathered for 6 1/2 years. The increase in the loop of the thin specimens weathered for 3 years is due to the same factors as that of the unweathered specimens (thin specimen controls). The diminished hysteresis loop of the specimen weathered for 6 1/2 years is understandable, if it is assumed that most of the new (additional) molecular arrangements have already taken place during the numerous cycles of sorption and desorption in the outdoor environment.

The influence of weathering on the size of the hysteresis in the isotherms of GRP sheet may be explained in a manner similar to that presented for the thin specimen material.

CONCLUSIONS

Sorption results indicate that the equilibrium sorbed water content of thin specimens from the exposed surface of weathered GRP composite is markedly higher (by a factor of up to 2) than the equilibrium sorbed water of regular sheets weathered for the same duration. This is probably due to the higher concentration of the polar groups in the thin specimen material of the exposed surface, which has a much higher proportion of degraded polymer matrix than the GRP sheet. The polar groups (e. g., $-\text{COOH}$, $-\text{OH}$, $-\text{CO}$) produced by the weather-induced degradation of GRP composite are strongly hydrophilic. Therefore, as the concentration of these hydrophilic groups increases, the water-sorptive capacity of the material will be enhanced.

The equilibrium amounts of sorbed water and rates of water sorption and desorption of GRP sheets exposed outdoors for up to 7 1/2 years, are increasing functions of weathering time. Higher amounts of sorbed water in conjunction with faster rates of water sorption and desorption will produce larger, alternating dimensional

changes (swelling and shrinkage), occurring at increased rates. This effect in combination with the action of the thermally-induced dimensional changes will result in greater environmental stress-fatigue on the GRP composite.

Acknowledgement

The author wishes to thank R. Lacroix for performing the experiments of this study. This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

NOMENCLATURE

- M_{∞} , equilibrium sorbed water content;
- p , absolute pressure at temperature of water reservoir;
- p_0 , absolute pressure at temperature of water bath;
- M_t , cumulative mass of water sorbed at time t ;
- $\bar{D}_s$, mean coefficient of sorption;
- $\bar{D}_d$, mean coefficient of desorption;
- l , thickness of sheet specimen;
- $t_{1/2}$, time at half-saturation (i. e. when $M_t/M_{\infty} = 1/2$).

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RÉSUMÉ

Effet de l'exposition sur l'absorption d'eau de feuilles de polyester renforcé de fibres de verre. — Les isothermes de sorption-desorption d'eau d'un matériau de revêtement mince en polyester renforcé à la fibre de verre (PRV), soumis et non soumis au vieillissement naturel, ont été déterminées pour des périodes allant jusqu'à 6 1/2 ans et pour toute la gamme des tensions de vapeur relatives. Le matériau de revêtement grandement dégradé de la feuille de polyester renforcé à la fibre de verre soumise au vieillissement naturel présente une caractéristique d'absorption d'eau plus grande que celle de l'ensemble du matériau exposé aux intempéries pour la même période, probablement en raison d'une concentration accrue des groupes polaires hydrophiles que produit la dégradation par les intempéries. On a constaté que la teneur en eau absorbée d'équilibre du matériau de revêtement soumis au vieillissement naturel est plus élevée que celle de la feuille exposée aux intempéries pendant la même période, par un facteur allant jusqu'à 2. En outre, la teneur en eau absorbée d'équilibre du matériau dégradé augmente beaucoup plus rapidement avec la durée du vieillissement que celle de la feuille de polyester renforcé à la fibre de verre.

Les isothermes de la feuille de polyester renforcé à la fibre de verre indiquent que la teneur en eau absorbée

d'équilibre est toujours plus grande dans les échantillons ayant été soumis au vieillissement naturel que dans la feuille n'ayant pas subi de vieillissement et qu'elle s'accroît avec la durée du vieillissement pour des périodes d'exposition aux intempéries allant jusqu'à 7 1/2 ans. Dans la gamme de tensions de vapeur relatives se situant entre 0,60 et 0,90 (humidité relative de 60 à 90%), la teneur en eau absorbée de la feuille de PRV ayant subi un vieillissement naturel de trois ans est environ 16 à 43% supérieure à celle de la feuille témoin (qui n'a pas subi de vieillissement), et de 37 à 60% pour une période de vieillissement de 7 1/2 ans. Les taux de sorption et de désorption d'eau de la feuille de PRV évalués par le coefficient de diffusion moyen combiné [$1/2 (D_{sDa})$], augmentent de façon marquée avec la durée de l'exposition aux intempéries. Les coefficients de diffusion moyens combinés, à une tension de vapeur relative de 0,975 pour les feuilles de PRV ayant subi un vieillissement naturel de trois ans, sont de 50% plus élevés que ceux de la feuille témoin, et de 90% plus élevés pour un vieillissement de 7 1/2 ans. L'absorption de plus grandes quantités d'eau, combinée à des taux de sorption et de désorption plus rapides, a pour effet d'amplifier les variations dimensionnelles alternantes (gonflement et retrait), à des taux accrus. Les contraintes alternantes qui en résultent, combinées avec celles induites thermiquement, produiront dans les matériaux composites de PRV une plus grande fatigue mécanique imposées par l'environnement.