

Non-Fickian diffusion of water in melamine–formaldehyde resins

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Integral absorption of bulk water in melamine–formaldehyde (1:2 mole ratio) resins has been studied. Diffusion is non-Fickian but can be quantitatively described by an equation incorporating a stress relaxation rate factor. This stress relaxation is irreversible and leads to structural degradation of the thermoset resin. The activation energy for diffusion of bulk water in the unfilled polymer is $143 \pm 8 \text{ kJ mol}^{-1}$ and $59 \pm 4 \text{ kJ mol}^{-1}$ in a cellulose-filled polymer (68% resin). The cellulose filler does not significantly alter the flexural properties of the resin nor does it prevent stress crazing, but it does reduce gross structural deterioration. A sharp 'advancing front' moving with $(\text{time})^{1/2}$ has been observed. When two such fronts meet in the centre of the sample, the diffusion mechanism is altered.

Keywords: Diffusion of water; melamine–formaldehyde resins; melamine resins; stress relaxation; cellulose filler; non-Fickian diffusion

INTRODUCTION

The diffusion of water in polymers has been the subject of numerous studies^{1,2}. It is of considerable practical importance in view of the environmental and packaging demands on polymers. Crosslinked melamine–formaldehyde resins are widely used in adhesives, moulding compounds, decorative laminates and (when suitably modified) in coatings. These resins, containing unreacted amino and methylol groups, might be expected to be hydrophilic, but the detailed interaction of water with the system has not been clarified. The structure of the resins themselves eludes direct analysis although many approaches have been made, for example by n.m.r. analysis of simple oligomeric resins^{3,4}.

This paper presents data for the diffusion of bulk water into crosslinked melamine–formaldehyde resins. Both the unfilled resin, and the more commercially important cellulose-filled resin, have been studied.

THEORY

Fick's first and second laws of diffusion (1855) adequately describe most diffusion processes. Their application to specific geometries has been worked out⁵. The present study requires equations which describe diffusion into a planar sheet of thickness l . For integral sorption at short times, the main result is

$$F = 4(Dt/l^2)^{1/2}/\pi^{1/2} \quad (1)$$

Here F is the fractional uptake, M_t/M_∞ , where M_t is the amount of diffusant sorbed at time t and M_∞ is the maximum amount absorbed. D is the diffusion coefficient. When D is constant, a plot of F versus $t^{1/2}$ is linear with slope σ_1 from which D can be found. When $F=0.5$, an average diffusion coefficient \bar{D} can be calculated from one time only, $t=t_{1/2}$, with

$$\bar{D} = 0.049l^2/t_{1/2} \quad (2)$$

Equation (2) has been used to discuss the diffusion of bulk water in polystyrene in a series of experiments similar to those reported here⁶. The diffusion of small molecules in polymeric systems is well understood in terms of free-volume theory⁷.

F is indeed found to be linear with $t^{1/2}$ ($t \leq t_{1/2}$) for most diffusion systems and for even higher t when D varies with concentration.

However, it is not unusual to observe that F is non-linear with $t^{1/2}$ and, typically, the absorption is initially slow but increases with time. This non-Fickian behaviour is often found for diffusion into glassy polymers below their T_g ⁵.

In the present work, such anomalous diffusion was the rule and an explanation was sought. Non-Fickian effects were studied by Crank⁸ who proposed a time-dependent diffusion coefficient. He considered two processes occurring in the glassy polymer—a rapid diffusion associated with instantaneous molecular rearrangements, and a much slower one associated with time-dependent relaxation towards an equilibrium value of the diffusant concentration. This analysis by Crank was advanced by later work of Long and Richman⁹, based on their detailed experimental observation of the surface concentration of diffusant in glassy polymers. This was found to be initially small but to increase with time (for the diffusion of methyl iodide into cellulose acetate, for example). Therefore they argued that diffusion was a two-stage process (with single, constant D) in which there was initial diffusion due to an instantaneously attained surface concentration and a slower process due to changing surface concentration. An equation which expressed the relationships between these concentrations was given as

$$C_s = C_0 + (C_e - C_0)(1 - e^{-\beta t}) \quad (3)$$

where C_s is the surface concentration, C_0 the initial value, and C_e the equilibrium value. β was a constant which Long and Richman tentatively related to the rate of stress

relaxation of the polymer structure. Using equation (3) Long and Richman derived an equation which gave an expression for integral absorption (their equation (3), ref. 8). This equation calculated both the sigmoidal and the 'two-step' absorption curves of F versus $t^{1/2}$ observed experimentally (the shape depends on the ratio of D/l^2 to β) and it was this equation which was used in the present work. It was found that variation of the initial surface concentration had little effect on the calculated results and it could be assumed that $C_0 \approx 0$. The integral adsorption equation then simplified to

$$F = 1 - 2e^{-\beta t} A^{1/2} \tan(4A)^{-1/2} - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp[-D(2n+1)^2 \pi^2 t/l]}{(2n+1)^2 [1 - (2n+1)^2 A \pi^2]} \quad (4)$$

where $A = D/\beta l^2$. The only two parameters in equation (4) (M_∞ and l being known) are D and β , which can then be varied to give a calculated F to compare with the experimental F .

As a diffusant penetrates a glassy polymer causing stress relaxation, the phenomenon of a distinct 'advancing boundary' is often observed¹⁰. This is a sharp division between the swollen, relaxed region, and the dry rigid region of the polymer. A recent paper by Shankar¹¹ has provided a theoretical analysis of this situation. Shankar makes the interesting observation that a plot of $\ln(1-F)$ against time will be linear but will show a distinct break in slope as is indeed found experimentally in both Fickian and non-Fickian diffusion. The break in slope is related to the time when the two advancing boundaries meet in the centre of the polymer. From the slope of the line after the break, σ_2 , the diffusion constant can be calculated

$$\sigma_2 = -D\pi^2/4l^2 \quad (5)$$

The D calculated from this analysis is that for diffusion in the swollen polymer and is two to three times the D calculated using equation (1). Shankar does not discuss anomalous diffusion.

Another model explaining anomalous moisture diffusion by a Langmuir-type adsorption has been suggested¹². This model assumes water diffusing in both a mobile and strongly bound phase. This model has not been followed here because the present results indicate there is very little water in a mobile phase (see below).

EXPERIMENTAL

Technique

Integral absorption of water was followed by measuring water uptake with time for various samples. Pogany⁶ describes the simple method—the sample was removed at time t from the constant-temperature water bath, quenched in ice-water, dried and rapidly, accurately, weighed before re-immersion. Total water uptake versus $\log t$ and F versus $t^{1/2}$ were then plotted.

In the one experiment where the absorption of water vapour rather than bulk water was studied, a Cahn magnetic balance was used and the sample was kept at constant temperature and humidity.

Micrographs were taken *via* optical and electron microscopy, and mechanical analyses were carried out on a DuPont 981 Dynamic Mechanical Analyser¹³ and an Instron.

Materials

The basic resin was made by a slight variation of the standard procedure¹⁴. One mole of melamine was reacted with 2 moles of formaldehyde (as 37% formalin methanol-stabilized) at 90°C, after adjusting the pH of the solution to 9.0 with 0.1 M NaOH, and adding 1% total weight of triethanolamine as a buffer. Reaction was allowed to proceed for about 60 min, or until 1 ml of solution became cloudy when diluted with 4–5 ml cold water.

The cooled syrup (~50% solids) was stable for 1 or 2 days, and was used for impregnating α -cellulose paper. The resin could also be vacuum dried, or spray dried, to give a water-soluble powder. A commercially available melamine-formaldehyde moulding resin from American Cyanamid Company, Cymel 405, could also be dissolved in water to form impregnating syrups.

Composites, usually of five sheets of paper, were formed by pre-curing treated sheets at 120°C for 10 min, and then fully curing them under pressure for 15 min at 130–175°C. The amount of resin (%) was calculated after pre-cure as

$$\frac{(\text{wt resin} + \text{paper}) - (\text{wt paper})}{(\text{wt resin} + \text{paper})} \times 100$$

A sample of Cymel 405 powder was pre-cured at 150°C for 20–40 min (until a 4–5 wt % loss was measured) and then ground to a fine powder. Compression moulding of this powder at 175°C gave a clear, very brittle polymeric glass. Most of this absorption work was carried out on glasses cured for 3 min. These were subsequently found (by dynamic mechanical analysis, d.m.a.) to be under-cured. The effect of cure time on the properties of these resins has been studied by Wohnsiedler *et al.*¹⁵

All samples were pre-conditions by drying at 50°C for 24 h, followed by cooling and storing in a desiccator for 2 days. This was taken to give a 'dry' polymer. It was found that after 3 months in the desiccator pre-conditioned cellulose-filled thermosets lost $\leq 1\%$ by weight, while the unfilled polymer lost $\sim 0.3\%$ and a network of internal cracks developed. The residual water was not considered important in the present work where the sample is being immersed in bulk water.

RESULTS

Filled thermoset resins are complex materials and there are several variables which could affect the diffusion of water in these systems. Four of the more important factors have been varied here—cure temperature, resin content, sample thickness and water temperature. These variables were examined using the series of samples detailed in Table 1.

All samples showed non-linear F versus $t^{1/2}$ plots. Figure 1 gives the results for samples E-1, 2. The full curves were computed from equation (4) and show a reasonable fit to the experimental points.

At 100°C in bulk water, leaching was evident in the samples as a decrease in weight after the maximum (M_∞) had been reached. (Time for weight to reach 99.9% of M_∞ is $13.7t_{1/2}$.¹⁶) The extent of this weight loss was $\sim 7\%$ for sample A-3 after 24 h in boiling water. Analysis by i.r. and h.p.l.c. of the extract showed this was similar to the initial, uncured resin, which implies that the boiling water is extracting unreacted resin, or perhaps even hydrolysing

Table 1 Total water uptake and $t_{1/2}$ values for prepared samples

Sample	Resin (%)	Thickness (cm)	Cure temp. (°C)	Water temp. (°C)	$t_{1/2}$ (min)	M_{∞} (%)
A-1	68	0.013	130	78	12.4	9.97
A-2	68	0.031	130	78	60.3	6.83
A-3	68	0.048	130	78	71.7	6.44
1st repeat	68	0.050	130	78	16.1	7.46
2nd repeat	68	0.050	130	78	16.8	7.46
A-4	68	0.074	130	78	129	5.20
B-1	68	0.050	130	100	18.4	6.45
B-2	68	0.050	130	78	87.1	6.98
B-3	68	0.051	130	50	558	6.65
B-4	68	0.050	130	24	3151	5.40
C-1	69	0.092	150	78	123	5.09
C-2	57	0.043	150	78	18.9	14.2
C-3	48	0.038	150	78	3.1	24.3
C-4	30	0.035	150	78	0.83	48.5
D-1 (A-3)	68	0.048	130	78	71.7	6.44
D-2	68	0.045	150	78	85.5	4.83
D-3	68	0.046	174	78	70.3	4.30
E-1	100	0.195	175*	100	150	7.78
E-2	100	0.195	175*	78	3000	8.14
E-3	100	0.078	175*	60	4326	5.06

* 3 min cure

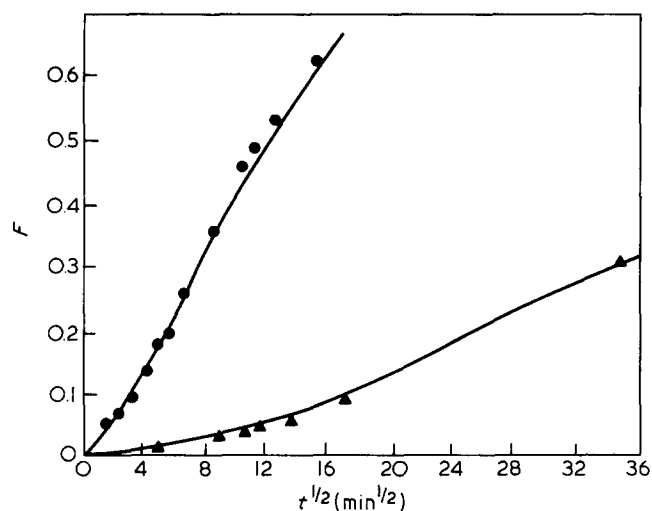


Figure 1 Fractional uptake vs $t^{1/2}$ for samples E-1 (●) and E-2 (▲) in water at 100° and 78°C respectively. Curves calculated using equation (4) with $D_1 = 1.97 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $\beta_1 = 7.5 \times 10^{-6} \text{ s}^{-1}$, and $D_2 = 1.15 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $\beta_2 = 1.62 \times 10^{-7} \text{ s}^{-1}$

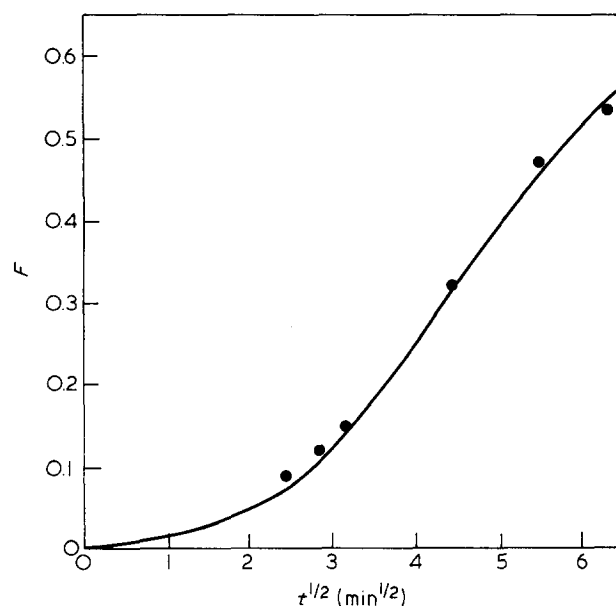


Figure 2 Fractional uptake vs $t^{1/2}$ for sample A-3 in 69% RH at 97°C. Curve calculated using $D = 1.08 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $\beta = 1.32 \times 10^{-8} \text{ s}^{-1}$

some of the crosslinking bonds. Leaching at 78°C was less severe (0–2% after 24 h) and most comparative measurements were made at this temperature. That leaching itself does not lead to non-Fickian diffusion is seen by the absorption of sample A-3 in 69% RH water vapour at 97°C—Figure 2 shows the usual non-linear curve. For this sample $M_{\infty} = 4.50\%$ and $t_{1/2} = 34 \text{ min}$.

Table 1 gives $t_{1/2}$ and M_{∞} results for the samples. Results were reproducible considering the many variables which had to be adjusted.

In an attempt to define the role of water in the system, differential scanning calorimetry (d.s.c.) measurements were run on filled and unfilled samples after 3 h in boiling water (when the amount of water absorbed is > 5%). The temperature scan was -40° to $+20^\circ \text{C}$. Water, if present in the system as 'free' or mobile water, will show a distinct and quantitative melting endotherm. This was confirmed

by running a series of water and water plus glass-fibre test samples. For all melamine resin samples (some containing 7–10% water), only extremely small endotherms were observed, indicating that most of the water taken up by the sample is strongly affected by the molecular framework. Similar, more comprehensive, experiments have been carried out recently on water absorbed in cellulose acetate membranes. Even 15 wt % water gave no melting endotherm in this material¹⁷.

DISCUSSION

The two main results of the present work are (a) the observed non-Fickian diffusion can be quantitatively and adequately explained in terms of stress relaxation; (b) the

Table 2 Diffusion coefficients vs. temperature for filled and unfilled samples

Sample	Temp. (°C)	D (10^{-10} cm 2 s $^{-1}$)	β (10^{-10} s $^{-1}$)	\bar{D} (equation (2)) (10^{-10} cm 2 s $^{-1}$)
E-1	100	1970	75000	2180
E-2	78	115	1617	94
E-3	60	5	31.7	11.5
B-1	100	1167	1170	1110
B-2	78	433	54	234
B-3	50	38	1.75	38
B-4	24	7.1	3.08	6.5

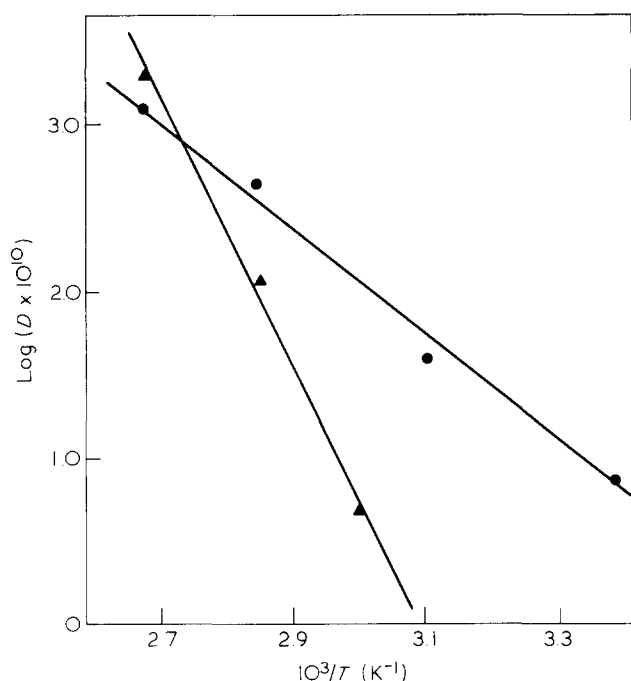


Figure 3 Arrhenius plot for filled (●) and unfilled (▲) polymer

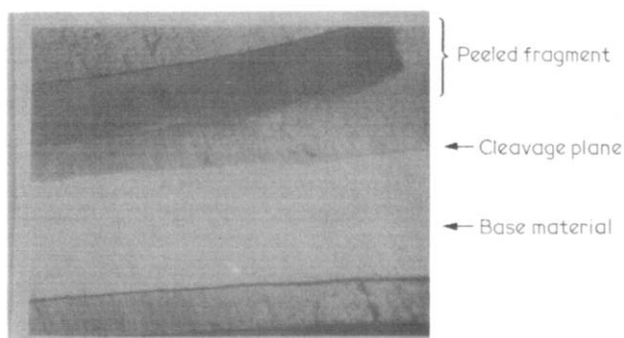


Figure 4 Surface of unfilled glass showing cleavage plane after 4 h diffusion of water at 100°C. Thickness of fragment = 0.55 mm

role of cellulose in the water absorption process is clarified.

The diffusion mechanism

The ability of equation (4) quantitatively to describe the observed anomalous water uptake is a strong indication of the correctness of Long and Richman's analysis. One diffusion coefficient is required which remains constant for the main diffusional process. It was found that this D was close to the value obtained from the simple formula using $t_{1/2}$ (equation (2)); see Table 2. Equation (2) is a

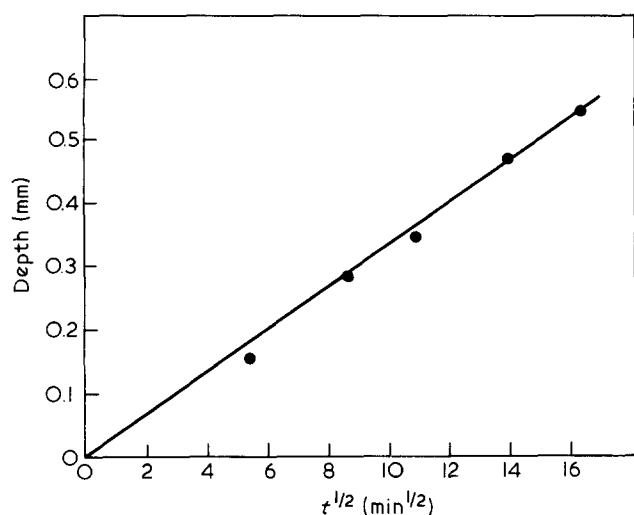
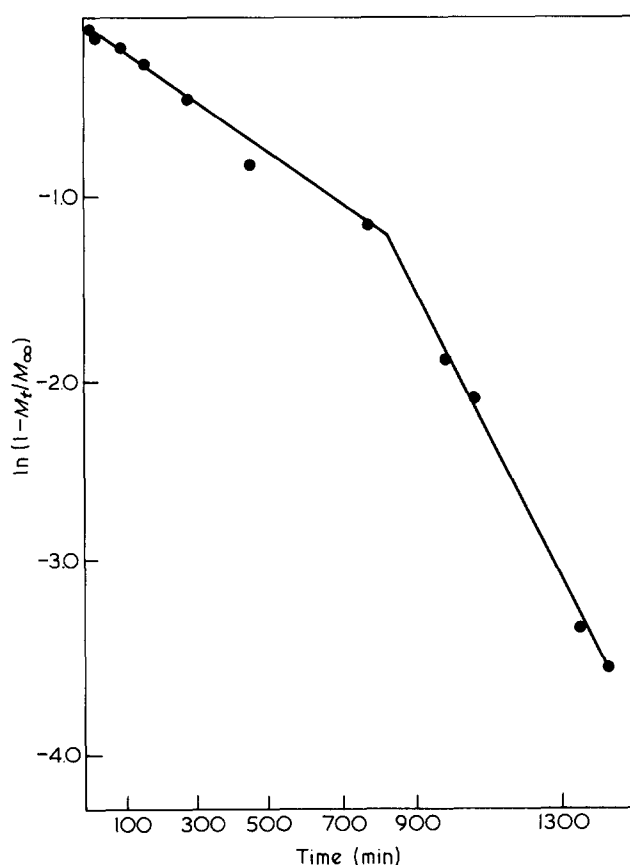
useful means of calculating an approximate average diffusion coefficient \bar{D} .

It would be unjustified to attach much quantitative significance to the β parameter without further experimental work on its relation to the rate of stress relaxation. However, it does seem to be larger by an order of magnitude in the unfilled as against the filled polymer. That diffusion of water is an activated process is expected (see Figure 3), with $E_a = 143 \pm 8$ kJ mol $^{-1}$ for the unfilled polymer, 59 ± 4 kJ mol $^{-1}$ for the filled polymer.

A sharp boundary front between the water-containing and dry polymer was clearly observed in the unfilled polymer during the early stages of diffusion. It was found that when samples E-1, 2, 3 were removed from the water bath and allowed to dry, gross surface fracturing resulted. A similar effect has been noted for novolac phenolic resins¹⁸.

To quantify the effect, the depth of water penetration with time for the glassy polymer was measured by the following experiment. Squares 2 cm \times 2 cm of the glassy sheet were coated sides and edges with silicone rubber and dried for 24 h at 50°C. They were then immersed in boiling water for various times up to 4 h, and then the diffused water was rapidly desorbed by drying at 50°C. The surfaces fractured. The samples were carefully embedded in polyester resin, sectioned, and the degree of penetration measured microscopically. Figure 4 shows the fragment broken off the main structure. It is remarkably uniform in thickness, showing that the strain is biaxial and cleavage is thus planar. This made measurement of the cleavage distance straightforward. This distance was linear with $t^{1/2}$ (Figure 5), which agrees with diffusion theory and is good evidence that Long and Richman's assumption of a single D is correct. (The average penetration of molecules is given¹⁹ by $(2Dt)^{1/2}$.) The slope is 4.55×10^{-4} cm s $^{-1/2}$, which means the advancing fronts meet after 12.7 h in sample E-1 ($l/2 = 0.0975$ cm). Time to equilibrium is 23.3 h. Samples dried out after reaching equilibrium show face-to-face cracking but no surface fracturing. If Shankar's analysis is correct, when the two diffusing fronts meet, there will be a change in the diffusion mechanism as shown by a break in the slope of $\ln(1-F)$ versus time. This plot is shown for a sample of the unfilled glass (Figure 6) in water at 95°C ($l/2 = 0.075$ cm). The time to the break in the slope is 13.8 h, in good agreement with the predicted value when the effects of different sample and lower temperature are taken into consideration. For this sample, D from equation (5) is 16.5×10^{-8} cm 2 s $^{-1}$, about three times \bar{D} from equation (2), 4.84×10^{-8} cm 2 s $^{-1}$, showing that diffusion in the fully swollen relaxed polymer is faster than when the diffusion is associated with stress relaxation.

It has been seen from the d.s.c. work that the absorbed water appears tightly associated with the molecular


 Figure 5 Depth of cleavage plane vs $t^{1/2}$ for sample E-1

 Figure 6 Plot of $\ln(1 - F)$ vs time for a sample of unfilled polymer in water at 95°C

structure. Dimensional changes with water uptake have not at present been studied in detail but thickness swell was of the order of 5–10% at equilibrium water uptake, but area changes were very small ($\sim 0.25\%$). What seems to be happening is as follows. According to Wohnsiedler's early paper²⁰, the number of crosslinking bonds in these resins is relatively small (one per 20–30 monomer units) and hydrogen bonding is an important factor in the structure. When the samples are cured, stress is built-in by the compression moulding process—under crossed polars, the glassy polymer shows a fine network of stress variations. However, diffusing water molecules block the

intramolecular bonding sites (by bonding to those sites themselves), thus decreasing the network of hydrogen bonds holding the structure together. The stresses relax irreversibly, and diffusion is non-Fickian. When the temperature is high, the rate of stress relaxation is also high (Table 2) and the structure is elastic enough to accommodate the diffusing water. The sample E-1 did not craze when immersed in water at 100°C. When the temperature is low, the structure is much more rigid and cannot adjust to the diffusing water. A sample of the glassy polymer in water at room temperature absorbed up to 0.75% of its weight over 30 days, at which time it developed large internal cracks and eventually it shattered into small fragments. It is the discontinuity between relaxed and stressed regions of the sample at low diffusion times which creates the biaxial forces and degrades the structure.

This model also explains why degree of cure seems to have only a marginal effect on the diffusion coefficient. Table 1 gives absorption data for filled polymer, samples D-1, 2, 3 for which ($\bar{D} \times 10^8$) is 2.62, 2.20 and 2.46 $\text{cm}^2 \text{s}^{-1}$ respectively. Table 3 gives values for unfilled glass. Although a greater degree of cure reduces M_∞ , \bar{D} is not greatly different between low and high cure. This agrees with Wohnsiedler's results¹⁵ on water absorption in these polymers. Surface crazing is much less obvious with more highly cured polymers and is best observed with a microscope. As cure advances, more crosslinked bonds are formed (Wohnsiedler has shown that the heat deflection temperature rises with degree of cure) and stress relaxation will be less pronounced, but the number of crosslinks will have a negligible effect on the porosity of the molecular framework for small water molecules.

The role of cellulose

Cellulose is the traditional, commercially important, filler for melamine-formaldehyde polymers. The present results give some indication of the role that cellulose plays in water absorption. Figure 3 is important—water diffuses into cellulose-filled polymer with considerably lower activation energy than into the unfilled polymer. The M_∞ values are generally higher by a factor of 2 for the filled polymer than the (cured) unfilled—compare values in Tables 1 and 3. For lower resin contents (samples C-2, 3, 4), poor resin-cellulose interaction is found and M_∞ values increase rapidly. These samples were non-transparent due to the presence of air in the central lumen of the cellulose fibres²¹. Resin contents $\geq 68\%$ gave semi-transparent composites as the lumen was then filled with resin. The temperature of cure has only a slight effect on the diffusional mechanism, as discussed. Thickness of the specimen does have a more pronounced effect (samples A-1, 2, 3, 4), a reflection of non-Fickian diffusion mechanisms. Table 4 gives diffusional coefficients and β

Table 3 Average diffusion coefficients for unfilled polymer in water at 95°C

Cure time (min)	M_∞ (%)	$\bar{D} \times 10^8$ ($\text{cm}^2 \text{s}^{-1}$)
3	4.78	4.52
5	2.46	3.27
10	2.32	4.50
15	2.51	5.92

$l = 0.150$ cm, cured at 175°C

Table 4 Diffusion coefficients vs. composite thickness (water at 78°C)

Sample	l (cm)	$D \times 10^8$ (cm ² s ⁻¹)	$\beta \times 10^{10}$ (s ⁻¹)
A-1	0.013	1.33	4.0
A-2	0.031	1.50	23.8
A-3	0.048	2.17	500
A-4	0.074	3.33	683

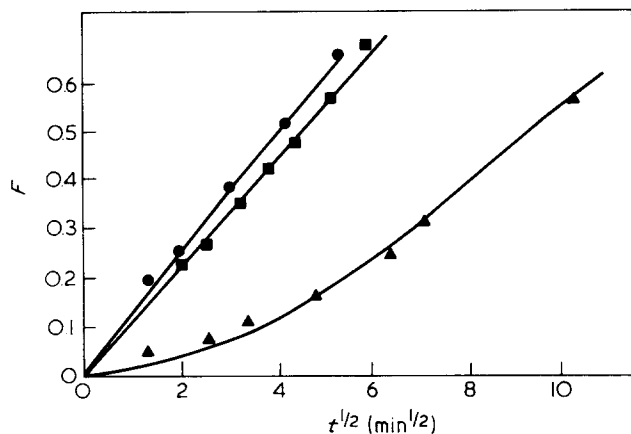


Figure 7 Fractional uptake for sample B-2 after recycling in water at 78°C: \blacktriangle , initial curve calculated using $D=4.33 \times 10^{-8}$ cm² s⁻¹ and $\beta=1.17 \times 10^{-8}$ s⁻¹; \bullet , first repeat, $D=12.7 \times 10^{-8}$ cm² s⁻¹ (equation (1)); \blacksquare , second repeat, reducing M_t values by 0.88%, $D=9.53 \times 10^{-8}$ cm² s⁻¹ (equation (1))

values for the samples, calculated from equation (4). The range of β values shows the importance of stress relaxation.

It has already been stated that the stress-relaxation causes gross degradation of unfilled (undercured) resin and microscopic crazing of more highly cured resins. Samples with $\geq 68\%$ resin should also show such crazing because the sample is largely glassy resin and impregnated cellulose. The formation of these crazes has been clearly demonstrated in recycling experiments. Samples of filled polymer (68% resin) were immersed for 16 h in water at 78°C, dried at 50°C and re-immersed once, twice or three times under the same conditions. (Such a recycling experiment could not be done with the glassy unfilled polymer because it fractured on drying.)

The water absorption curves are shown in Figure 7, from which it is obvious that one cycle only has been enough to alter the diffusion process. It has become Fickian. The diffusion coefficient, calculated from equation (1), is 12.7×10^{-8} cm² s⁻¹. This is three times the 4.33×10^{-8} cm² s⁻¹ from equation (4) in the initial, non-Fickian process. Once strains have been relaxed, diffusion can occur by normal (Fickian) processes. Although there was no visible physical change in the samples during recycling, cracks were observed under the microscope, notably along the resin-fibre interface. In the second re-immersion, 0.88% was deducted from each M_t to give a line through the origin. This factor is probably due to initial, rapid water uptake by immediate capillary filling of the cracks.

The cellulose fibres play the important role here of preventing fragmentation of the surface—the resin, though crazed, is held together by the fibre network. Similarly, studies of the mechanical wear of filled and

unfilled resins show the cellulose reinforcement distributes stresses and reduces gross fragmentation²².

To study this effect further, an isothermal d.m.a. experiment was carried out on D-2 samples, after one, two and three re-immersions in water at 78°C. The amplitude of vibration was increased and the damping factor $\tan \delta$ recorded. Any cracks in the system should increase the damping. The results are shown in Figure 8 where it is quite obvious that recycling increases the damage to the samples.

Further d.m.a. experiments were carried out at constant frequency over the temperature range 20°–300°C and showed that there was surprisingly little difference in modulus or damping curves between the filled and unfilled resins. The only noticeable difference was at higher temperatures when the unfilled had a slightly lower modulus, and lower blistering temperature (274°C) than the filled (288°C). Three hours in boiling water had very little effect on the modulus values, although significantly a complete run on the glass was not possible due to cracking. The modulus of the filled sample was slightly lower for $200 < T < T_g$ when wet, but redrying this sample returned the modulus curve to the initial values. Static measurements confirmed this result, and are given in Table 5.

Wohnsiedler also found similar results in his study of cure versus physical properties¹⁵. He attributed this constancy of modulus to the strength of secondary hydrogen bonds.

Returning finally to the main theme of bulk water diffusion, the cellulose does clearly increase the rate of

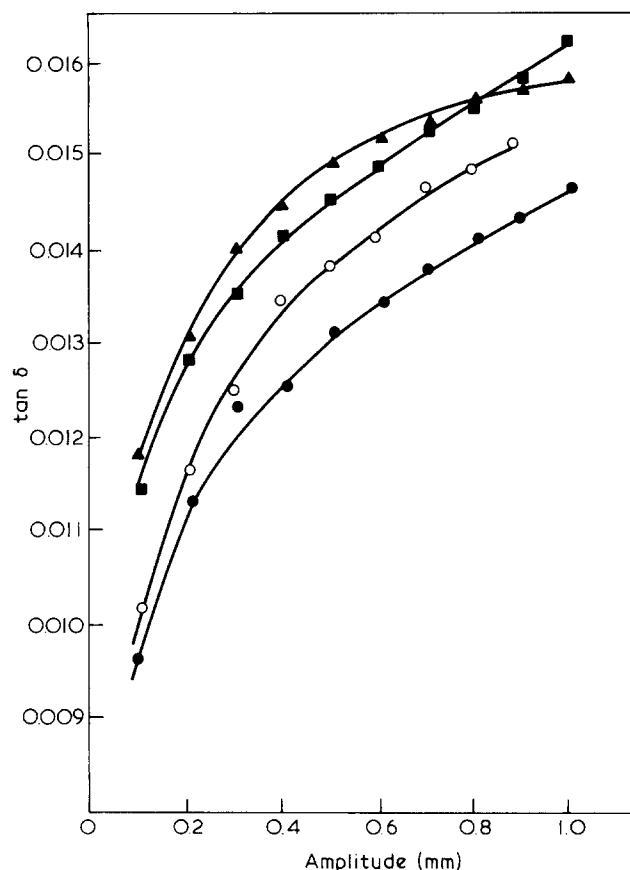


Figure 8 Loss factor ($\tan \delta$) against vibrational amplitude for samples of D-2 after 16 h in water at 78°C followed by 24 h drying at 50°C: \bullet , control; \circ , 1 immersion; \blacktriangle , 2 immersions; \blacksquare , 3 immersions

Table 5 Static flexural properties of filled and unfilled resin

Sample		Flexural modulus (GPa)	Stress (MPa)
E-1	dry	8.8	—
	wet	5.7	—
E-1 (15 min cure)	dry	8.6	166
	wet	8.8	189
A-3	dry	9.1	148
	wet	9.2	147
	redried	8.6	137

Note: dry, redried = 24 h at 50°C
wet = 3 h in water at 100°C

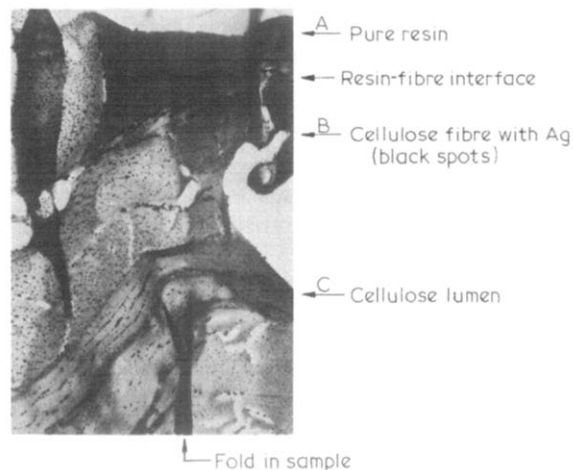


Figure 9 TEM ($\times 20000$) of AgNO_3 -stained filled sample. Region A, pure resin; B, cellulose fibre with deposited silver; C, fibre lumen

diffusion at room temperature (Figure 3). The cellulose fibres provide a 'path of least resistance' for the water molecules and the amount of water adsorbed is greater than for the unfilled polymer. This effect is clearly seen in Figure 9, a transmission electron micrograph of a filled sample after treatment with sodium bromide (2 h at 80°C) and then silver nitrate (2 h at 80°C). The black specks are areas of reduced silver, and are clearly associated with the cellulose fibre. Surprisingly little silver has penetrated the resin. The cellulose, although apparently well impregnated with resin, is still more porous than the bulk resin.

CONCLUSIONS

The above discussion can be summarized to give a fairly clear and consistent pattern. The main conclusion is that diffusion of bulk water into melamine-formaldehyde thermosets is non-Fickian because the diffusion causes irreversible stress relaxations and structural degradation.

In addition equation (4), using assumed single diffusion coefficients coupled with stress relaxation factors, calculates fractional uptake values in good agreement with experimental values. Cellulose filler in the resin has negligible effect on the flexural properties of the resin. Stress crazing is on a microscopic level but is localized along the resin-fibre interface. The sample retains its integrity and allows recycling of the sample between wet and dry conditions, with increasing damage to the structure. The cellulose provides a more porous route for diffusing water molecules.

Several factors in this complex system remain to be quantitatively defined. Accurate studies of dimensional changes, comparison of absorption at various humidities, and desorption experiments would all add to our understanding of these resins. Such studies are being actively pursued in these laboratories.

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