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WATER SORPTION CHARACTERISTICS OF GRP
COMPOSITE : EFFECT OF OUTDOOR WEATHERING

by A. Blaga

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RESUME

A partir des isothermes complets de l'équilibre sorption-désorption établis à 23°C, l'auteur détermine que les panneaux de plastique armé de fibres de verre vieillis à l'extérieur pendant trois ans absorbent plus de vapeur d'eau que des panneaux non vieillis. Les résultats cinétiques de sorption et de désorption à 23°C et deux niveaux de pression relative ($p/p_0 = 0.80$ et $p/p_0 = 0.975$) montrent que les panneaux vieillis absorbent la vapeur d'eau à une vitesse beaucoup plus grande que les panneaux non vieillis. Une plus grande quantité d'eau sorbée et des vitesses de sorption et de désorption plus élevées entraînent des modifications dimensionnelles plus grandes et plus rapides (gonflement et rétrécissement), ce qui accélère les effets généraux de la contrainte-fatigue exercée par l'environnement sur le panneau armé de verre.

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Water Sorption Characteristics of GRP Composite: Effect of Outdoor Weathering

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The complete sorption-desorption equilibrium isotherms determined at 23°C indicate that glass fiber-reinforced polymer (GRP) sheets weathered outdoors for 3 years absorb larger amounts of water vapor than the non-weathered sheets. Sorption and desorption kinetic results at 23°C and two levels of relative pressure ($p/p_0 = 0.80$ and $p/p_0 = 0.975$) show that the weathered sheets absorb water vapor at considerably higher rates than the non-weathered sheets. Larger amounts of sorbed water, and faster sorption and desorption will result in respectively greater magnitudes and higher rates of dimensional changes (swelling and shrinking). This accelerates the overall effects of environmentally exerted stress-fatigue on the GRP composite.

INTRODUCTION

Generally, polymer-based materials are not water soluble but they are capable of absorbing varying amounts of water, depending on their chemical nature and formulation, as well as on the humidity and temperature of the environment to which they are exposed. Sorbed water can produce changes in the chemical and physical nature of the material by itself or in conjunction with other chemical or physical agents such as heat and ultraviolet light (1-4). Sorption and desorption of water from plastic material causes swelling and shrinking. These dimensional changes are cyclical because of fluctuations of humidity in the environment. The combined effect of moisture- and temperature-induced dimensional changes produces a stress fatigue, particularly intense in the outer layers of the sheet, resulting in surface deterioration (3-5).

The purpose of the present paper is to report results of a study of the effect of weathering on the water sorption characteristics of glass fiber-reinforced polymer (GRP) sheet.

EXPERIMENTAL

Materials

Specimens used in the water-vapor sorption experiments were prepared from 0.8 mm (1/32 in.) thick commercial GRP sheet produced by a continuous process. The GRP sheets consisted of approximately 25 weight percent of silane-treated glass fiber (E-glass) in the form of chopped strand mat and 75 weight percent of 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.

Water Sorption Apparatus

The apparatus consisted of a series of 6 glass tubes, each containing one calibrated spring balance (McBain-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 vacustat (mercury manometer) and a thermostated water source (reservoir). The lower part of the tubes were placed in a thermostated water bath controlled at $23 \pm 0.02^\circ\text{C}$ and immersed to a depth such that the water level was about 8 cm above the upper ends of the specimen.

The range of constant water vapor 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 to that (p_0) at the temperature of the thermostated water bath.

Procedures

The method used to determine the isotherms (Figs. 1 and 2) consisted in increasing the vapor pressure in steps in the evacuated system (essentially air-free) at constant temperature ($23 \pm 0.2^\circ\text{C}$), and obtaining equilibrium values at each step (instead of drying the specimens between successive determinations).

Sorption- and desorption-time experiments were carried out with the same equipment and specimens as described previously. At zero time, the relative vapor 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 vapor pressure was used as initial pressure in sorption and as final pressure in desorption. Two series of

Fig. 1. Equilibrium water sorption isotherms of GRP control sheet.

Fig. 2. Effect of weathering on the equilibrium water sorption isotherms of GRP sheets (edges sealed).

experiments were carried out, using relative vapor pressures of 0.80 and 0.975 as final pressures for sorption and as initial pressures for desorption (Figs. 3-5).

Fig. 3. Effect of weathering on the rate of sorption and desorption of GRP at $23 \pm 0.2^\circ\text{C}$, and $p/p_0 = 0.80$ (edges sealed).

Fig. 4. Effect of edge surface on the rate of sorption and desorption of GRP at $23 \pm 0.2^\circ\text{C}$ and $p/p_0 = 0.975$.

Fig. 5. Effect of weathering on the rate of sorption and desorption of GRP at $23 \pm 0.2^\circ\text{C}$ and $p/p_0 = 0.975$ (edges sealed).

The specimens were washed thoroughly with distilled water and rinsed with ethanol. Two test specimens were used for each determination of equilibrium sorbed water and for sorption-desorption time experiments. Prior to the actual sorption experiments, the specimens were evacuated to constant weight (as indicated by the quartz spring balance). The corrected weight was then used as a basis for the calculation of the amount (percent) of sorbed or desorbed water, using the formula $\{(W_{H2O}/W_{GRP}) \times 100\}$, where W_{H2O} and W_{GRP} are the weight of water-sorbed and dry GRP specimen, respectively.

In assessing the effect of outdoor weathering on the sorption isotherms and on the sorption-desorption kinetics of GRP sheets, the edge surfaces were sealed by

dipping them in molten paraffin wax. This was done to simulate the situation usually encountered in use where the edges are at a sufficient distance from most main surfaces that they do not have any influence on the sorption process. However, the edge surface may affect the water sorption characteristics of the composite material in the regions near the periphery of a GRP panel.

THEORETICAL

Mean Coefficients of Sorption and Desorption

Plots of the cumulative, relative amounts of water sorbed and desorbed by GRP sheets vs the square root of time shown in Figs. 3-5 indicate that the sorption process is either Fickian or pseudo-Fickian (7). Indeed, both the sorption and desorption curves are linear for relative amounts of water sorbed and desorbed up to 60 to 70 percent of the equilibrium amount. Above the linear part, both the sorption and desorption curves are concave with respect to the time axis with no inflexions in either sorption or desorption curves.

For an infinite plane sheet (where lateral dimensions are very much greater than thickness) exposed to an atmosphere of vapor at constant pressure and temperature, which absorbs through both surfaces via a process controlled by a constant diffusion coefficient, the solution of Fick's second law can be written as:

$$M_t/M_\infty = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-D(2n+1)^2 \pi^2 t/l^2] \quad (1)$$

where M_t and M_∞ are cumulative total masses of water sorbed or desorbed from a sheet of thickness l at time t and at equilibrium ($t = \infty$); n is a positive integer and D is the diffusion coefficient. A further assumption is that the sheet material is initially free of vapor. It has been shown (7, 8) that the value of t/l^2 for which $M_t/M_\infty = 1/2$, conveniently written as $(t/l^2)_{1/2}$, is given by:

$$(t/l^2)_{1/2} = -\frac{1}{\pi^2 D} \ln \left\{ \frac{\pi^2}{16} - \frac{1}{9} \left(\frac{\pi^2}{16} \right)^9 \right\} \quad (2)$$

the error being about 0.001 percent (9). In deriving the above equation, it is assumed that the thickness of the sheet remains constant (it is not swelling or shrinking) throughout the sorption-desorption process (10). For systems in which the total amounts of sorbed or desorbed penetrant (water) are small compared to the mass of the polymer-based material, the change in thickness is negligible (11). By solving for D and carrying out the arithmetical operations, the relation becomes

$$D = 0.049/(t/l^2)_{1/2} = 0.049 (l^2/t)_{1/2} \quad (3)$$

Thus, when the coefficient of diffusion (D) is constant and if the half time ($t_{1/2}$, half-saturation time) of a sorption experiment is known, the value of D can be determined by this simple formula. If, however, the diffusion coefficient is concentration dependent, the above formula will yield a mean value, $\bar{D}$, of the diffusion coefficient for the concentration range over which the

sorption (or desorption) takes place (9-10). The combined mean of the values of the mean diffusion coefficients for paired* sorption and desorption curves, i.e., $1/2(\bar{D}_s + \bar{D}_d)$, is a better approximation of $\bar{D}$ than either $\bar{D}_s$ or $\bar{D}_d$ separately.

RESULTS AND DISCUSSION

Equilibrium Water Sorption-Desorption Isotherms

The water sorption-desorption isotherms of GRP control sheets and those weathered outdoors for 3 years, are presented in Figs. 1 and 2. The isotherms are partly of type III B.E.T. As for many water-polymer systems, hysteresis is observed in all the sorption isotherms. The isotherms are nearly linear over most of the relative pressure range for all specimens of GRP sheets, which implies that the sorption follows the law of ideal solutions (Henry's law); the type III behavior occurs at higher relative pressures. This indicates a lack of strong polymer-water interaction for equilibrium concentration of sorbed water in the linear region of the isotherms. The subsequent rapid increase of equilibrium sorbed water as a function of the relative vapor pressure ($p/p_0 > 0.80$) confirms that the water-water (penetrant-penetrant) interactions are inherently stronger than the water-polymer interaction. It is well-known that water is associated through hydrogen bonding to form stable clusters or aggregates of molecules, a phenomenon which has been reported to occur with some polymeric materials (12). Possibly, clustering of water molecules is initiated at polar centers (e.g., $-\text{CO}-$, $-\text{COO}-$, $-\text{COOH}$, $-\text{OH}$) in the polymer matrix.

Figure 1 shows that the isotherms of the GRP sheets with sealed edge surfaces coincide over most of their range with those of sheets with non sealed edges, indicating that the edges have no significant effect on the amount of sorbed water at equilibrium.

Effect of Outdoor Weathering on the Equilibrium Sorbed Water Content

In Fig. 2, the isotherm of the weathered GRP sheet is compared with that of the non weathered material. Although the isotherms are very similar, the equilibrium content of the sorbed water is consistently higher in the weathered than in the non weathered sheet. In the range of relative pressure of 0.30 to 0.80 (30 to 80 percent RH), the content of sorbed water is about 20 to 26 percent higher in the weathered sheet than in the control sheet (Table 1). At relative pressures of 0.975 and 1.00**, the sorbed water is 13 and 15 percent higher, respectively, in weathered sheets than in the non-weathered material.

This difference can be attributed to oxidative photo-degradation of the matrix during weathering, which produces additional hydrophilic groups (13, 14) in the resin molecules and thus results in the much larger sorptive affinity for water. Also, the polyester resin has a relatively large number of ester linkages, $-\text{CO}-\text{O}-$,

*For which the initial concentration for desorption is equal to the final concentration for sorption.

**Estimated by extrapolation.

Table 1. Effect of Outdoor Weathering on the Equilibrium Water Sorption* at $23 \pm 0.2^\circ\text{C}$

Experiment no.	Sample description**	Equilibrium sorbed water			
		$p/p_0 = 0.30$	$p/p_0 = 0.80$	$p/p_0 = 0.975$	$p/p_0 = 1.00^{***}$
1	Control sheet, with non-sealed edges	0.29	0.82	1.24	1.35
2	Control sheet, with edges sealed with paraffin wax	0.27	0.81	1.24	1.35
3	Sheet weathered outdoors for 3 years, exposed horizontally with no backing in accordance with ASTM D1435. Edges sealed with paraffin wax	0.34	0.97	1.40	1.35

*Data used in the Table have been taken from Figs. 1 and 2.

**Flat, colorless sheets, with smooth surface, made by a continuous process; specimens used were rectangular, 38 mm long, 12 mm wide and 0.80 mm thick, weighing approximately 0.6 g.

***The equilibrium sorbed water at $p/p_0 = 1.00$ (100 percent RH) was estimated from the isotherms by extrapolation (Figs. 1 and 2).

which during weathering undergo hydrolytic reactions to produce carboxyl ($-\text{COOH}$) and hydroxyl groups ($-\text{OH}$). It can thus be assumed that as the magnitude of these changes increases with weathering, the sorptive capacity of the material will become larger and larger.

Higher amounts of equilibrium sorbed water will induce larger swelling stresses in the weathered GRP sheets. Also, higher concentrations of sorbed water may result in faster and more extensive hydrolytic degradation of the polyester matrix and/or of the glass-resin bond of the GRP composite. Furthermore, larger amounts of sorbed water will affect mechanical and various other physical properties to a greater extent than in non-weathered material.

Repeating sorption and desorption on the control sheets had no significant effect on the equilibrium isotherms over most of the relative vapor pressure range. Similarly, when the determination of the sorption isotherm was repeated on the weathered sheet, only a very slight change in the amount of water sorbed at equilibrium was observed on both the upper and lower curve of the hysteresis loop, but the general shape of the isotherm was unchanged. These results demonstrate that the difference between the amounts of water sorbed at equilibrium by the weathered and non-weathered specimen is caused by exposure to outdoor weathering.

Rate of Water Vapor Sorption and Desorption

At the relative vapor pressure of 0.80, the sorption and desorption curves of the control sheet intersect (Fig. 3). Between the relative sorbed water concentration at the intersection point and 0.97, the desorption becomes gradually much slower than sorption. The difference between the two rates is greater for sheets with non sealed edges (curves not shown); the mean coefficient for desorption is about 16 percent higher than the mean coefficient for sorption in sheets with non-sealed edges, but only 9 percent higher for sheets with sealed edges (Table 2).

At the highest relative vapor pressure ($p/p_0 = 0.975$), the sorption and desorption curves for the sheets with non-sealed edges coincide over the entire relative amount of water sorbed or desorbed (Fig. 4). Thus in these sheets the mean coefficients for sorption and desorption have the same value and are thus independent of sorbed water content (11). When the sorption and desorption is confined to the two faces of the sheet (edge surfaces being sealed), the rate of desorption is higher than the rate of sorption over the range of relative water sorbed or desorbed (Fig. 4). The mean diffusion coefficient for desorption is approximately 16 percent higher than for sorption. The combined mean coefficient of diffusion ($\bar{D}$) calculated from the mean coefficients for

Table 2. Rate of Water Sorption and Desorption in GRP Sheet at Constant Temperature ($23 \pm 0.2^\circ\text{C}$)

Experiment no.	Sample description	Relative vapor pressure p/p_0	Equilibrium amount of sorbed water*, $M_x\%$	Time of half-concentration (50 percent) change (t_1)*, 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 $\bar{D} = \frac{1}{2}(\bar{D}_s + \bar{D}_d)$ $10^9 \text{ cm}^2 \text{ s}^{-1}$
				Sorption	Desorption			
1	Control sheet, with non sealed edge	0.80	0.94	42.25	36.60	2.06	2.38	2.22
2	Control sheet, with sealed edges	0.80	0.93	54.76	50.41	1.59	1.73	1.66
3	Sheet weathered for 3 years	0.80	1.04	37.21	38.69	2.34	2.25	2.30
4	Control sheet, with non sealed edges	0.975	1.23	40.96	40.96	2.13	2.13	2.13
5	Control sheet, with sealed edges	0.975	1.22	52.29	51.12	1.47	1.70	1.58
6	Sheet weathered for 3 years	0.975	1.38	39.06	35.52	2.23	2.45	2.34

*Obtained from the corresponding graphs.

** $\bar{D}_s$ and $\bar{D}_d$, mean coefficients for sorption and desorption, respectively, were calculated by the formula, $\bar{D} = 0.049 (l^2/t_1)$, where l is the thickness and t_1 , the time corresponding to 50 percent change in concentration ($M/M_x = 0.50$).

sorption and desorption is 25 percent lower for sheets with sealed edges than for sheets with non-sealed edges at both the lower and the higher relative vapor pressures (Table 2).

Effect of Weathering on the Rate of Water Vapor Sorption and Desorption

The sorption- and desorption-time curves for sheets with sealed edge surfaces, controls and weathered outdoors for 3 years, are shown at relative pressures of 0.80 and 0.975 respectively in Figs. 3 and 5. The rates of water sorption and desorption of weathered sheets are considerably higher than those of non weathered sheets. This is also evident from the calculated mean coefficients for sorption and desorption, which are drastically higher in weathered sheets (Table 2). For example, at the lower relative pressure ($p/p_o = 0.80$), the mean diffusion coefficients for sorption and desorption of the weathered sheets are 47 and 30 percent, respectively, higher than the corresponding coefficients of control sheets; at the higher relative pressure ($p/p_o = 0.975$), these coefficients are 52 and 44 percent larger than in the control sheets. The combined coefficients of diffusion at the two relative pressures are 29 and 48 percent higher for the weathered sheets than the corresponding coefficients of the control sheets. These results clearly indicate that weathering greatly influences the rates of movement of water vapor in and out of GRP sheet materials.

Although optical and scanning electron microscopy (SEM) did not reveal any significant changes in the exposed surface, some yellowing of the weathered samples was visually observed. The yellowing is due to the formation of carbonyl groups in conjugation with double bonds, as a result of UV-induced photo-oxidative degradation (13, 14). These photo-oxidative processes produce polymer-chain scissions and cross-linking. Chain scissions result in an increased number of chain ends, and an accumulation of these at certain sites produce submicroscopic voids. An increased number of such voids, which are usually concentrated in the surface region, may result in higher sorption rates.

As dimensional measurements indicated, exposure to outdoor weathering did not cause any reduction in sheet thickness. Thus the GRP did not undergo significant erosion. This is reasonable, since these sheets are made from resin with improved resistance and have been exposed for only 3 years.

Faster rates of sorption and desorption in conjunction with larger amounts of sorbed water will result in higher rates of the dimensional changes (swelling and shrinking). This accelerates the overall effect of environmentally exerted stress-fatigue on the GRP composite. Furthermore, it should be emphasized that weathering affects only a very thin layer (about 10 to 15 μm) of the GRP sheet. These results refer to about 1 to 2 percent of the total sheet thickness. Experiments now in progress

indicate that when only the weathered material is tested, the change in the water sorption characteristic can be very great indeed.

CONCLUSIONS

The sorption-desorption isotherms of GRP sheet determined over the entire range of relative vapor pressure (p/p_o) are partly of the type III in the B.E.T. classification. Equilibrium isotherms (at $23 \pm 0.2^\circ\text{C}$) indicate that weathered GRP sheets absorb larger amounts of water than non-weathered sheets over the entire vapor pressure range.

Furthermore, sorption and desorption kinetic studies at two levels of relative pressure ($p/p_o = 0.80$ and $p/p_o = 0.975$) show that weathered sheets absorb and desorb water vapor at considerably higher rates than non-weathered sheets. Higher amounts of equilibrium sorbed water will induce larger swelling stresses in the weathered GRP sheets. Data on the effect of weathering on swelling stresses will be published in a separate publication.

Sorption-desorption experiments should be carried out on specimens with sealed edges. When such experiments are performed to study the effect of weathering, the exposed sheets should be very thin.

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