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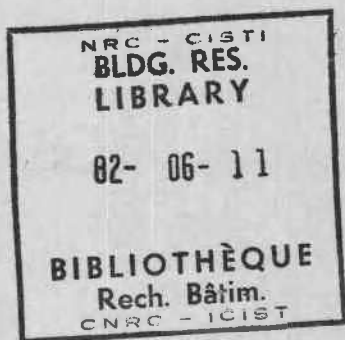Council Canada   de recherches Canada

LENGTH CHANGES INDUCED BY SORPTION AND DESORPTION

OF MOISTURE IN GLASS-FIBER REINFORCED POLYESTER

(GRP) COMPOSITE AND THE EFFECTS OF WEATHERING

by A. Blaga

ANALYZED

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SOMMAIRE

Le changement de longueur en fonction de la quantité d'eau
adsorbée par un plastique renforcé de fibre de verre ou PRFV
(23 °C) indique que, lorsque le point d'équilibre de la
teneur en eau excède une certain valeur critique, il se
produit une diminution marquée du taux relatif de déformation
par gonflement $(\Delta L/L_0)$ en fonction de la quantité d'eau
adsorbée $(\Delta W/W_{GRP})$, à la fois dans les matériaux
témoins et dans les matériaux vieillis. Ce changement est
attribué à la microhétérogénéité de la résine matrice, qui
est formée d'un mélange de particules de microgel dense
(îlots de résine très réticulée) enrobées dans une phase
continue de résine moins dense (moins réticulée). À des
concentrations d'équilibre inférieures à la valeur critique,
toute l'eau ou la plus grande partie de l'eau adsorbée est
contenue dans la phase moins dense de la résine, plus
facilement imprégnée. Comme cette phase est moins rigide
parce que moins réticulée, elle gonfle beaucoup plus que la
phase microgel qui adsorbe presque toute l'eau au-dessus de
la concentration critique.

Le gonflement linéaire dans la feuille vieillie est inférieur
à celui de la feuille témoin. Le vieillissement résulte par
ailleurs en des taux inférieurs de gonflement au-dessous de
la valeur critique de la teneur en eau adsorbée à
l'équilibre, mais il entraîne des taux bien plus élevés au-
dessus de cette valeur.

LENGTH CHANGES INDUCED BY SORPTION AND DESORPTION OF MOISTURE IN GLASS-FIBER REINFORCED POLYESTER (GRP) COMPOSITE AND THE EFFECTS OF WEATHERING

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ANALYZED

ABSTRACT

Blaga, A., 1982. Length changes induced by sorption and desorption of moisture in glass-fiber reinforced polyester (GRP) composite and the effects of weathering. *Durability of Building Materials*, 1: 67—84.

   The length change—sorbed water isotherm of GRP composite (23°C) indicates that for equilibrium water contents higher than a certain critical value a marked decrease in the relative rate of swelling strain ($\Delta L/L_0$) per unit rate of sorbed water ($\Delta W/W_{GRP}$) occurs in both the control and the weathered material. The change in rate is attributed to the microheterogeneity of the matrix resin, which consists of a mixture of dense microgel particles (highly cross-linked resin islands) embedded in a less dense continuous resin phase (cross-linked to a lesser degree). At equilibrium concentrations lower than the critical value, most or possibly all of the sorbed water is contained in the less dense phase of the resin, which is more easily penetrated by the water. As this phase is less restrained because of fewer cross-links, it swells to a greater extent than the microgel phase, which absorbs most of the water above the critical concentration.
   The amount of linear swelling in the weathered sheet is lower than that of the control sheet. Weathering also results in lower rates of swelling below the critical value of equilibrium sorbed water content, but induces considerably higher rates above that value.

1. INTRODUCTION

   Water is an important factor in most environments in which plastics are used. It may produce chemical degradation and various physical changes in materials; such changes contribute to the overall deterioration of useful properties. A GRP composite is particularly susceptible to the action of water and other weather factors.
   The chemical action of water results in scission of the polyester molecular chain by hydrolysis (Blaga, 1980; Norman et al., 1970), thus reducing the strength of the resin and its resistance to fracture. The chemical action of water can also reduce the strength of the bond between glass and resin (Norman et al., (1970), lowering the strength of the GRP composite. As a physical agent migration of water in and out of the material, as a result of fluctuations

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in humidity and temperature, induces differential dimensional changes in the composite. These moisture-induced differential dimensional changes, in conjunction with those resulting from temperature variations, play an important role in the distribution and build-up of internal stresses and in the change in mechanical behaviour. These stresses are cyclical because of fluctuations of humidity and temperature in the environment, producing a stress-fatigue that is particularly intense in the outer layers of the sheet and which leads to deterioration of the material (Norman et al., 1970; Blaga, 1972; Blaga and Yamasaki, 1973, 1976).

Thus, it is important to understand the relation between the amount of water contained in a material and its effect on the dimensional change (strain response) at various relative humidities. The water sorption characteristics (sorption—desorption isotherms and rates) of GRP and the effect of weathering on these characteristics have been reported previously by the author (Blaga, 1981). However, the reported results on moisture-induced strain behaviour during sorption and desorption of environmental water by virgin GRP composite are very few and incomplete, and none is available on weathered material. The purpose of this paper is to report the dimensional changes (swelling and shrinking) induced in polyester (GRP) composite over the entire range of relative vapour pressure. The effect of weathering on these dimensional changes and on the resulting stresses is also considered.

2. EXPERIMENTAL

2.1 Materials

The GRP specimens used in this study were prepared from 0.8 mm thick commercial sheet manufactured by a continuous process. By weight the composition of the sheet material was 75% resin and 25% silane-treated glass fiber (E-glass) reinforcement in the form of chopped strand mat. The resin (matrix) was an acrylic modified, thermosetting, UV stabilized, general purpose resin, 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.

2.2 Apparatus and procedures

The apparatus consisted of a series of 6 glass tubes, each containing one calibrated spring balance (McBaine—Bakr type) sensitive to weight changes of 1.2×10^{-5} g. The tubes were connected by a suitable valving system and through a manifold to a vacuum line, a micrometer, a McLeod gauge (mercury manometer) and a thermostatted water source. The lower part of the tubes was placed in a water bath controlled at $23 \pm 0.2°C$ and immersed to a depth such that the water level was about 80 mm above the upper end of the specimen.

The different constant water vapour pressures were obtained by setting the temperature of the water source at the required level. The relative pressures were determined by calculating the ratio of the absolute pressure at the temperature of the water reservoir (p) to the pressure at the temperature of the thermostatted water bath (p_0).

The method used to determine the isotherms consisted of increasing in steps the vapour pressure in the evacuated system at constant temperature and obtaining equilibrium values at each step (instead of drying the specimens between successive determinations).

The GRP specimens were thoroughly washed with distilled water, rinsed with ethanol and dried. The edge surfaces of the two control and the weathered specimens were sealed by dipping them in molten paraffin wax. This was done to simulate the situation usually encountered in actual use where the edges are at a sufficient distance from most main surfaces (of GRP sheet) that they do not have any influence on the sorption process. The edge surface, however, may affect the water sorption characteristics of the composite material in the regions near the periphery of a GRP panel.

Two test specimens were used for the determination of equilibrium sorbed water during the sorption and desorption experiment. For each pair of specimens used in the sorption—desorption experiments, three companion specimens were mounted on a modified Tuckerman optical extensometer (Sereda and Feldman, 1963), placed in a vacuum cell equipped with an optical window and connected to the sorption system. This permitted dimensional changes to be measured at each vapour pressure to a sensitivity of 2×10^{-6} mm/mm. Prior to starting the sorption experiment, the mounted specimens were evacuated to constant weight (as indicated by the quartz spring balance). The corrected weight was then used as the basis for the calculation of the percentage sorbed water, using $(W_{H_2O}/W_{GRP}) \times 100$, where W_{H_2O} and W_{GRP} are the weight of water sorbed and dry GRP specimen, respectively.

3. RESULTS AND DISCUSSION

3.1 General considerations

The take up of vapours or liquids by flawless solid organic polymeric materials normally occurs by a process of activated diffusion (Rogers, 1965). Solid polymers have low energy surfaces and thus are not readily wetted (Bowers and Zisman, 1964). Consequently their behaviour in the presence of liquids and even vapours can be expected to differ from that of inorganic solids (e.g., oxides or minerals). Mechanistically, the penetrant dissolves in the surface layers of the solid polymer and migrates into the bulk of the material under a concentration gradient (Rogers, 1965). The penetration of water may also occur by capillary or Poiseuille type flow through microcracks, pinholes or other flaws. In polymers, pore structure in the

usual sense is absent (Boucher, 1976), and the amount of inner surfaces associated with microcavities, microvoids, or superficial crack surfaces, is relatively small. Therefore, the water taken up by a solid polymeric material is mostly absorbed water such that a mixture similar to that of a true solution is created (Machin and Rogers, 1970). The thermodynamic properties of the whole polymer are thus altered, in accordance with the various theories of polymer solutions (Carpenter, 1970). As the dividing line between absorption and adsorption onto internal or molecular surfaces is not generally clear, the non specific term sorption is used to designate the overall process of water gain by polymer solids. Similarly, the term desorption is used to describe the over-all process by which the sorbed substance leaves the solid polymer when the relative pressure decreases. The weight of water sorbed at constant temperature is expressed as a function of the relative vapour pressure (p/p_0) and is usually referred to as sorption isotherm or weight change isotherm.

Sorption and desorption of gases, vapours and liquids generally result in dimensional change of the solid material (Barrie, 1968; Adamson, 1980; Hale, 1976). The results are usually given in the form of relative dimensional change (e.g., $\Delta L/L_0$) as a function of the amount of gas or liquid sorbed (e.g., $\Delta W/W_0$) at constant temperature (Boucher, 1976).

3.2 Length and weight change isotherms

The length change isotherms of the weathered and non-weathered GRP sheets during sorption and desorption are presented in Fig.1. The relative length change $(\Delta L/L_0)$ is an approximately linear function of the relative vapour pressure (p/p_0) during sorption and desorption in both the weathered and non-weathered (control) sheets. The sorption branch of the weathered sheet coincides with that of the control sheet. Furthermore, the length change (linear strain) induced by moisture during sorption and desorption in both the control and weathered sheet is reversible for relative pressures higher than 0.60. In the p/p_0 range below 0.60, the amount of shrinkage strain induced by desorption is somewhat higher than the swelling strain resulting from sorption, again for both the control and weathered sheets, with the weathered sheet undergoing slightly more deformation.

Thus, these results seem to indicate that when length change is related to relative pressure, weathering has very little or no influence on the moisture-induced deformation behaviour of GRP composite. This is in contrast to what is found when the length change is evaluated as a function of sorbed water content, as shown in the following discussion.

In Figs.2 and 3 the length change isotherms of both the control and the weathered sheet, respectively, are compared with the corresponding weight change isotherms. The shapes and slopes of both the sorption and desorption branches of the weight isotherms are generally different from those of the length isotherms. For example, the weight change isotherms are nearly
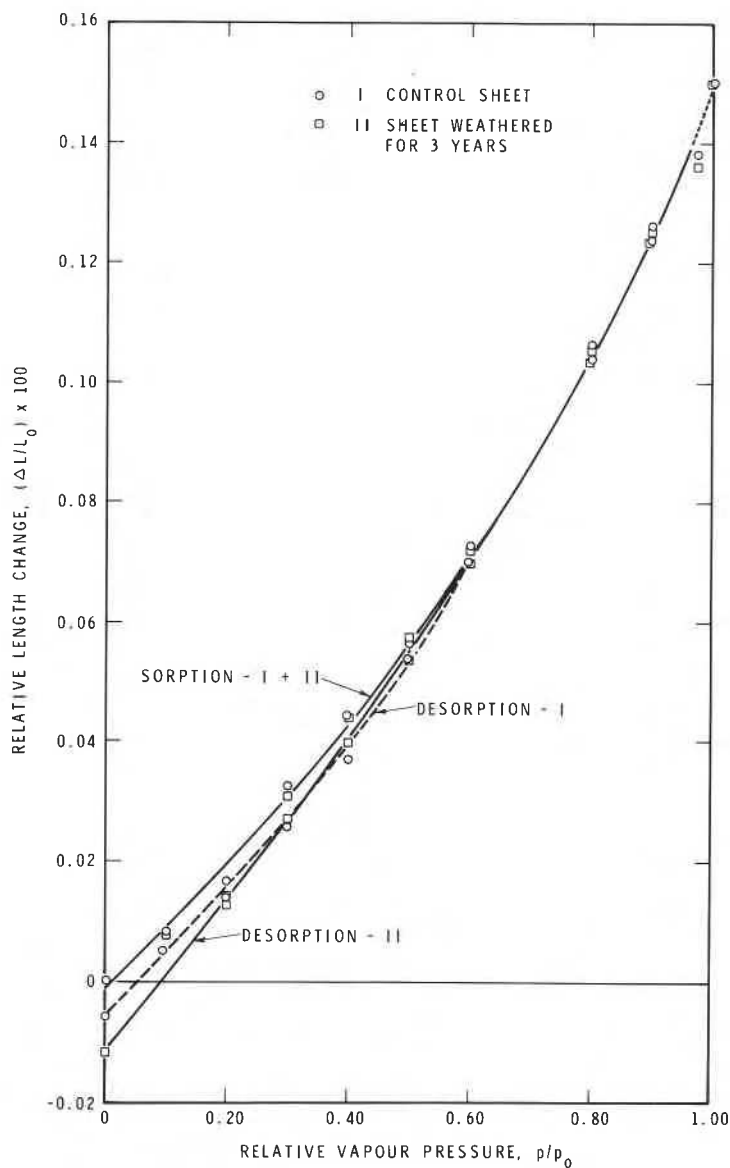
Fig.1. Length change isotherm of GRP sheet (sealed edges) at 23 ± 0.02°C.

linear for relative vapour pressures up to 0.80 for both the control and the weathered sheet. This implies that the sorption process follows the law of ideal solutions (Henry's law) for water sorbed at p/p_0 values lower than 0.80, the sorbed water being randomly distributed within the polymer (Machin and Rogers, 1970). The linear portion of the control sheet weight change sorption is very different from that of the corresponding length change isotherm (Fig.2), but that of the weathered sheet follows quite close-
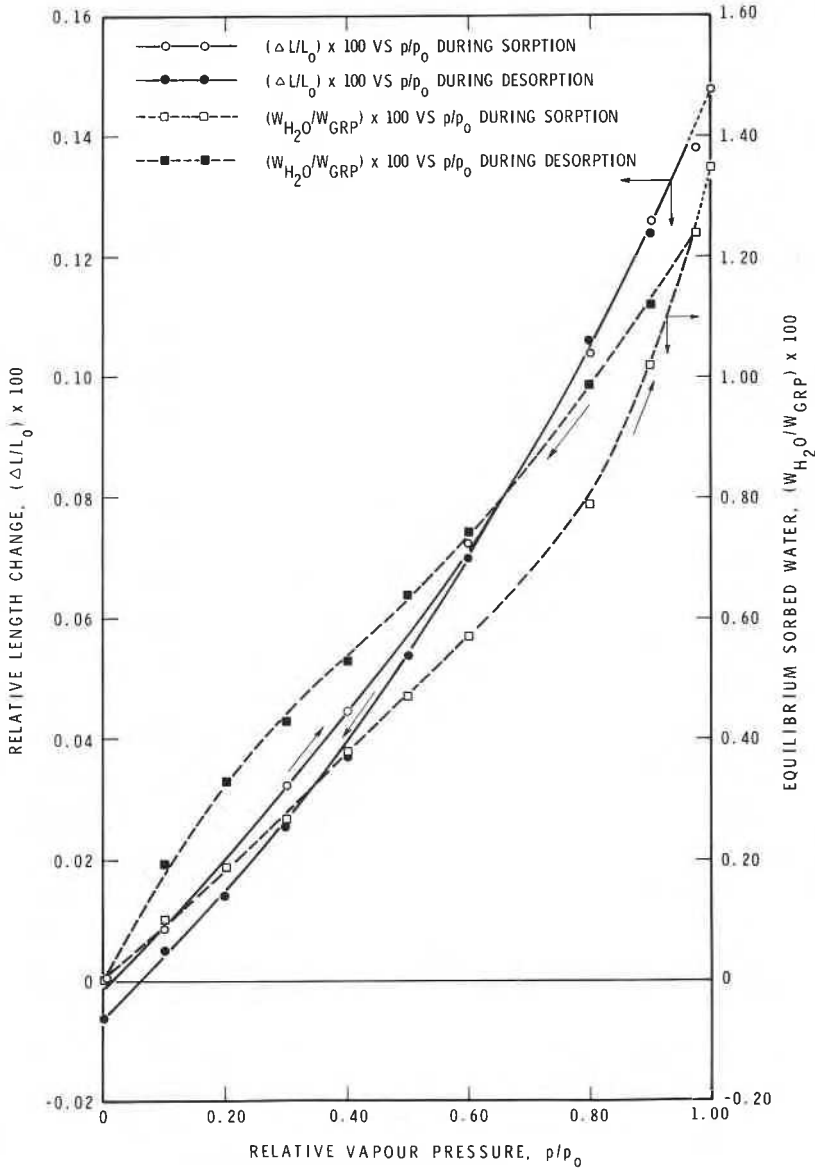
Fig.2. Length change and equilibrium water sorption isotherms of GRP control sheet (sealed edges).

ly the length change isotherm during sorption (Fig.3), over the lower half of the p/p_0 range.

For p/p_0 values greater than 0.80, the weight sorption isotherms show Type III B.E.T. behaviour for both the control and the weathered sheet. This rapid increase in equilibrium sorbed water as a function of relative
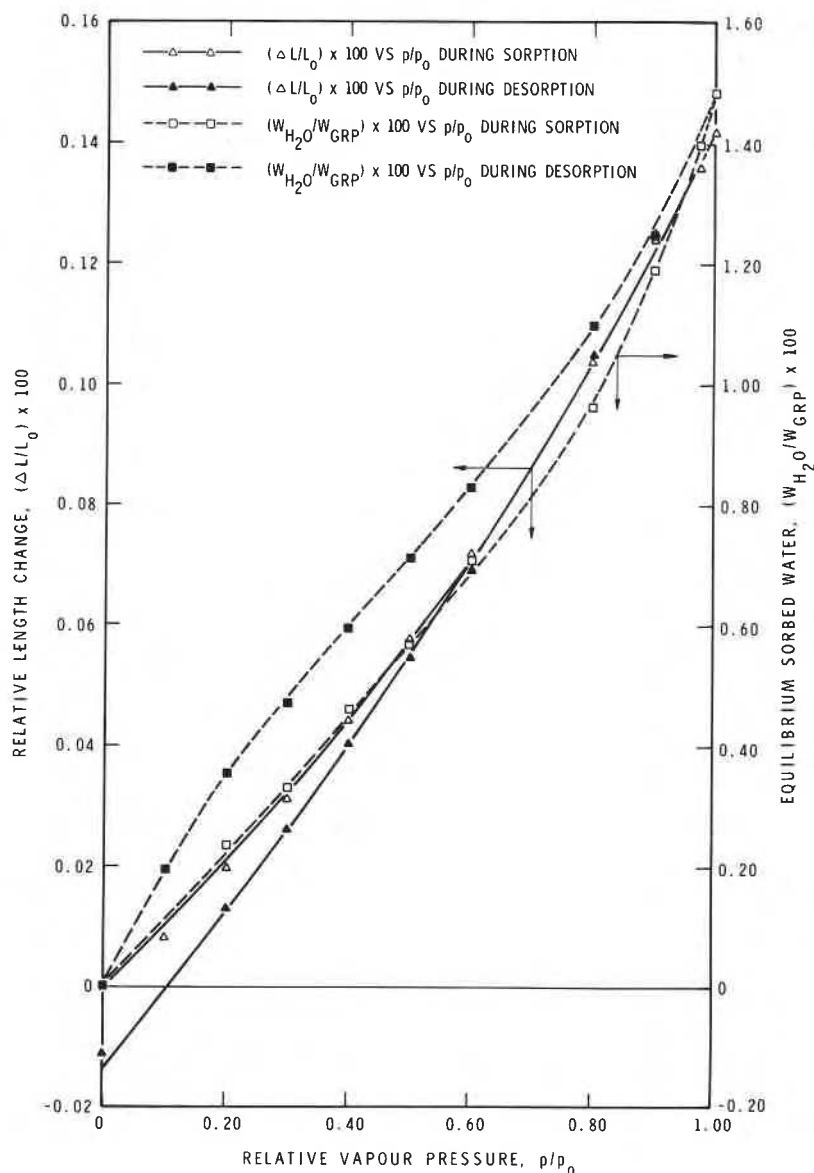
Fig.3. Length change and equilibrium water sorption isotherms of GRP sheet weathered for 3 years.

vapour pressure above 0.80 indicates that the water—water (penetrant—penetrant) interaction is inherently stronger than the water—polymer inter-action, probably resulting in the formation of clusters or aggregates of water molecules. This has been reported to occur with some polymers (Barrie and Platt, 1963). The desorption branch of the weight isotherm is almost linear

over the entire relative vapour pressure range and is well above the sorption branch, forming a wide hysteresis loop, a common occurrence in most water —polymer systems (Barrie, 1968). Thus, the occurrence of hysteresis in the weight isotherm is in contrast to the moisture-induced reversible deformation behaviour in the length change isotherm for $p/p_0 > 0.60$, with only slight irreversibility for $p/p_0 < 0.60$. The origin of irreversibility of the weight isotherm in polymeric materials is still controversial. One tentative suggestion is that there are more active sites available during desorption than during sorption (Barrie, 1968), resulting in higher equilibrium water content for a given relative vapour pressure.

3.3 Length changes induced by sorbed water

The moisture-induced deformational behaviour (hygroelasticity) of polymeric materials is usually assessed by plotting the relative dimensional change versus the relative weight change resulting from sorption and desorption of water in the liquid or vapour state (Adamson, 1980; Ishai, 1975; Marom, 1977; Cohen and Marom, 1978). This approach leads to a better understanding of the effects of water uptake on the swelling (or shrinkage) strain of the polymeric material.

In Figs.4 and 5, the percentage length changes ($100 \times \Delta L/L_0$) are plotted versus the percentage weight changes ($100 \times \Delta W/W_{GRP}$) produced by water sorbed at equilibrium over the relative vapour pressure range ($p/p_0 = 0.00$—1.00) during sorption and desorption. The mean rates of dimensional changes (swelling and shrinkage) per unit rate of sorbed water over the ranges of water sorption are given in Tables 1 and 2. In Tables 3 and 4 selected values are presented showing the relation between p/p_0, equilibrium amount of sorbed water and dimensional changes.

As in the sorbed water weight change—relative humidity isotherm (W/W_{GRP} vs. p/p_0), a hysteresis was observed in the length change—weight change sorption—desorption isotherm ($\Delta L/L_0$ vs. W/W_{GRP}) of weathered and non-weathered GRP sheets (Figs.4 and 5). It is suggested that the occurrence of hysteresis in the length change—weight change sorption—desorption isotherm is due to the weight change component.

3.3.1 Swelling strain of GRP composite

The sorption branch of the curves (length change isotherms) for the control sheet (with either sealed or non-sealed edges) and weathered sheet may be considered for the purpose of discussion to be composed of two approximately linear portions (Figs.4 and 5). In the control sheets (sealed or unsealed) the relative rate of swelling ($\Delta L/L_0$) per unit rate of sorption of water ($\Delta W/W_{GRP}$) in the portion of the curve below 1.00% sorption is greater than that in the second portion, above 1.00%, by a factor of 2.7—2.8. The corresponding factor for similar rates for the weathered sheet (with sealed edges) is 1.7 (Table 1).
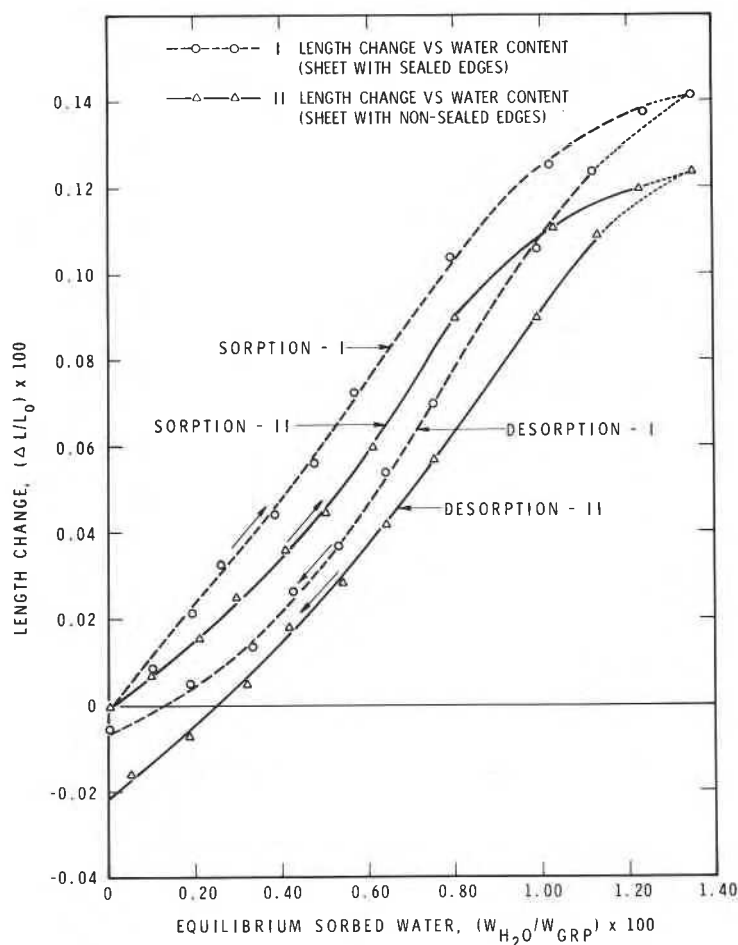
Fig.4. Effect of edge surface on length changes induced by sorbed water in GRP control sheet.

It is suggested that the considerable difference in rates between the initial and final stages of swelling is due to microheterogeneity in the matrix resin. Studies by microscopic techniques (Morgan and O'Neal, 1975; Solomon et al., 1967) have indicated that the fully reacted, finally cured thermosetting resin consists of a mixture of highly cross-linked microgel particles (micelles) embedded in a less highly cross-linked continuous phase. Although the micelles are comparatively more dense, they contain a portion of the total molecular free volume. Given their higher density, however, the micelles are less easily penetrated by water molecules than is the surrounding matrix.

Thus it is proposed that for equilibrium concentrations lower than 1.00%, most or all of the sorbed water is contained in the less dense fraction of the resin, which constitutes the largest proportion, is more easily penetrated by water, and can swell to a larger extent as it is less restrained due to fewer
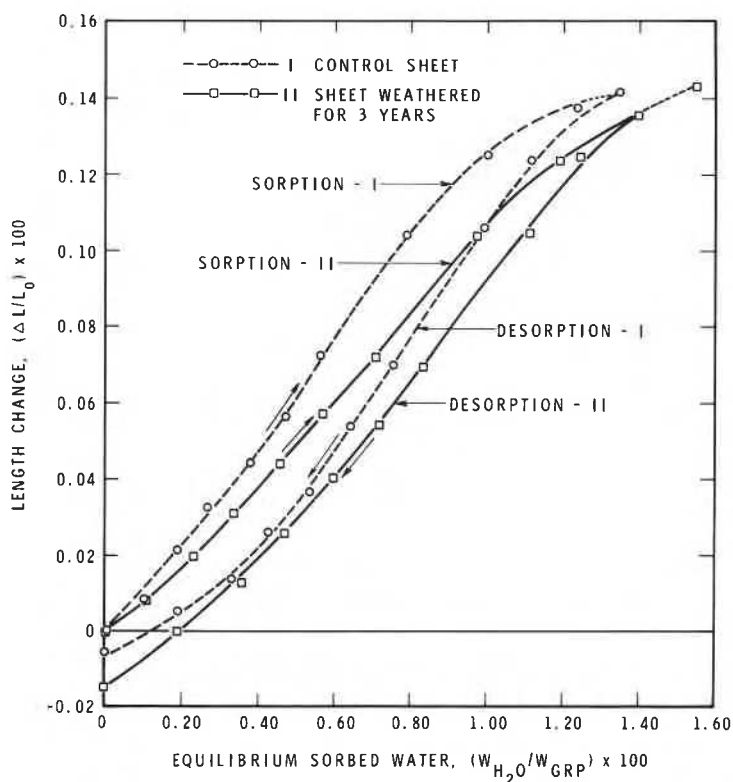
Fig.5. Effect of weathering on length changes induced by sorbed water in GRP sheet (sealed edges).

TABLE 1

Rate of swelling of GRP sheet during water sorption

Expt. No.	Sample Description	Mean Rate of Swelling[a]			R_1/R_2[b]
		Range of Sorbed Water ($100 \times W_{H_2O}/W_{GRP}$)			
		0.00—1.00	1.00—1.35	1.35—1.55	
1	Control sheet with non-sealed edges	1.11×10^{-1}	4.14×10^{-2}	—	2.7
2	Control sheet with sealed edges	1.26×10^{-1}	4.43×10^{-2}	—	2.8
3	Sheet weathered for 3 years (sealed edges)	1.08×10^{-1}	6.36×10^{-2}	6.36×10^{-2}	1.7

[a]Calculated by the formula $\dfrac{(\Delta L_2 - \Delta L_1)/L_o}{(\Delta W_2 - W_1)/W_{GRP}}$

[b]R_1 and R_2 designate the average rates of swelling of the first and second portions of the length change—sorption isotherms, respectively.

TABLE 2

Rate of shrinking of GRP sheet during water desorption

Expt. No.	Sample Description	Mean Rate of Shrinking[a]			
		Range of Sorbed Water ($100 \times W_{H_2O}/W_{GRP}$)			
		1.55—1.35	1.35—1.20	1.20—0.40	0.40—0.00
1	Control sheet with non-sealed edges	—	6.00×10^{-2}	1.25×10^{-1}	9.00×10^{-2b}
2	Control sheet with sealed edges	—	7.33×10^{-2}	1.37×10^{-1}	7.00×10^{-2}
3	Sheet weathered for 3 years (sealed edges)	5.50×10^{-1}	1.00×10^{-1}	1.23×10^{-1}	8.50×10^{-2}

[a]Calculated by the formula $\dfrac{(\Delta L_2 - \Delta L_1)/L_0}{(\Delta W_2 - \Delta W_1)/W_{GRP}}$

[b]Caused by the contribution of greater permanent shrinking than in the control sheet with sealed edges.

cross-links. The slower rate of swelling for equilibrium water concentrations above 1.00%, i.e., for concentrations representing amounts > 74% of that sorbed at p/p_0 of 1.00 (Table 3), reflects the slower diffusion into the high density micelles and, because of their highly cross-linked state, swell to a much lesser extent than the surrounding lower density material.

Concentrations lower than 1.00% represent equilibrium amounts of water that are sorbed at relative vapour pressures between zero and 0.90 (90% RH) by the controls and between zero and 0.82 by the weathered sheets (Table 3, Figs.4 and 5; Blaga, 1981). Consequently, GRP sheets exposed to variable relative humidities lower than these levels will undergo swelling at considerably higher rates. Cyclic variations of humidities within this range will produce a more severe stress-fatigue (Blaga and Yamasaki, 1973) than at higher RH, ultimately resulting in higher rates of deterioration of the GRP composite.

The sheet with sealed edges swells to a greater extent and has consistently higher relative rates of swelling than the sheet with non-sealed edges (Fig.4 and Table 1). The initial slope of the sorption branch indicates that the relative rate of swelling per unit rate of water sorption by the sheet with sealed edges is 14% greater than that of the sheet with non-sealed edges. For the last stages of water sorption, the rate of relative swelling of the sheet with sealed edges is, however, only about 7% higher than that of the sheet with non-sealed edges . The lower rates of swelling of sheet with non-sealed edges may be due to the presence of water sorbed in microcavities, small amount of open pores and pockets at the glass—resin interface located in the edge region (Figs.6 and 7). The pockets are usually produced by water attack on the glass—resin interface, resulting in partial debonding, as a result of lack of adhesion during fabrication and during cutting of the sheet. The water

TABLE 3

Results on sorption and linear swelling of GRP composite

Expt. No.	Description of Sample	Relative Vapour Pressure p/p_0	Water Content[a] (%)	Percent of the Max. Water Sorbed (Equil. Amt. at $p/p_0 = 1.00$)	Linear Swelling Strain $(\Delta L/L_0) \times 10^4$
1	Control sheet with non-sealed edges	0.00	0.00	0.00	0.00
		0.50	0.50	37.04	4.60
		0.82	0.84	62.22	9.45
		0.90	1.00	74.07	10.85
		1.00	1.35	100.00	12.35
2	Control sheet with sealed edges	0.00	0.00	0.00	0.00
		0.50	0.47	34.81	6.10
		0.82	0.85	62.96	11.20
		0.90	1.00	74.07	12.65
		1.00	1.35	100.00	14.20
3	Control sheet weathered for 3 years (sealed edges)	0.00	0.00	0.00	0.00
		0.50	0.57	36.77	4.90
		0.82	1.00	64.52	10.85
		0.90	1.17	75.48	12.25
		1.00	1.55	100.00	14.35

[a]Equilibrium amount. Further details on the relation between sorbed water in GRP composite and p/p_0 are given by Blaga, 1981.

TABLE 4

Results on desorption and linear shrinking of GRP composite

Expt. No.	Description of Sample	Relative Vapour Pressure p/p_0	Water Content[a] (%)	Percent of the Max. Water Sorbed (Equil. Amt. at $p/p_0 = 1.00$)	Linear Shrinkage Strain $(\Delta L/L_0) \times 10^4$
1	Control sheet with non-sealed edges	1.00	1.35	100.00	12.35
		0.95	1.20	88.89	11.00
		0.50	0.64	47.41	3.30
		0.275	0.40	29.63	1.45
		0.00	0.00	0.00	−2.15
2	Control sheet with sealed edges	1.00	1.35	100.00	14.20
		0.95	1.20	88.89	13.10
		0.50	0.64	47.41	3.40
		0.275	0.40	29.63	2.15
		0.00	0.00	0.00	−0.65
3	Control sheet weathered for 3 years (sealed edges)	1.00	1.55	100.00	14.35
		0.95	1.35	87.10	13.25
		0.87	1.20	77.42	11.75
		0.50	0.72	46.45	1.95
		0.245	0.40	25.81	1.90
		0.00	0.00	0.00	−1.50

[a]Equilibrium amount of water at p/p_0 given on the same line, before desorption to the p/p_0 on the next line. Further details on the relation between sorbed water and p/p_0 are given by Blaga, 1981.

sorbed in these flaws does not induce swelling. Thus, experiments on the relation between equilibrium sorbed water and dimensional changes should be carried out on specimens with sealed edges.
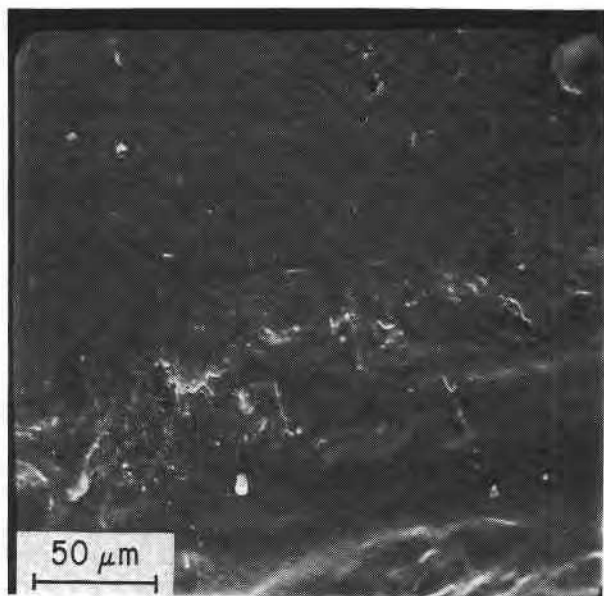
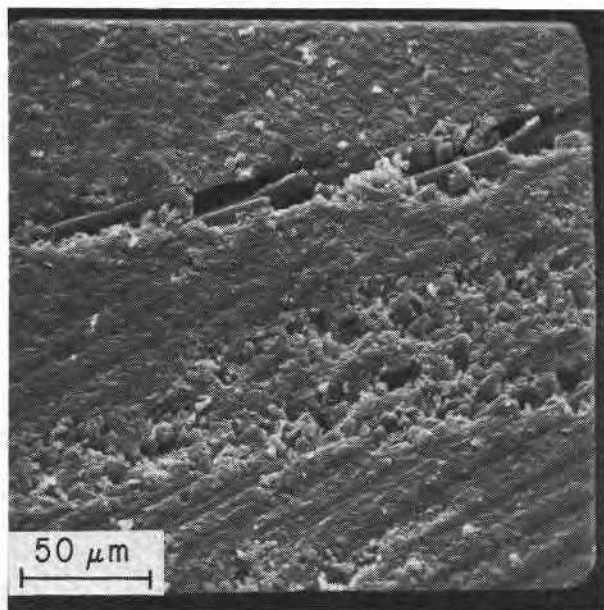Fig.6. SEM Micrograph of wax-sealed edge surface of GRP control sheet.

Fig.7. SEM Micrograph of non-sealed edge surface of GRP control sheet.

3.3.2 Effect of weathering

The length change isotherm of the weathered sheet is very similar to that of the control sheet. The amount of swelling is, however, generally lower in

sheet weathered for three years than for non-weathered sheet (Fig.5). Furthermore, weathering of GRP sheet results also in a decrease in the rate of swelling for equilibrium sorbed water concentrations below 1.00%, but induces higher relative rates of swelling for concentrations greater than 1.00%. For example, the relative rate of swelling is about 14% lower for sorbed water concentrations up to 1.00% in weathered sheet than in the control. For concentrations higher than 1.00%, i.e., when the sorbed water is > 65% of the equilibrium amount at p/p_0 = 1.00, (Table 3), the weathered sheet has 44% higher rates of relative swelling per unit rate of water sorption than the control. The lower amount of swelling in the weathered sheet in comparison with the control is probably due to an increased proportion of molecular free volume*, microvoids and microcavities in the resin, and pockets at the glass—resin interface, as a result of deterioration. As stated earlier, the water sorbed at these sites does not induce swelling. This may also account for the initial lower rates of swelling in the weathered sheet than in the non-weathered sheet. Probably, during the initial stage, more water is sorbed in the microvoids and other flaws, which are present to a greater extent in the weathered sheet than in the non-weathered material, and this results in lower rate of swelling. After the GRP composite has sorbed 1.00% of water, i.e., 65% of the equilibrium amount at p/p_0 = 1.00, most or all of the voids and cavities are filled. For concentrations higher than 1.00%, therefore, most of the water being sorbed diffuses into the bulk of the resin, resulting in an increased relative rate of swelling as evidenced by the higher slope for the weathered sheet compared with that of the control (Fig.5 and Table 1). It may be stated that the above explanation does not include the possible restraining effect of the glass fiber. This question cannot be resolved until the experiments are repeated with resin alone.

These results indicate that there is a critical concentration of equilibrium sorbed water at which a marked change in the rate of relative swelling strain occurs. It is possible that the concentration at which the marked change in swelling occurs will vary with the extent and distribution of the microgel particles, the microgel and the continuous phase densities, and these, in turn, will be determined by the formulation of the resin and process conditions used in the fabrication of the composite. The value of the concentration of sorbed water will be associated with a corresponding critical value of the relative humidity, below which the GRP composite undergoes the greatest deterioration.

3.3.3 Shrinkage strain

The extent and rate of linear shrinking is considerably higher for the sheet with sealed edges than for that with non-sealed edges (Fig.4). The over-all deformational response of the sheet material with free edge surfaces during desorption is analogous to that exhibited during sorption for similar

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*Submicroscopic voids or holes caused by packing irregularities of the polymer molecules.

reasons, i.e., desorption of water contained in microcavities, pockets along the fiber close to the edge surface, and other flaws that do not result in dimensional changes.

The desorption branches of the length change isotherms (Figs.4 and 5 and Table 2) of the control and weathered sheet may be divided for easier comparison into three and four portions, respectively, according to their average slopes. The initial (water content between 1.55% in the weathered sheet or 1.35% in the control and 1.20%) and final stages (water content 0.40—0.00%) of water desorption have lower rates of shrinkage per unit rate of desorption than the intermediate stage (1.20—0.40%) in both control and weathered sheets. During the initial stages, part of the water that is desorbed was probably contained in flaws, because it can leave the composite with greater ease than the water more intimately associated (dissolved) with the polymer molecules. Migration of the water from these sites does not result in dimensional changes (Rogers, 1965) so that the overall rate of shrinking is reduced. The mechanism for the equally low rate in the final stages is different. Part of the water being desorbed was probably contained in the microgel particles which, due to their highly cross-linked state, undergo relatively low dimensional change, resulting in a lower rate of shrinking.

The extent of shrinkage in the weathered sheet is much lower than in the control sheet (Fig.5). The relative rates of shrinking per unit rate of desorption are also lower in the weathered sheet than in the control for most of the desorption isotherm.

The initial portion of the desorption curve is influenced by changes induced in the composite by weathering that results in larger over-all equilibrium amounts of sorbed water (Blaga, 1981). In the next portion of the curve (between 1.35 and 1.20% sorbed water content) desorption causes an approximately 36% higher rate of shrinking in the weathered than in the control sheet (Table 2). This conclusion should, however, be treated with caution. Desorption corresponding to the initial portion of the curve (between 1.55 and 1.35% water content) of the weathered sheet evidently involved mostly loss of water located at the various flaws that do not induce dimensional changes, and this accounts for the lower rate in comparison with other parts of the isotherm. In the next portion of the curve, most of the water leaving the composite was probably that more intimately mixed with the resin, resulting in higher shrinkage. In the control sheet, however, desorption between 1.35 and 1.20% of sorbed water concentrations constitutes the initial stage and thus may also involve mostly water leaving from flawed sites. This, therefore, accounts for the lower rate of relative shrinking in the control than in the weathered sheet. Desorption between 1.20 and 0.40% water content results in approximately 10% lower rate of shrinking in the weathered than in the control sheet. The rate of shrinking in the final stage, desorption between 0.40 and 0.00% water content, is 21% higher in the weathered than in the control sheet.

Complete desorption of the water induces a relatively small permanent shrinkage in both the control and the weathered sheet, being higher in the latter. This shrinkage may be attributed to post cross-linking during the experminentation as a result of the reaction of residual ethylenic bonds under the influence of the free radicals still present in the matrix resin (Blaga and Yamasaki, 1973). This process is promoted by the hydrolytic action of the sorbed water on the polyester chain, causing chain breakage that imparts a greater freedom of movement to the resulting molecular segments. Thus, the heretofore inaccessible free radicals can be reached by the reactive groups. It is also reasonable to believe that this occurs not only in the sheet weathered for three years, but also in the non-weathered sheet which was subjected to cycles in relative humidities over a relatively long period of time (about 60 weeks overall). The larger permanent shrinkage in the weathered sheet may be due to changes in the molecular structure produced in the outdoor exposure, which favour increased cross-linking by the water-assisted process during sorption. There is also the possibility of strain relaxation associated with the fiber reinforcement.

As the reinforcing glass is practically impervious to water and has lower surface area, net dimensional changes (swelling and shrinkage strains) induced by sorption and desorption of water in the GRP composite are due essentially to the matrix resin. This does not consider the possible restraining effect of the glass fiber.

It is suggested that these water-induced stresses, in conjunction with those resulting from the fluctuations in temperature, result in a system of stresses that is particularly intense at the glass—resin interface. These stresses, induced by both humidity and temperature fluctuations, may be acting in the same direction or in opposite directions. They are cyclical and result in a stress-fatigue that affects the durability of the GRP composite (Blaga and Yamasaki, 1973). Their effect on the durability depends to a great extent on the nature, value and distribution of internal (residual) stresses (Chambers and McGarry, 1959; McGarry, 1964).

CONCLUSIONS

The length change—p/p_0 isotherm indicates that the moisture induced deformational behaviour is a reversible phenomenon for p/p_0 values between 0.60 and 1.00, with some slight deviation for values of p/p_0 lower than 0.60. The length change isotherm of the weathered sheet is essentially identical with that of the control, with only a slight deviation of the desorption branch at low vapour pressures ($p/p_0 < 0.20$). All this is in contrast to conclusions derived from considerations of length change—weight change sorption—desorption isotherms.

The relation between the equilibrium sorption and the resulting dimensional changes (swelling and shrinkage strains) and the effect of weathering on this relation is relatively complex. The length change—sorbed water isotherms

indicate that when the equilibrium water content in the GRP composite has reached a certain fraction (critical value) of the possible maximum (the equilibrium concentration at $p/p_0 = 1.00$), a marked decrease in the rate of swelling strain occurs in both the control and the weathered sheet. This change in the rate of swelling is believed to be due to the microheterogeneity of the matrix resin, which consists of a mixture of dense microgel particles (highly cross-linked resin islands) embedded in a less dense continuous phase (resin cross-linked to a lesser degree). At concentrations of sorbed water lower than the critical value, most or possibly all of the water is contained in the less dense phase of the resin, which is more easily penetrated by water and constitutes the largest proportion of the matrix. As the continuous phase is less restrained by cross-links, it swells to a greater extent than the microgel phase, which probably contains most or all of the equilibrium sorbed water above the critical concentration.

Although the weathered GRP composite consistently absorbs greater equilibrium amounts of water, the amount of its linear swelling is lower than that of the control. Weathering also results in lower rates of swelling below the critical value of equilibrium sorbed water content, but induces considerably higher rates above that value. The lower amount and reduced rate of swelling below the critical value of sorbed water content is believed to be due to an increase in molecular free volume and a greater proportion of possible larger flaws, such as microvoids and microcavities in the resin and glass-resin interfaces, as a result of deterioration. The sorption of water at these sites does not result in swelling. Higher rates of swelling above the critical concentration may occur because, at this point, most or possibly all of the additional flaws produced by weathering have been filled and, subsequently, the water begins to diffuse from the flaws into the bulk of the matrix-resin (continuous and microgel) phases. Owing to an increased proportion of sites that do not induce dimensional changes, the amount of shrinkage strains is lower in the weathered than in the control sheet. For the same reason, weathering also results in lower relative rates of shrinking per unit rate of water sorbed over the major portion of the concentration range. The above analysis does not take into account any effect of the re-inforcing glass fiber. This question will be resolved with future experiments involving resin alone.

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