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# Diffusion of moisture into two-phase polymers

## Part 2 *Styrenated polyester resins*

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The moisture absorption and desorption behaviour of a styrenated isophthalic unsaturated polyester resin has been examined. This resin system is believed to have a two-phase structure comprising particles of the dense phase embedded in a less dense matrix. The model developed in Part 1, which describes the diffusion behaviour of a two-phase resin system, has been applied to this system and the diffusion coefficients for both the dense and less dense phases calculated. The diffusion coefficient of the dense phase is found to be 30 times lower than that of the less dense matrix. The volume fraction of the former was estimated at 0.16, which was lower than expected. It is postulated that the microgel particles have a dense core and become progressively less dense towards the periphery.

## 1. Introduction

Absorption and desorption of moisture by various resins and composites has been a subject of interest for a number of years. Several authors have investigated the diffusion characteristics of epoxy resins and their composites [1–9] and, to a lesser extent, polyester resins and their composites [10–12]. In the majority of cases it has been assumed that moisture absorption is a concentration-independent Fickian diffusion process [1–5, 10–12]. While this model may be applicable to the initial stages of the diffusion process in a wide range of resins and composites it often fails to describe the entire diffusion process.

Fujita [13] has observed that for true Fickian diffusion the absorption curve should exhibit the following features:

(i) The curve should be linear up to and exceeding 60% of the equilibrium moisture content ($M_\infty$).

(ii) Above the linear portion the sorption curve should be concave to the abscissa, irrespective of any dependence of the diffusion coefficient ($D_x$) on the moisture concentration.

(iii) When the initial and final moisture concentrations are fixed, a series of sorption curves for films of different thicknesses are superposable to a single curve if replotted as a reduced curve of $M(t)/M_\infty$ against (time)$^{1/2}$/thickness where $M(t)$ is the percentage moisture content as a function of time $t$.

For a concentration-independent diffusion coefficient, as suggested by Shen and Springer [1], reduced absorption and desorption curves should coincide.

In many cases it is assumed that if the experimental sorption curves are consistent with the criteria (i) and (ii) above then the system can be described using a Fickian approach. However, this convention should be applied with caution since sorption data may conform to these criteria but fail to satisfy criterion (iii).

It is often found that the final stages of moisture absorption deviate from Fickian behaviour. Some authors attempt to explain this by means of a Langmuir-type diffusion process [7–9], in which the absorbed water can be divided into mobile and strongly bound types. While this model may be applicable to some polymer systems, an additional factor which needs consideration is the presence of a disperse phase. In the previous paper [14] a simple model which describes the diffusion behaviour of a two-phase resin system was developed. In the present paper this approach is applied to an isophthalic unsaturated polyester resin system which is believed to have a two-phase structure [15–18].

## 2. Experimental procedure

Crystic 272 (Scott-Bader & Co. Ltd, Northampton, UK), an isophthalic unsaturated polyester resin, was cured with 2 parts per hundred of resin (phr) and of a 50% methyl ethyl ketone peroxide solution (Catalyst M, Scott-Bader & Co. Ltd) and 0.45 phr of a cobalt naphthenate solution (Accelerator E, Scott-Bader & Co. Ltd). This formulation has a gelation time of 6 to 12 h depending on ambient temperature, and no exotherm is observed. This slow-gelling formulation enables reproducible void-free castings to be produced.

Resin specimens suitable for accurate absorption and desorption measurements were prepared by casting the activated resin between two vertical glass plates separated by a gasket of PVC tubing coated with industrial mould wax. The glass plates were lined with Melinex release film in order to prevent the resin adhering to the glass. Cast resin plates of approximately 5 mm thickness were produced using this technique. Specimens 20 mm × 80 mm were cut from the plates using a water-cooled diamond saw and then all the faces of the specimen were polished to a better than 1 μm finish using cerium oxide.

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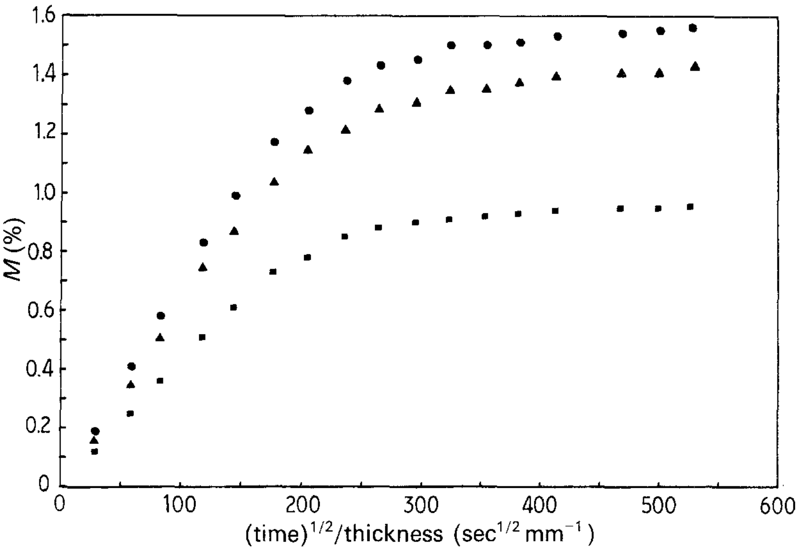

*Figure 1* Moisture absorption $M(t)$ against (time)$^{1/2}$/thickness at 50° C: (●) immersion, (▲) 96% r.h., (■) 75% r.h.

After cutting and polishing, all the specimens were post-cured in an air-circulating oven at 130° C for 1.5 h. This procedure resulted in a fully post-cured resin [17]. On cooling from the post-curing temperature the specimens were placed in a vacuum oven and dried to a constant weight, at 50° C. This procedure is necessary to ensure that the specimens are completely dry prior to testing.

Dry specimens were exposed to relative humidities of 96 and 75 r.h., and some were immersed in distilled water. The relative humidities were created by the use of saturated solutions of $K_2SO_4$ (96% r.h. at 50° C) and NaCl (75% r.h. at 50° C), and the temperature was maintained by placing the humidity chambers in an air circulating oven at $50 \pm 1°$ C. The specimens were periodically weighed in order to monitor the absorption of moisture by the specimen with time. Once the specimens reached equilibrium moisture content they were then transferred to a vacuum oven where they were dried under vacuum at 50° C. The desorption process was again monitored by periodic weighing of the specimens.

The thicknesses of the specimens when dry and at equilibrium moisture content were measured and the maximum amount of swelling due to moisture uptake was found to be less than 0.5%.

## 3. Results and discussion

Shen and Springer [1] have developed expressions for the diffusion of moisture in fibre-reinforced composite materials, which are based on the similarities between heat conduction and moisture diffusion in composite materials. Adopting this approach, expressions for the diffusion of moisture in an isotropic two-phase system have been developed in the previous paper [14]. In that paper the validity of the model was demonstrated using a thermoplastic elastomer. In this paper the model is applied to an isophthalic unsaturated polyester resin system which exhibits the type of absorption curve that has been associated with a two-phase structure.

The absorption curves for the resin, in the form of percentage moisture content as a function of time, $M(t)$, plotted against (time)$^{1/2}$/thickness for each of the relative humidities, or immersion, to which they had been exposed are shown in Fig. 1.

The absorption curves for the resin specimens immersed in water and exposed to relative humidities of 96 and 75% r.h. show the two regions indicative of the two-phase structure of the resin (Fig. 2). They also clearly show the influence of relative humidity on the equilibrium moisture content of the specimens ($M_\infty$). It has been noted that an important factor in

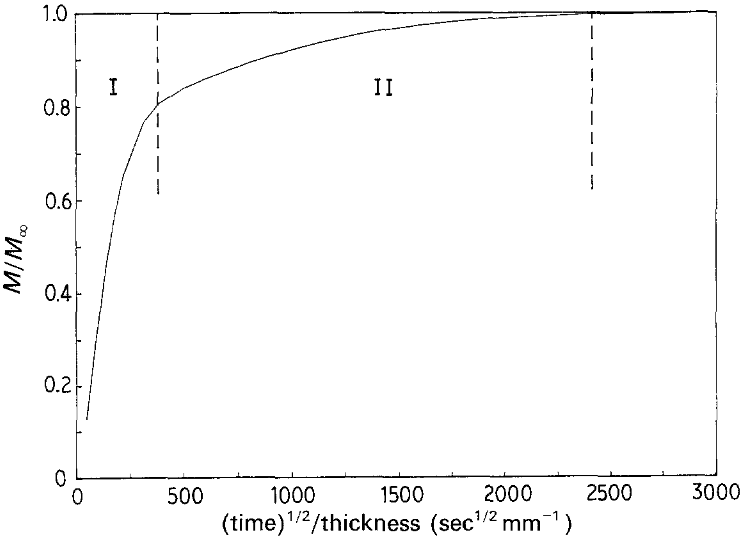

*Figure 2* Schematic absorption curve for a two-phase resin system showing absorption into both the dense and less dense phases (Region I) and the dense phase alone (Region II).

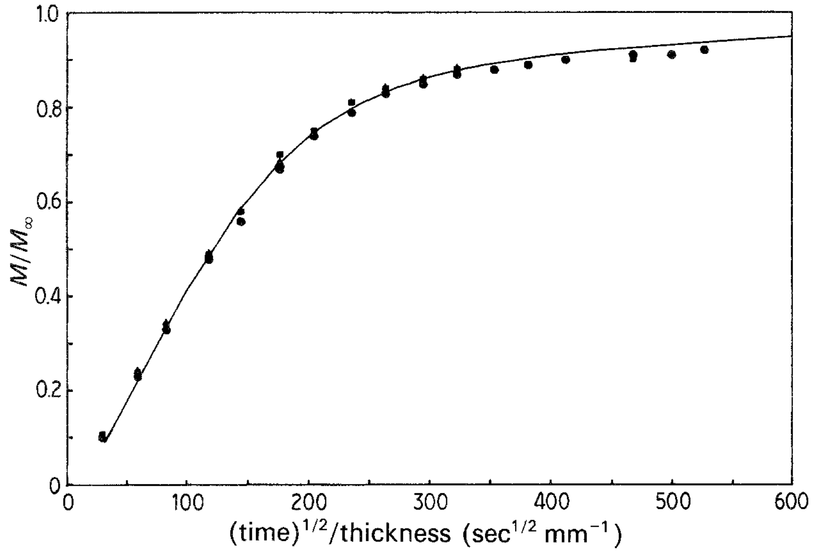

*Figure 3* Comparison of the theoretical and experimental moisture absorption curves. The theoretical curve was calculated from the data given in Table I. (●) Immersion, (▲) 96% r.h., (■) 75% r.h.

determining the ultimate concentration of absorbed moisture by a resin, or composite, is the relative humidity of the environment.

From these curves the diffusion coefficients of the dense and less dense phases of the resin ($D_d$ and $D_l$, respectively) and the resin as a whole ($D_x$) can be calculated from the equations

$$D_x = \pi\left(\frac{m_x h}{4M_\infty}\right)^2 \tag{1}$$

$$D_d = \pi\left(\frac{m_d h}{4(M_\infty - M_l)}\right)^2 \tag{2}$$

and

$$D_l = \pi\left(\frac{(m_x - m_d)h}{4M_l}\right)^2 \tag{3}$$

where $M_\infty$ = equilibrium moisture content of the resin, $M(t)$ = equilibrium moisture content of the less dense phase, $m_x$ = slope of $M(t)$ against (time)$^{1/2}$/thickness in Region I (Fig. 2), $m_d$ = slope of $M(t)$ against (time)$^{1/2}$/thickness in Region II (Fig. 2), and $h$ = thickness of specimen.

The "edge effect" correction calculated by Shen and Springer [1] must then be applied in order that the true diffusion coefficients may be determined (Table I); this states

$$D_a = D(1 + h/l + h/n)^{-2} \tag{4}$$

where $l$ = length, $n$ = width and $D$ = diffusion coefficient (either $D_x$, $D_d$ or $D_l$).

In a number of cases [19–21], specimens exposed to high humidities and temperatures exhibited non-Fickian absorption behaviour with increasing water uptake after reaching an apparent $M_\infty$. This has been found to be the result of regions of microstructural damage usually in the form of microcracks, into which bulk water penetration is possible. In the specimens used in this investigation no visible deterioration was observed using optical microscopy, even in the specimens which were immersed in water for periods in excess of 80 days. Any suggestion that a microstructural degradation mechanism could be operating in Region II of the absorption curves is, therefore, highly unlikely. In addition there was no evidence of leaching during immersion in water since all the specimens returned to their original weights, within experimental error (as shown in Fig. 4 below), on desorption.

Theoretical absorption curves were calculated using the equation derived in a previous paper [14]:

$$M(t) = V_d\left\{1 - \exp\left[-7.3\left(\frac{D_d t}{h^2}\right)^{0.75}\right]\right\} + (1 - V_d)\left\{1 - \exp\left[-7.3\left(\frac{D_l t}{h^2}\right)^{0.75}\right]\right\} \tag{5}$$

The values of $D_x$, $D_d$ and $D_l$ obtained from Equations 1, 2 and 3, using experimental values of $m_x$ and $m_d$, were not sufficiently accurate for detailed analysis. However, these values of $D_x$, $D_d$ and $D_l$ can be used for an iterative computation using Equation 5 in order to obtain more self-consistent values, and these are shown in Table I. The relationship given in Equation 5 also involves the volume fraction of the dense phase ($V_d$) and this value of $V_d$, also shown in Table I, is unique for any given values of $D_x$, $D_d$ and $D_l$ and must, therefore, be considered to be a material property. It is not possible to vary $V_d$ independently of $D_x$, $D_d$ and $D_l$ and so the theoretical curve in Fig. 3 will only fit the experimental data under a well-defined set of conditions. It is also noted that no correction factor was necessary for the samples exposed to different relative humidities, and this demonstrates that in this system the diffusion is independent of concentration.

The volume fraction of the dense phase calculated from Equation 6 below ($V_d$ = 0.16) is lower than

TABLE I Moisture diffusion coefficients from absorption ($D$) and desorption ($D'$) data for fully cured crystic 272 polyester resins exposed to different environments at 50° C (the subscripts x, d, l refer to resin, dense and less dense phases, respectively)

| Variable | Environment | | |
|---|---|---|---|
| | 75% r.h. | 96% r.h. | Immersion |
| $D_x$ ($10^{-5}$ mm$^2$ sec$^{-1}$) | 8 | 8 | 8 |
| $D_d$ ($10^{-5}$ mm$^2$ sec$^{-1}$) | 0.6 | 0.6 | 0.6 |
| $D_l$ ($10^{-5}$ mm$^2$ sec$^{-1}$) | 10 | 10 | 10 |
| $V_d$ | 0.16 | 0.16 | 0.16 |
| $D_x'$ ($10^{-5}$ mm$^2$ sec$^{-1}$) | 8 | 8 | 8 |

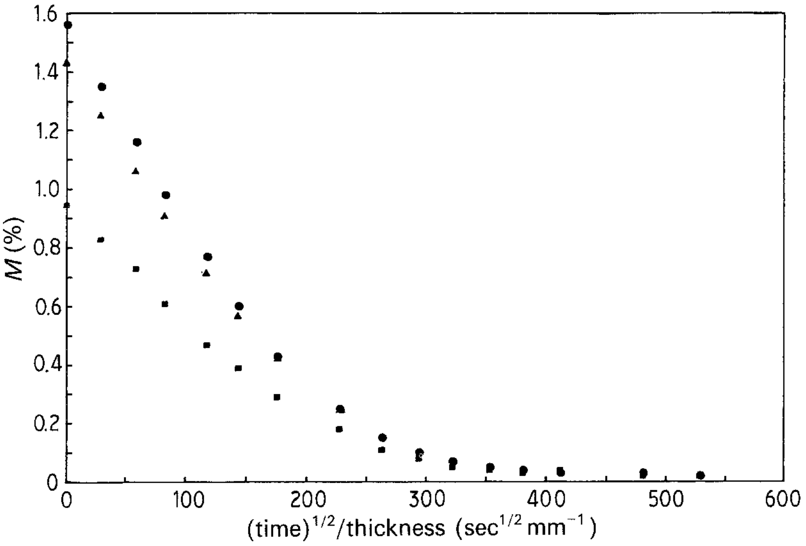

*Figure 4* Moisture desorption $M(t)$ against (time)$^{1/2}$/thickness at 50° C under vacuum, for samples previously exposed to (●) immersion, (▲) 96% r.h., (■) 75% r.h.

would be predicted from the work of Bergmann and Demmler [16]. These authors suggest a structure of dense phase microgel particles, of 50 nm radius, separated by 5 nm of less dense material. If we assume that these microgel particles are arranged in a cubic array then $V_d$ for the system is 0.45. However, in such an analysis it is assumed that the dense phase is in the form of discrete particles of uniform density, which is unlikely for this system. The probability is that the microgel particles have a dense core, but become progressively less dense towards the periphery of the particles. This implies that there is a variation in diffusivity across the particles, which may explain why $V_d$ is lower than expected. In the present case

$$V_d = \frac{(B_D + 2)[(D_x/D_l) - 1]}{(B_D - 1)[2 + (D_x/D_l)]} \quad (6)$$

where

$$B_D = \frac{D_d}{D_l} \quad (7)$$

The desorption curves for these specimens given in Fig. 4 are also of interest. According to Fujita [13], the reduced absorption and desorption curves should coincide when the diffusion is independent of moisture concentration. A comparison of the diffusion coefficients, calculated from the two-phase model, reveals that the absorption and desorption curves are identical (Table I). The desorption curves would, therefore, tend to confirm the existence of a heterogeneous microstructure in these resins. Further evidence for the two-phase structure of the free-radical-cured polyester resins has been provided by chemical degradation [15], pulsed and broad-line NMR spectroscopy [16] and thermomechanical measurements [17] and from scanning microscopy [22]. From these various studies, a microstructure consisting of microgel particles embedded in a less densely cross-linked phase has been proposed. This is entirely consistent with both the absorption and desorption data obtained for these resins. The rate at which moisture absorbs into, or desorbs from, the resin is controlled by the diffusion characteristics of the less dense phase of the material, as this is the continuous phase. Were the dense phase of the material to be the continuous phase a completely different moisture profile would be observed.

In this paper we have shown that anomalous moisture absorption curves can also be explained by the presence of a dispersed phase of differing diffusion coefficient and that care must be taken when interpreting data of this type. While moisture absorption data alone are insufficient to confirm this hypothesis, absorption data in conjunction with desorption data suggest a two-phase structure of the type proposed by Bergmann and Demmler [16].

## 4. Conclusions

From the results of this study it is evident that the isophthalic unsaturated polyester resin system Crystic 272 has a two-phase structure. The diffusion coefficients of both the dense and less dense phases, as well as the material as a whole, can be calculated from the absorption curves. Using the mathematical relationships which have been developed it is possible to calculate the volume fraction of the dense phase of the material from a knowledge of these diffusion coefficients. The diffusion coefficient for the resin, calculated from the desorption data, appears to be dominated by the desorption of moisture from the less dense phase. This suggests that the two-phase structure is comprised of particles of the dense phase embedded in the less dense phase.

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