

Influence of temperature and hydrostatic pressure on moisture absorption in polymer resins

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Polyester resins are widely used as the matrix in glass fibre-reinforced polymer composites. Moisture absorption has an adverse effect on their mechanical properties. Examination of two cured unsaturated polymers, Stypol R1067/32 and R1067/26, at various temperatures and hydrostatic pressures has shown that the saturation level of moisture in R1067/26 is independent of both temperature and pressure, but in R1067/32 at 5 °C the level depended on pressure. The temperature dependences of the diffusivities were found to be well described by Arrhenius expressions. The diffusivities were found to decrease slightly with increasing pressure, the effect being largest at the highest temperature, in qualitative agreement with theories based on changes in the free volumes in the polymers.

1. Introduction

Polyester resins are widely used as the matrix in glass fibre-reinforced polymer (GFRP) composites. The adverse effects of moisture absorption on the mechanical properties of these materials are well known, and it is therefore important to determine the moisture characteristics of any potential polymer matrix under different conditions of temperature and relative humidity. In applications where a composite is in contact with water at high pressure, it is also important to investigate the effects of pressure on the moisture absorption.

Relatively little work has been reported in the open literature on the moisture absorption characteristics of polyester resins or of GFRP. Springer *et al.* [1] studied the effects of exposure to different temperatures and relative humidities on the mechanical properties of GFRP. Other work in this area has been reported by Apicella *et al.* [2] and Jacquemet and Lagrange [3], where the effects of different resin chemical structures on the absorption and mechanical properties of GFRP were investigated. The moisture absorption characteristics of glass fibre-reinforced polyester composites under hydrostatic pressure have been studied by Nakashino and colleagues [4–6], with uncertain results, by Pollard *et al.* [7, 8], and by Avena and Bunsell [9], at room temperature.

The present study has concentrated on the effects of hydrostatic pressure and temperature on the moisture absorption characteristics of two resins with different chemical structures. Experiments have been per-

formed on specimens immersed in water and held at one of four temperatures, 5, 25, 40 and 70 °C and subjected to one of four pressures, 1, 25, 50 and 75 bar*.

2. Materials

The two resins investigated were formulated to have different water absorption characteristics, and were supplied by Freeman Chemicals Ltd, Ellesmere Port. One was designated Stypol R1067/32, and the other Stypol R1067/26, the latter having the higher moisture saturation level. Both resins are fumarate polyesters cross-linked with styrene monomer but with different chain-extending portions within the molecules.

Differential scanning calorimetry measurements were made on samples of both materials using a Mettler Thermal Analyser. Values obtained for the glass transition temperatures, T_g , were found to be 185 ± 3 °C for Stypol R1067/32 and 191 ± 5 °C for Stypol R1067/26. Values of approximately 150 °C were obtained for the T_g s using a Polymer Laboratory dynamic mechanical thermal analyser (DMTA). The differences between the DSC and DMTA results have not been explained, but it is important to note that both methods give values well above the maximum temperature of 70 °C used in the moisture absorption experiments.

*1 bar = 10^5 Pa.

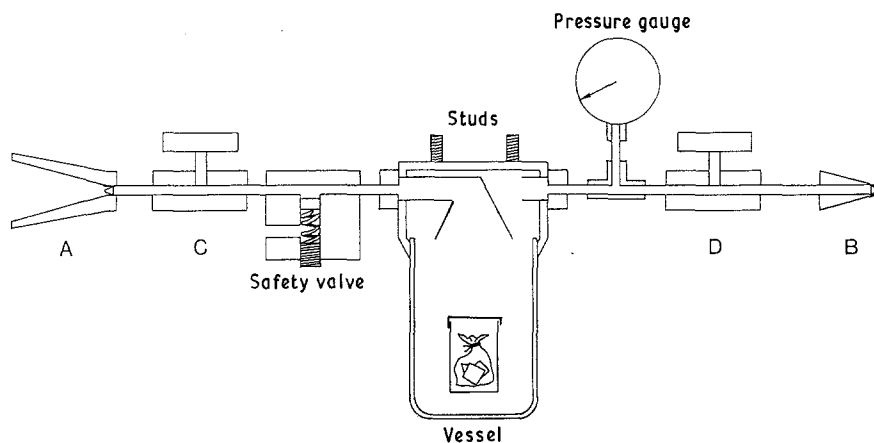


Figure 1 Pressure vessel and plumbing.

3. Experimental procedure

For each material a total of 48 specimens were used, each having approximate dimensions $25 \times 25 \times 3.5 \text{ mm}^3$. The samples were initially dried in a desiccator containing silica gel crystals at room temperature, and when they showed no significant further weight loss, the weights of all the samples were recorded. Weighings were made on an Oertling NA 114 electronic balance with a sensitivity of $2 \times 10^{-4} \text{ g}$.

Three samples of each material were subjected to each of the different environments employed. The weight of every sample was monitored by weighing at regular intervals.

Fairey Arlon filter casings, rated at 414 bar, were used for the twelve high-pressure vessels. The high-pressure plumbing associated with each vessel is shown in Fig. 1. Three vessels were maintained at 5°C by immersion in a cold-water bath, the temperature being maintained using a cooler unit, a temperature-controlled heater and a circulator. Two sets of three vessels were maintained at 40 and 70°C , respectively, by employing made-to-measure heating bands with suitable temperature controllers. Each pressure vessel was provided with a small pressure gauge to monitor any changes in pressure, but a separate, more accurate, gauge was used to ensure that the correct pressures were obtained initially.

4. Results

4.1. Temperature effects

Figs 2 to 5 display the variations of moisture absorption for both materials as functions of the square root of time and of the temperature at pressures of 1 and 75 bar. The curves are essentially Fickian for temperatures at or below 40°C . It is clear that the diffusivity, as determined by the initial slope, increases with temperature, and it is generally larger for Stypol R1067/26 than for Stypol R1067/32. The deduced values of the diffusivity are listed in Table I for all the environments studied. Corrections were applied to take account of edge effects [10].

The samples held at 40°C reached saturation after approximately 35 d immersion for Stypol R1067/26, at a level of $\approx 1.7\%$ moisture content, and after approximately 25 d for Stypol R1067/32, at a level of $\approx 0.85\%$ moisture content. Samples held at the lower temperatures 5 and 25°C were approaching the 40°C saturation level after 100 d.

The results for the two sets of specimens held at 70°C indicated pronounced interaction between the polymers and water. For Stypol R1067/32, a saturation level of approximately 0.95% moisture content was reached after 9 d immersion, but then the specimens began to lose weight owing to decomposition of their surfaces. After 25 d immersion, the

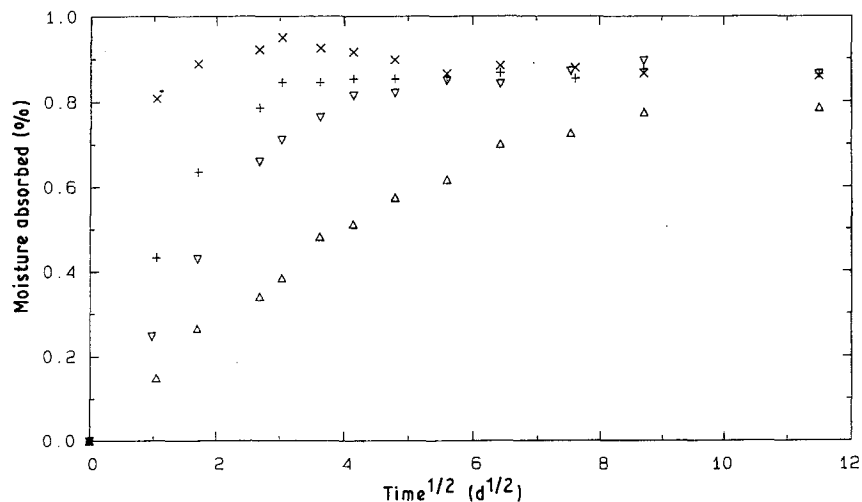


Figure 2 Stypol R1067/32. Variation of moisture absorption with square root of time at a pressure of 1 bar at (Δ) 5°C , (∇) 25°C , (+) 40°C and (\times) 70°C .

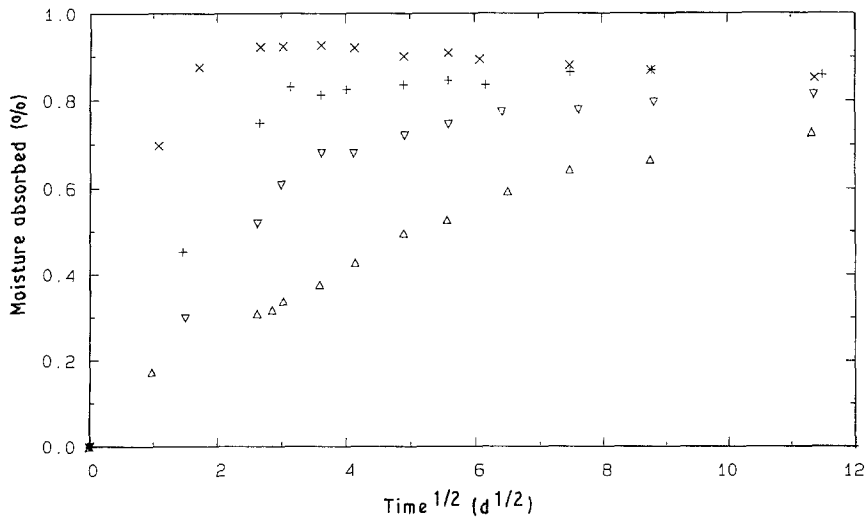


Figure 3 Stypol R1067/32. Variation of moisture absorption with square root of time at a pressure of 75 bar at (Δ) 5°C, (∇) 25°C, (+) 40°C and (\times) 70°C.

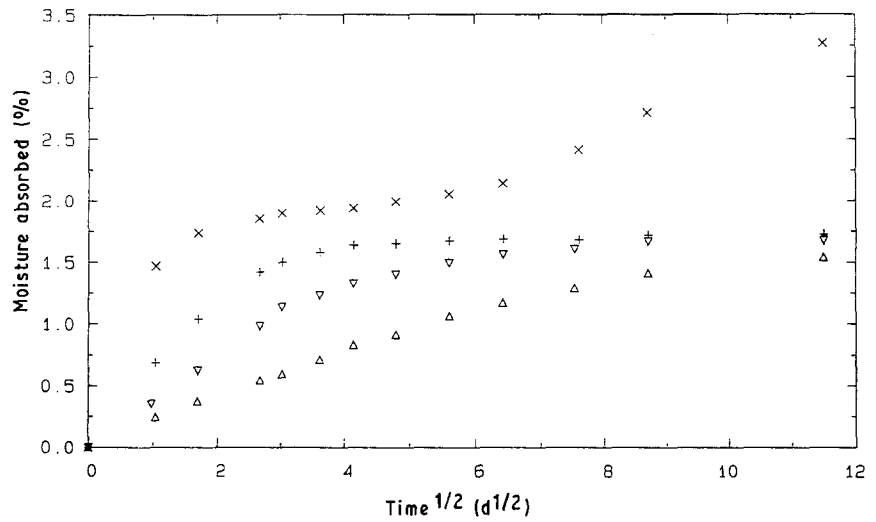


Figure 4 Stypol R1067/26. Variation of moisture absorption with square root of time at a pressure of 1 bar at (Δ) 5°C, (∇) 25°C, (+) 40°C and (\times) 70°C.

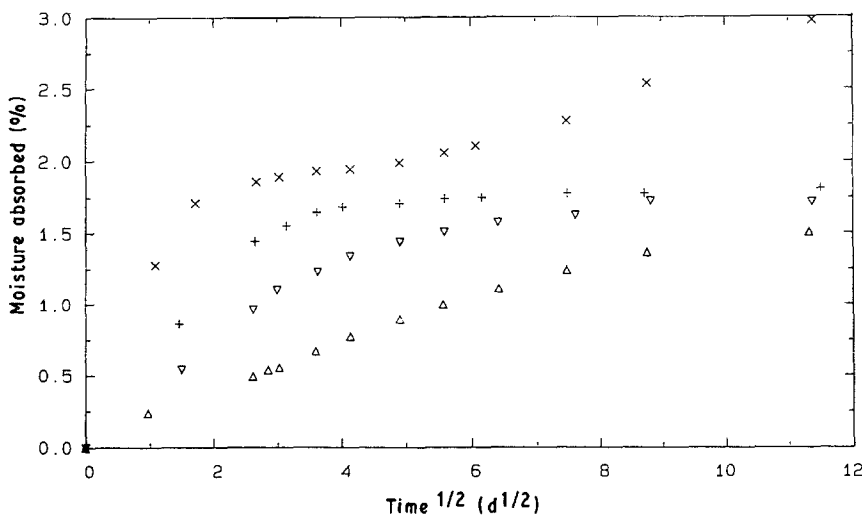


Figure 5 Stypol R1067/26. Variation of moisture absorption with square root of time at a pressure of 75 bar at (Δ) 5°C, (∇) 25°C, (+) 40°C and (\times) 70°C.

weight of the specimens remained constant at a level of $\approx 0.85\%$ moisture content, essentially the saturation level of the samples held at 40°C. In the case of the Stypol R1067/26 specimens, an initial saturation plateau at $\approx 1.7\%$ moisture content was reached after approximately 9 days immersion. However, after approximately 20 days, the weight of the samples began to increase relatively quickly, reaching a value of

$\approx 3.0\%$ moisture content after 100 d, and it was still rising.

4.2. Pressure effects

The effects on the moisture absorption of different hydrostatic pressures at constant temperature are illustrated in Figs 6 to 9. It can be seen that, in general,

TABLE I Diffusivity data. Diffusivities $\times 10^{12} \text{ m}^2 \text{ sec}^{-1}$

Material	P (bar)	Diffusivity ($10^{-12} \text{ m}^2 \text{ sec}^{-1}$) at			
		5°C	25°C	40°C	70°C
Stypol R1067/32	1	0.32 ± 0.05	1.3 ± 0.3	3.5 ± 0.6	10 ± 1
	25	0.27 ± 0.05	1.0 ± 0.2	3.3 ± 0.6	10 ± 2
	50	0.30 ± 0.05	0.9 ± 0.2	3.1 ± 0.5	7 ± 1
	75	0.28 ± 0.05	1.1 ± 0.2	2.5 ± 0.4	8 ± 1
Stypol R1067/26	1	0.19 ± 0.02	0.64 ± 0.65	1.9 ± 0.1	7.3 ± 0.7
	25	0.20 ± 0.02	0.66 ± 0.07	1.7 ± 0.1	5.7 ± 0.5
	50	0.21 ± 0.02	0.63 ± 0.06	1.6 ± 0.1	6.3 ± 0.5
	75	0.15 ± 0.01	0.48 ± 0.04	1.5 ± 0.1	4.7 ± 0.6

increased pressure has little effect on the absorption compared to atmospheric pressure, except in the case of Stypol R1067/32 specimens at 5°C where, as can be seen from Fig. 6, the absorption at elevated pressures is significantly lower than at atmospheric pressure, and almost independent of pressure between 25 and 75 bar.

5. Discussion

The moisture saturation levels of the two materials, $\approx 0.85\%$ for Stypol R1067/32 and $\approx 1.7\%$ for Stypol

R1067/26, appear to be independent of temperature between 5 and 40°C. The decrease in weight of Stypol R1067/32 after 9 d immersion at 70°C is because of local disintegration of the surface of the polymer. This behaviour at 70°C is consistent with other reported work [11, 12]. As can be seen from Fig. 7, increased hydrostatic pressure had no effect on the surface disintegration.

In contrast, the specimen of Stypol R1067/26 at 70°C did not show signs of surface blistering. However, the second stage increase in moisture up-take, after an apparent initial saturation, is assumed to

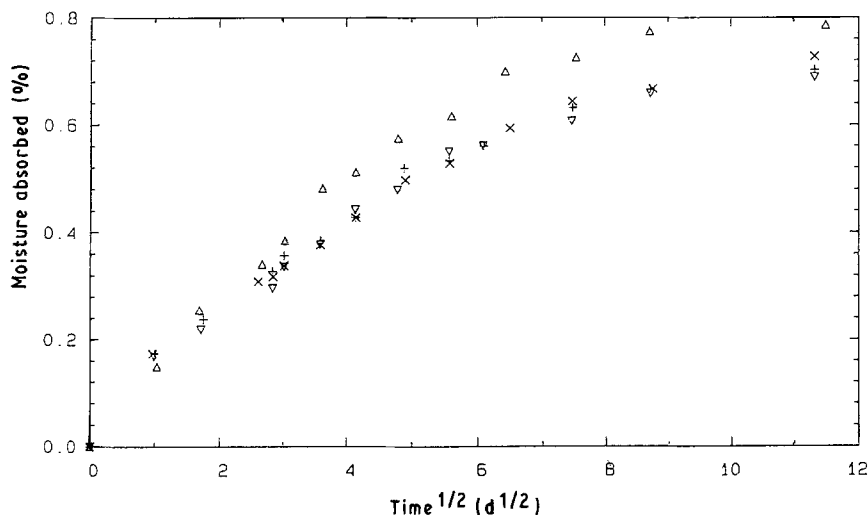


Figure 6 Stypol R1067/32. Variation of moisture absorption with square root of time at a temperature of 5°C at (Δ) 1 bar, (∇) 25 bar, (+) 50 bar and (\times) 75 bar.

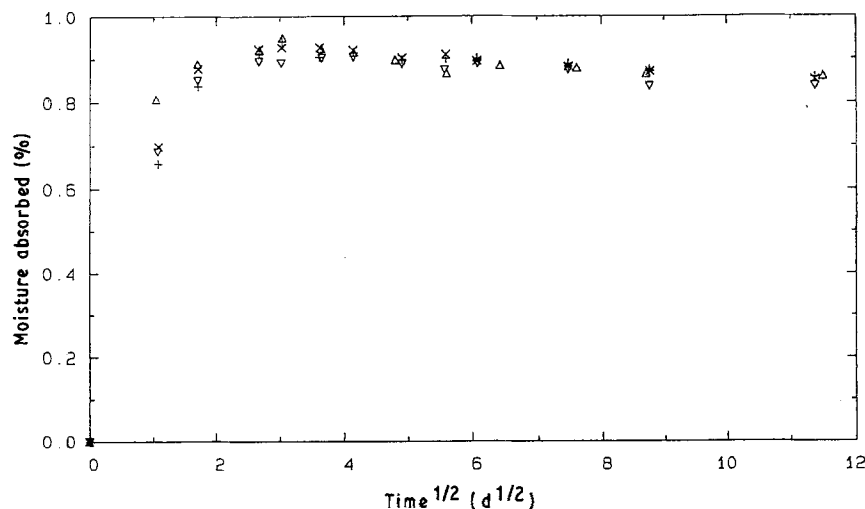


Figure 7 Stypol R1067/32. Variation of moisture absorption with square root of time at a temperature of 70°C at (Δ) 1 bar, (∇) 25 bar, (+) 50 bar and (\times) 75 bar.

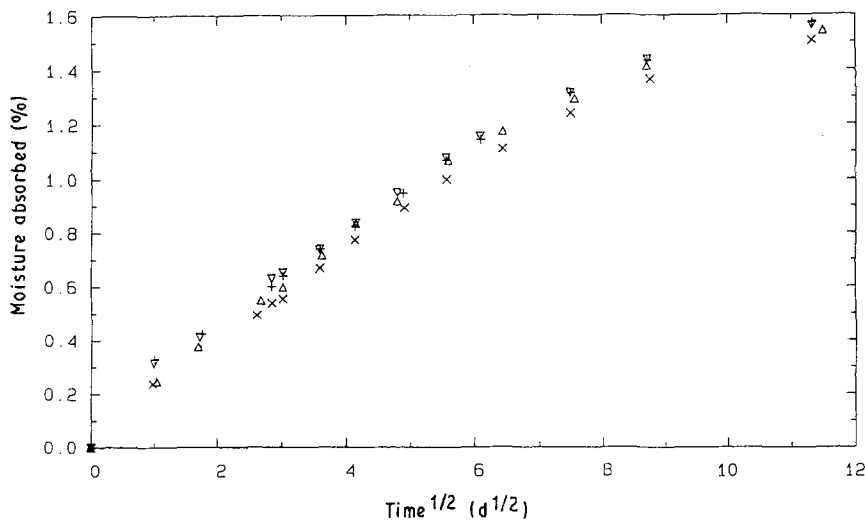


Figure 8 Stypol R1067/26. Variation of moisture absorption with square root of time at a temperature of 5°C at (Δ) 1 bar, (∇) 25 bar, (+) 50 bar and (×) 75 bar.

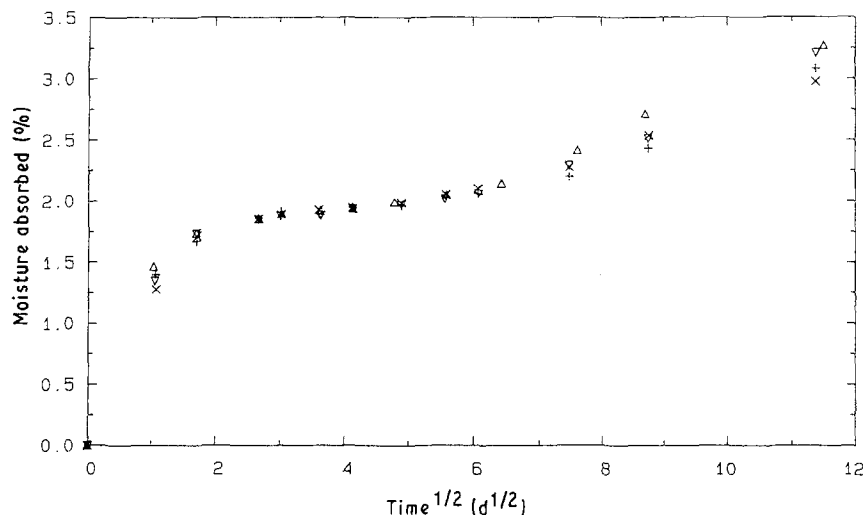


Figure 9 Stypol R1067/26. Variation of moisture absorption with square root of time at a temperature of 70°C at (Δ) 1 bar, (∇) 25 bar, (+) 50 bar and (×) 75 bar.

result from hydrolysis of the polymer. It would have been interesting to have followed the absorption for a longer time, but this was not possible.

It was found that the diffusivities, D , at constant pressure increased with increasing temperature, and the results were well represented by the Arrhenius expression

$$D = D_0 \exp(-Q/T) \quad (1)$$

with the parameters D_0 and Q given in Table II. The errors indicated in the table were deduced from a least squares fit of $\ln D$ against T^{-1} . It is interesting to note

TABLE II Parameters D_0 and Q in the Arrhenius expressions representing the diffusivities

Material	Pressure (bar)	$D_0(10^{-5} \text{ m}^2 \text{ sec}^{-1})$	Q (K)
Stypol R1067/32	1	3 ± 2	5100 ± 400
	25	8 ± 1	5400 ± 400
	50	9 ± 2	4800 ± 500
	75	2 ± 1	4900 ± 200
Stypol R1067/26	1	6 ± 4	5400 ± 200
	25	1.2 ± 0.6	5000 ± 100
	50	1.5 ± 0.6	5000 ± 100
	75	2 ± 2	5200 ± 300

that the diffusivity of Stypol R1067/32 is higher than that of Stypol R1067/26, although the saturation moisture concentration in Stypol R1067/32 is lower than in Stypol R1067/26.

The effects of hydrostatic pressure on the diffusivity were found to be much smaller than those of temperature. The variations of the diffusivities with pressure are displayed in Figs 10 and 11. The large uncertainties at 70°C arise because it was not practicable to take more than one measurement of weight during the first day. From Figs 10 and 11, a decrease in diffusivity with increasing pressure can be seen at 40 and 70°C. The behaviour is less clearly seen at the two lower temperatures.

A theory of the effects of stress, σ , on the diffusion of water in resins was proposed by Fahmy and Hurt [13]. By considering changes in the free volume, it was shown that the diffusivity, D , depends on stress, σ , as

$$D(\sigma) = D(0) \left(1 + \frac{C\sigma}{G} \right) \quad (2)$$

where G is the shear modulus of the resin, and C is a parameter. For epoxy resins, Fahmy and Hurt found that $6 \leq C \leq 10$, and assuming that similar values are appropriate for polyesters, with $G = 3 \times 10^9$ Pa it is estimated that $C\sigma/G \approx 0.05$ at 75 bar. It should be noted that σ is negative for compressive stresses, and

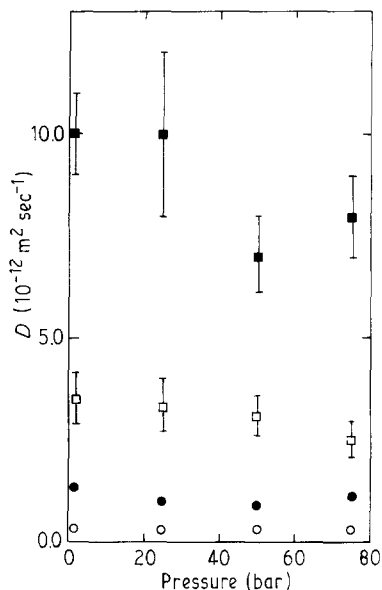


Figure 10 Stypol R1067/32. Variation of diffusivity with pressure at (○) 5°C, (●) 25°C, (□) 40°C and (■) 70°C.

hence Equation 2 predicts that D decreases linearly with increasing hydrostatic pressure.

The results displayed in Figs 10 and 11 suggest that the pressure dependence of D is greater at higher temperatures. The variations of C/G with temperature deduced from the present data are displayed in Fig. 12. The dependence of C/G on temperature is approximately linear for both materials, and mechanical measurements suggest that this can be attributed almost completely to changes in modulus G with temperature. For example, for Stypol R1067/32 the modulus decreases by a factor 1.9 when the temperature is increased from 0 to 80°C while C/G changes by a factor 2.2.

The pressure dependence of the diffusivities could also be considered in terms of the parameters D_0 and Q in Equation 1, but it can be seen from the values presented in Table II that there are no systematic trends in either D_0 or Q for either material.

There does not appear to be any simple description of the dependence of the diffusivity on temperature and pressure. The discussion above suggests that an

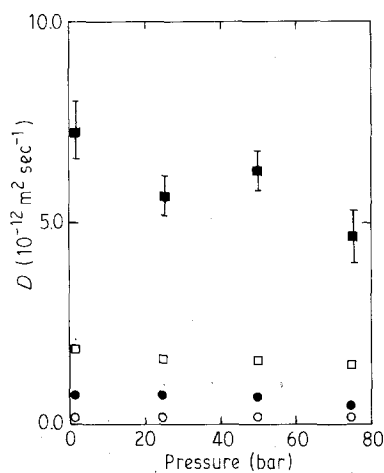


Figure 11 Stypol R1067/26. Variation of diffusivity with pressure at (○) 5°C, (●) 25°C, (□) 40°C and (■) 70°C.

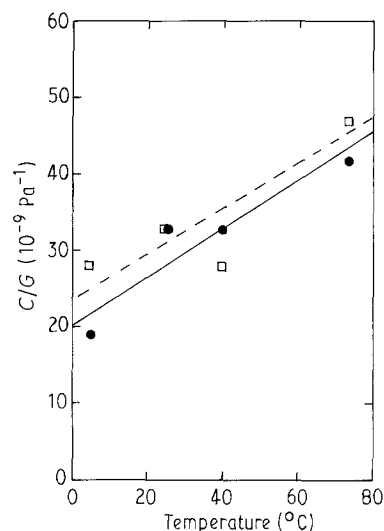


Figure 12 Variation of C/G with temperature. (●, —) Stypol R1067/32; (□, ---) Stypol R1067/26.

empirical relationship of the form

$$D(T, \sigma) = D_0(\sigma) \exp[-Q(\sigma)/T] \times \{1 + [A + B(T - 273)] \sigma\} \quad (3)$$

may be useful, where parameters A and B are used to fit the variation of C/G with temperature. The values of $D_0(\sigma)$ and $Q(\sigma)$ are as given in Table II. For Stypol R1067/32, the results displayed in Fig. 12 indicate that $A \approx 20.3 \times 10^{-9} \text{ Pa}^{-1}$ and $B \approx 0.575 \times 10^{-9} \text{ Pa}^{-1} \text{ K}^{-1}$.

The diffusivities discussed above were derived from the initial slopes of the moisture absorption curves. The effects of pressure on the moisture saturation level appear to be very small, except possibly for the case of Stypol R1067/32 at 5°C. The results for the latter are displayed in Fig. 6 and, although saturation was not reached, it can be seen that the absorption at 1 bar is significantly higher than at 25, 50 or 75 bar.

6. Conclusions

The experiments on Stypol R1067/32 and Stypol R1067/26 at temperatures at or below 40°C indicated that the saturation moisture level was independent of temperature. At 70°C, Stypol R1067/32 developed blistering, while Stypol R1067/26 showed marked hydrolysis, but no blistering, after 100 days.

It was found that the effects of temperature on the diffusivities of both materials could be well described by Arrhenius expressions.

Hydrostatic pressure was found to have no effect on the saturation moisture levels, except for Stypol R1067/32 at 5°C. The diffusivities were found to decrease slightly with increasing pressure, the effect being largest at higher temperatures, consistent with theories based on changes in the free volumes of the polymers.

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