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Influence of hydrostatic pressure on the moisture absorption of glass fibre-reinforced polyester

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The moisture absorption characteristics of glass fibre-reinforced polyester in simulated deep sea water environments have been investigated. Test panels of unsaturated isopthalic polyester resin reinforced with woven E-glass were prepared by hand lay-up and the mass gain occurring during immersion in sea water pressurized up to 80 MPa was monitored. Moisture ingress followed a modified form of Fick's second law of diffusion. The saturation moisture content was shown to be linearly dependent upon the vapour pressure equivalent of hydrostatic pressure. In the case of diffusivity, a systematic relationship with hydrostatic pressure was not observed.

1. Introduction

Fibre-reinforced polymeric materials are being increasingly exploited for the manufacture of components in space, air, ground and water vehicles as well as for sports equipment and building components because of their high specific strength, corrosion resistance and manufacturing flexibility.

Glass fibre-reinforced polyester (GFRP) is probably the most frequently used member of this family of materials and it has been successfully employed for the fabrication of the structural shell of submersible vehicles. Because some of these vehicles may have to operate at depths of 4000 m, the potential for degradation due to moisture absorption is of importance. Such vehicles have been in use for a number of years at depths of 1500 m but little research appears to have been undertaken into the effects of sea water at high pressure on GFRP.

Dukes and Griffiths' work [1] identifies the degradation of mechanical properties following sea water immersion and suggests that high hydrostatic pressure accelerates the deterioration. Several other papers have also identified a degrading effect on mechanical properties due to marine environments [2–4]. Finally the considerable amount of work undertaken in the related field of aerospace-type composites in humid environments also shows that moisture absorption can lead to a deterioration in mechanical properties. It follows that the first stage towards establishing deteriorating mechanisms is to characterize experimentally and theoretically moisture absorption under the influence of hydrostatic pressure. Experimental studies have been reported by Nakanishi and co-workers [3–5] of the effect of pressure on moisture absorption but the results were somewhat variable and no attempt was made to fit a theoretical model to the data. Fahmy and Hurt [6] studied the diffusion of water in epoxy resins under the influence of tensile and compressive stress but did not extend their analysis to saturation levels of moisture.

The present paper reports a study of the influence of hydrostatic pressure on the moisture absorption of a glass fibre-reinforced polyester composite together with a theoretical diffusion model consistent with the experimental results. The work was part of a larger investigation into the effect of hydrostatic pressure on the mechanical properties of a series of composites with polyester and epoxy matrices reinforced with glass or carbon fibres.

2. Experimental details

2.1. Materials and fabrication of test panels

The matrix of the composite was an unsaturated isophthalic polyester resin and the reinforcement consisted of layers of heavyweight, twill E-glass fibre roving with a silane finish. For sub-sea applications, the high glass transition temperature of high-temperature cured thermosetting resins is not of particular benefit because the temperatures encountered underwater are low. This makes ambient temperature-cured resins adequate which simplifies curing procedures.

A hand lay-up method of manufacture was adopted for cost benefit reasons associated with the manufacture of small numbers of complex-shaped commercial products. However, in order to maintain the uniformity of thickness of the plane test panels they were

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pressed to a standard thickness. The method of manufacture is specified below.

The mould plates were treated with release agent and catalysed, accelerated resin was applied to the bottom plate. One layer of woven rovings fabric, 300 mm square, was laid into the resin and lightly worked to cause the resin to fill the weave. This sequence of applying resin and fabric was repeated with the warp direction of the fabric being rotated through 90° on successive layers. When lay-up was complete time was allowed for the resin to fully wet-out the rovings and then a roller was applied to remove excess resin and with it any entrapped air.

Fresh resin was applied to the surface of the laminate and the mould top plate was lowered towards 3 mm thick stops placed around it. Pressure was applied to close the mould, with a further removal of excess resin, and the assembly was clamped and allowed to cure for 12 h. The panel was removed from the mould and postcured, unrestrained at a temperature of 60° C.

Each cured panel was nominally 3 mm thick and 300 mm square, comprising three reinforced laminae.

2.2. Moisture absorption test procedure

Rectangular specimens measuring approximately 20 mm × 40 mm × 3 mm were used for the majority of tests. Where practical, five replicates from different regions of the test panel were taken. No sealants were applied to the specimen edges because trials had failed to identify a suitable material and method for sealing. Edge effects were taken into account in the analysis. In each test, specimens were fully immersed in natural sea water with the exception of a comparison test in deionized water.

Immersion under hydrostatic pressure took place in one of three pressure vessels, one was maintained at 15 MPa, one at 35 MPa and a third at 70 MPa. Immersion at controlled temperature was carried out in closed containers of sea water which were placed in thermostatically controlled environments.

The following general method was adopted. Specimens were conditioned for approximately 8 weeks in a desiccator, rinsed in water, surface dried and weighed to within 0.1 mg, thus establishing the initial weight. They were then immersed in sea water under the particular test conditions. At appropriate intervals they were removed, rinsed and dried as above, reweighed and replaced.

3. Results and discussion

3.1. Initial trials at atmospheric pressure

The first phase of the investigation determined the repeatability of the test method, the influence of water purity, and whether or not temperature could be traded for time as a means of accelerating exposure trials.

Fig. 1 shows the moisture content dependency with time for five panels with five specimens cut from each panel. Data for each panel are shown separately, and the vertical size of the symbols represents the standard deviation of different specimens cut from the same panel. It can be seen that the moisture absorption behaviour was similar for all the specimens, and that there was more variation between, than within, panels.

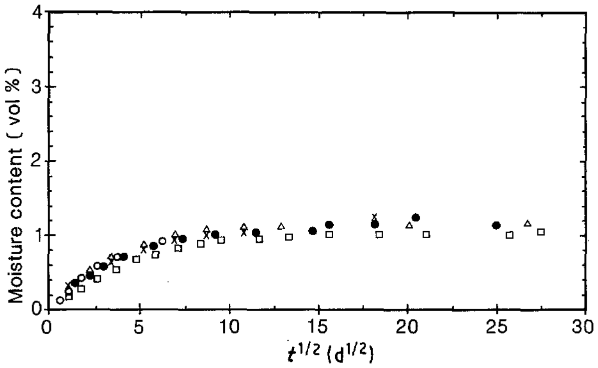

Figure 1 The variation of moisture absorption between specimens of glass/polyester taken from different test panels and immersed in sea water at ambient temperature and pressure. Panel: (×) 003, (□) 004, (△) 009, (○) 012, (●) 014.

Fig. 2 shows that there was no difference between the moisture absorption from deionized water and from sea water, indicating that water purity is not of any significance.

Fig. 3 illustrates the moisture absorption behaviour at 40, 60 and 80° C compared with that at ambient temperature. The results show that increasing temperature increases the rate of moisture absorption but that the material was unable to withstand exposure at 80° C and after an initial rapid weight increase the specimens started to lose weight. The specimens developed a cracked and blistered appearance and the weight loss was due to erosion of resin. Initially it appeared that exposure at 60 and 40° C served only to accelerate the diffusion process, but after an exposure time approaching one year these specimens showed signs of damage and those at 60° C were beginning to lose weight. It was concluded that temperature had influence beyond simply accelerating the diffusion process and that it was not reasonable to use raised temperature as a means of accelerating the moisture pick-up of composites. It follows that those examples in the literature (e.g. [7–9]), where conclusions have been drawn about a materials' resistance to moisture following short-term immersion in boiling water, should be treated with caution.

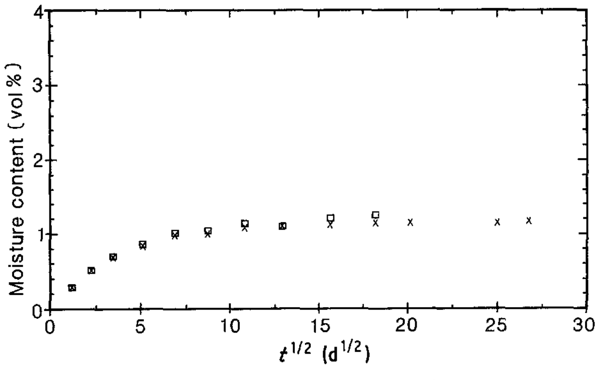

Figure 2 The variation of moisture absorption between specimens of glass/polyester immersed in (×) sea water or (□) deionized water at ambient temperature and pressure.

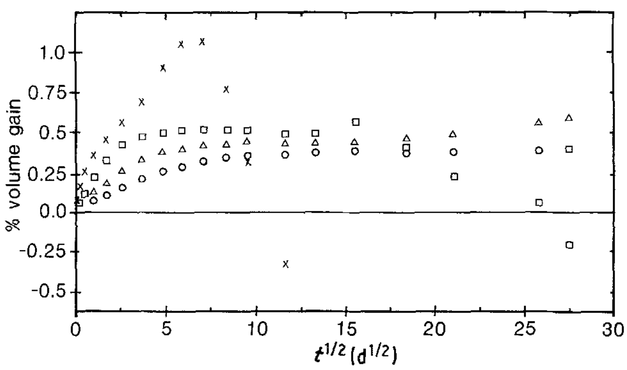

Figure 3 The influence of temperature on moisture absorption by specimens of glass/polyester immersed in sea water at atmospheric pressure. (×) 80° C, (□) 60° C, (△) 40° C, (○) ambient temperature.

3.2. Theoretical basis

Several mathematical models for the uptake of moisture by composite materials have been reported, the most frequently used being that of Shen and Springer [10] who applied Fick's second law of diffusion to the transport of water molecules in resin matrices. They presented an approximate analytical solution for the moisture content in a thin composite plate based upon the Fickian moisture concentration (c) relationship

$$\frac{\delta c}{\partial t} = \left(\frac{\partial}{\partial x}\right) D_x \left(\frac{\partial c}{\partial x}\right) \qquad (1)$$

where t is time. This led to an equation of the form

$$M = \left\{1 - \exp\left[-7.3\left(\frac{D_x t}{s^2}\right)^{0.75}\right]\right\} \times (M_m - M_i) + M_i \qquad (2)$$

where M_i is the initial, constant moisture content of the material, M_m is the maximum, i.e. saturated, moisture content and for a material exposed on two sides to the same environment, s is equal to the thickness. D_x is the diffusivity of the material in the direction normal to the surface.

Application of Equation 2 to the experimental situation comprising a thin plate specimen with moisture entering predominantly through the largest surface, a completely dry initial moisture content and immersion in water at constant temperature allows the relationship illustrated in Fig. 4 to be derived as an approximation for the diffusivity.

$$D_x = \pi\left(\frac{s}{4M_m}\right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \qquad (3)$$

where M_1 and M_2 are linearly related when moisture content is plotted against the square root of time, t, and M_m the saturation moisture content is approached asymptotically.

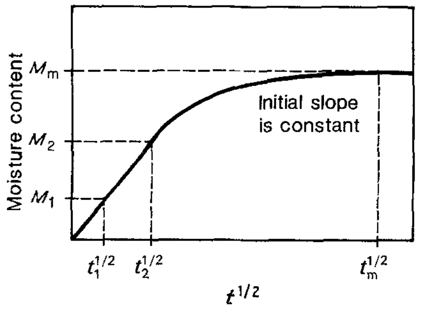

Figure 4 Illustration of the change of moisture content with the square root of time.

It can be seen from Figs 1 to 3 that the experimental data follow Equation 3 thus substantiating the Shen and Springer method of analysis as a basis for establishing values of diffusivity and moisture content and the influence of hydrostatic pressure upon them.

3.3. Relationship between edge and face diffusivity

The specimens used in the investigation were of necessity fairly squat and anisotropic which could lead to enhanced moisture absorption through the edges. Considerable effort was expended in trying to find a satisfactory method of sealing the specimen edges, but none was found. An alternative approach was adopted which established the relationship between the moisture absorption through faces and edges.

This consisted essentially of measuring the moisture absorption during immersion of a series of specimens having different face area to edge area ratios. The tests were undertaken at atmospheric pressure at nine different ratios, three replicates per ratio with gain in mass measured at 0.25, 1, 3, 8 and 15 days.

Following Shen and Springer, the moisture absorption through one face is given by

$$m = 2g(c_m - c_i) A \left(\frac{D_x t}{\pi}\right)^{1/2} \qquad (4)$$

where m is the mass of the water absorbed, c is the moisture concentration, A is the cross-sectional area and D_x is the diffusivity normal to the face.

The total amount of moisture entering the specimen is then

$$\begin{aligned} m &= 2g(c_m - c_i)\left(\frac{t}{\pi}\right)^{1/2} [A_F(D_F)^{1/2} + A_E(D_E)^{1/2}] \\ &= K[A_F(D_F)^{1/2} + A_E(D_E)^{1/2}]\, t^{1/2} \\ \frac{m}{A_F(t)^{1/2}} &= K\left[(D_F)^{1/2} + \frac{A_E}{A_F}(D_E)^{1/2}\right] \qquad (5) \end{aligned}$$

where suffix F relates to the specimen faces and suffix E relates to the specimen edges. The assumption is made that interaction between the six faces of the specimen can be neglected.

It follows from this result that if the weight gain factor, $m[A_F t^{1/2}]^{-1}$, is plotted against the edge area: face area ratio, A_E/A_F, then a straight line relationship is expected where the slope is given by $K(D_E)^{1/2}$ and the intercept by $K(D_F)^{1/2}$. The ratio of the edge diffusivity to the face diffusivity can then be obtained. The procedure adopted was to plot the relationship separately for each value of t used, extract the values of $K(D_E)^{1/2}$ and $K(D_F)^{1/2}$ by means of a least squares fit and then plot the extracted values against time using the values at $t = 0$ as the best estimate. This latter plot is shown in Fig. 5.

The extrapolated value for $K(D_F)^{1/2}$ is 3.73 and that for $K(D_E)^{1/2}$ is 2.63. This leads to a face diffusivity: edge diffusivity ratio of 2.0 which implies that moisture is more readily absorbed through the specimen faces than through the specimen edges and hence that there

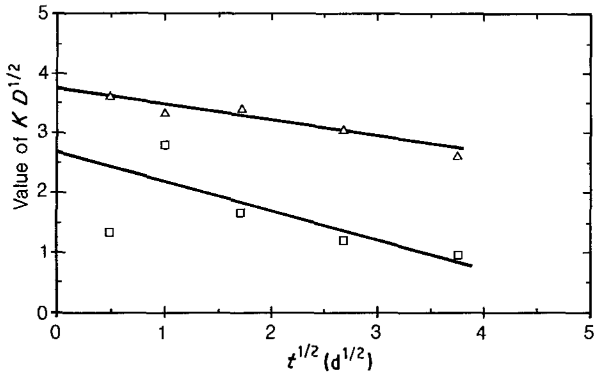

Figure 5 Estimation of face diffusivity : edge diffusivity ratio of glass/polyester laminate by extrapolation of data. (△) $K(D_F)^{1/2}$, (□) $K(D_E)^{1/2}$.

is no capillary effect associated with the fibre reinforcement in this particular type of composite.

Table I shows the face diffusivities for the atmospheric pressure immersion tests providing the data for Figs 1 to 3, after correction for the edge effects, together with the maximum moisture contents.

3.4. Effect of hydrostatic pressure on moisture absorption

Long-term exposure tests were carried out on specimens immersed at atmospheric pressure, 15, 35 and 70 (10 MPa being equivalent to approximately 1000 m sea water depth), for periods of up to 730 days. The results are shown in Fig. 6. They indicate that hydrostatic pressure did not have a large effect on moisture absorption, contrary to expectation.

In order to characterize the influence of pressure on moisture absorption in the immersed environment it was decided that vapour pressure was a more appropriate parameter to use than relative humidity. It has been established [11, 12] that weight gain behaviour at 100% relative humidity is similar to that following immersion in water at the same temperature. A relationship between external pressure and vapour pressure has been derived by Tabor [13] of the form

$$P_1 = P_0 + \frac{H\varrho_v}{\varrho_l} \qquad (6)$$

where P is the vapour pressure, ϱ_v is the vapour density, ϱ_l is the liquid density and H is the hydrostatic pressure.

TABLE I Moisture absorption characteristics of glass/polyester immersed in sea water at atmospheric pressure

Test condition	Measured saturation moisture content (vol %)	Calculated face diffusivity (10^6 mm^2 sec^{-1})
Panel 003	1.23	0.111
Panel 004	1.05	0.113
Panel 009	1.15	0.139
Panel 014	1.22	0.109
009, sea water	1.15	0.139
009, deionized water	1.28	0.117
004, 80° C	2.82	0.690
004, 60° C	1.34	1.085
004, 40° C	1.12	0.273
004, ambient	1.05	0.113

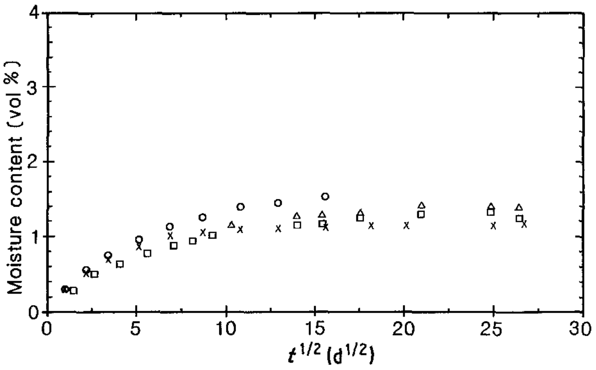

Figure 6 The influence of pressure on moisture absorption by specimens of glass/polyester immersed in sea water at ambient temperature. (×) Atmospheric pressure, (□) 15 MPa, (△) 35 MPa, (○) 70 MPa.

At room temperature the ratio of vapour density to liquid density is small, thus the increase in vapour pressure with external pressure is also small. Table II indicates the vapour pressure values corresponding to the various hydrostatic pressures used. When saturation is reached, equal numbers of water molecules are absorbed by the surface as evaporate from it, which should lead to a linear relationship between the saturation moisture content and the vapour pressure. Fig. 7 plots the experimental data and shows a straight line relationship described by the equation

$$M_m = 6.67 \times 10^{-4} P \qquad (7)$$

where M_m is expressed as % and P is measured in Pascals.

3.4. Effect of hydrostatic pressure on diffusivity

In order to establish the influence of pressure on diffusivity a further series of experiments was carried out where specimens were immersed at different pressures for short periods (up to 16 days, because only the initial behaviour was required). The diffusivity was calculated for each condition using Equation 3 and the correction described in Section 3.3. The saturation moisture content at each pressure was required to calculate diffusivity and this was obtained from Equation 7. The results are set out in Table II. It is not possible to draw a firm conclusion from the data. The absence of a systematic relationship between diffusivity and vapour pressure indicates that diffusivity is independent of pressure. This concurs with Shen and Springer's analysis, which assumes that diffusivity is independent of moisture concentration. However, relatively large changes in diffusivity have only a small effect on moisture absorption characteristics. Furthermore because of the sensitivity to experimental error only large changes in pressure are likely to have a discernable effect. In these circumstances it is possible

TABLE II Moisture absorption characteristics of glass/polyester at various hydrostatic pressure

Immersion pressure (MPa)	Vapour pressure (MPa)	Predicted saturation moisture content (vol %)	Calculated face diffusivity (10^6 mm^2 sec^{-1})
0	1.704	1.14	0.110
10	1.829	1.22	0.128
20	1.954	1.30	0.130
40	2.204	1.47	0.096
80	2.703	1.80	0.077

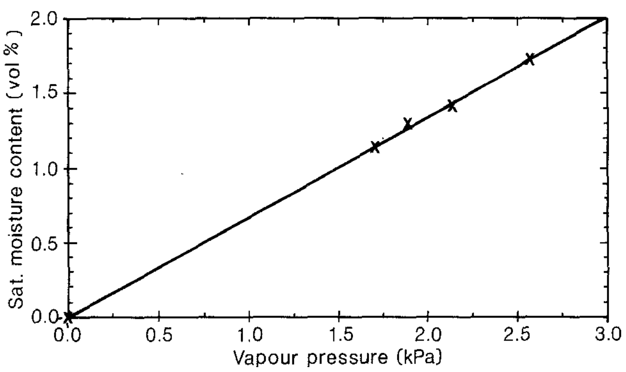

Figure 7 The relationship between saturation moisture content and theoretical vapour pressure for specimens of glass/polyester immersed in sea water at various hydrostatic pressures.

that the decrease in diffusivity at the highest pressures employed is significant. The maximum pressure used exerted a triaxial compressive stress of 80 MPa, which is of the same order as the uniaxial compressive strength of the matrix. Sufficient "tightening up" of the matrix structure could therefore occur to reduce the diffusivity of water molecules compared to that in the unstrained condition.

4. Conclusions

1. The form of Fick's second law of diffusion developed by Shen and Springer has been found to apply to the ingress of moisture in glass fibre-reinforced polyester composites at ambient temperatures and pressures up to 80 MPa.

2. The influence of hydrostatic pressure on saturation moisture content has been established by relating hydrostatic pressure to vapour pressure and showing that the saturation moisture content is linearly dependent upon vapour pressure. However, the increase in saturation moisture content was not as large as was expected, an increase in hydrostatic pressure from atmospheric to 70 MPa increased the vapour pressure by 53% and the saturation moisture content by the same percentage.

3. The influence of hydrostatic pressure on diffusivity was investigated in a similar manner. The results did not allow a clear conclusion to be drawn other than that the maximum effect would be a 30% reduction in diffusivity at the highest pressure used.

4. A brief investigation of the effect of elevated temperature on moisture ingress led to the separate conclusion that long-term exposure to hot water leads to degradation of the polyester matrix.

5. The use of high temperatures for accelerated ageing tests on polyester composites provides unreliable data.

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