

## MODELLING THE PROCESS OF ABSORPTION AND DESORPTION OF WATER BY COATINGS MADE OF EPOXY RESIN

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**Abstract**—The behaviour of coatings made of epoxy resin when in contact with water at 80° is studied. The process of water absorption is controlled by transient diffusion with a constant diffusivity, and 4% of water is absorbed at equilibrium. The drying process of the pre-saturated resin is controlled by transient diffusion through the resin and evaporation from the surface. At the end of the drying at 80°, c 16% of the initial water remains in the resin. If after drying the resin is immersed a second time in water, at 80° a higher rate of absorption with a higher diffusivity is observed. Mathematical models, with analytical expressions as well as mathematical models, are successfully tested for the processes of absorption and desorption.

### NOMENCLATURE

- $C$  = concentration of water in the resin at time  $t$  and position  $x$ ,  
 $C_{eq}$  = concentration of water in the resin after infinite time,  
 $C_o$  = concentration of water on the surface of the coating;  
 $C_{ext}$  = concentration of water on the surface, at equilibrium with the surrounding atmosphere;  
 $D$  = diffusivity of water in the coating,  
 $\Delta t$  = finite increment in time,  
 $\Delta x$  = slice thickness of space,  
 $F_o$  = rate of evaporation of pure water,  
 $l$  = half-thickness of the coating,  
 $M_t$  = total amount of water which has entered the resin at time  $t$ ,  
 $M_\infty$  = total amount of water after infinite time,  
 $M, N$  = dimensionless numbers,  
 $\rho$  = density of water.

### INTRODUCTION

Epoxy resins are often used for high performance coatings, as well as for the polymeric matrix in composites. Many studies have been made on the compositions of these epoxy resins, and on the process of cure. Because of the low thermal conductivity of the resin associated with the high exothermicity of the process of cure, the reaction gives rise to high temperature within the resin. These facts are of concern for thick samples, being responsible for discolouration or degradation of the final material, cracking or crazing or even distortion of the moulding [1-4].

The cure of the resin deposited as a coating is also difficult to achieve, because it is not easy to heat the resin. The problem is how to achieve the cure of the resin coating at room temperature, or at a temperature c 50°, and to know the time required to obtain

a good result. As the properties of the final material largely depend on the state of cure, various models have been built to describe the process by taking into account the heat conduction and the heat evolved by the reaction [5-8]. Another model has been constructed and tested for the cure of coatings made of epoxy resin, performed at low temperature, and it could predict the state of cure in terms of the parameters such as the temperature and time. A mechanical property such as hardness has been chosen to follow the cure, and correlations were obtained between this property and the state of cure [9].

The purpose of this paper is to study the matter transfer taking place between an epoxy resin coating and water kept at 80°, when they are in contact. The subsequent process of desorption of the water which has entered the resin is also examined, by considering various conditions of drying. The process of absorption is assumed to be controlled by transient diffusion, while the process of desorption is explained by diffusion of the water through the solid and evaporation on the surface.

### EXPERIMENTAL PROCEDURES

#### Material

The material was obtained by mixing the epoxy resin (Lopox 200—CDF Chimie, Orkem), and the hardener (D 2605—CDF Chimie, Orkem) containing an anhydride of Me THP and an accelerator with 0.75% of an aromatic amine (type 1, 195—CDF Chimie). The binary mixture was prepared at room temperature with continuous stirring. The composition in weight percent was, following previous work [10], epoxy resin (56%) and hardener (44%).

#### State of cure of the resin

The kinetics of cure are followed by calorimetry (DSC 111—Setaram) heating at a constant rate of 5°C/min from room temperature up to the end of reaction. The kinetic parameters are determined by using the Freeman and Caroll

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technique, by assuming that the cure reaction follows an Arrhenius equation.

#### Preparation of the coating

The resin mixture is deposited on steel sheets, the epoxy coating having an average thickness of 1 mm. After curing for 44 hr, part of the coating is studied by calorimetry, showing that the extent of cure reaches 90% at this time.

#### Matter transfer studies

The resin coating is removed from the steel plate and then immersed in water at constant temperature. The kinetics of absorption are followed by weighing the resin coating at intervals. When equilibrium is reached for the absorption of water, the resin coating is dried in air under various conditions:

- (i) at 20° up to equilibrium, followed by drying at 80° and 100%;
- (ii) at 80°.

### THEORETICAL

The following assumptions are made:

- (i) the thickness of the coating remains constant during absorption and desorption, as the amount of water absorbed is very small;
- (ii) the process of absorption is controlled by transient diffusion through the thickness of the coating, with a constant diffusivity as obtained from experiment;
- (iii) the process of desorption is controlled by transient diffusion of water through the solid and evaporation from the surface;
- (iv) the rate of evaporation is proportional to the difference between the actual concentration of water on the resin surface and the concentration of water on the surface which is at equilibrium with the vapour pressure of water in the surrounding atmosphere, the coefficient of proportionality being the rate of evaporation of pure water under the same conditions;
- (v) during absorption, the concentration of water on the coating surface reaches equilibrium as soon as the coating is immersed in water.

#### Mathematical treatment

**Absorption.** The one-dimensional diffusion in the medium of thickness  $2l$  is expressed by Fick's law with constant diffusivity:

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where  $C$  is the concentration of water in the resin at time  $t$  and position  $x$ .

The initial and boundary conditions are:

$$t = 0 \quad -l < x < l \quad C = 0 \quad (2)$$

$$t > 0 \quad x = \pm l \quad C = C_{eq} \quad (3)$$

The solution of equation (1) with these conditions is [11]:

$$\frac{C_{eq} - C_{xt}}{C_{eq}} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \frac{(2n+1)\pi x}{2l} \cdot \exp\left[-\frac{(2n+1)^2\pi^2}{4l^2} Dt\right] \quad (4)$$

where  $C_{xt}$  is the concentration of water in the resin at time  $t$  and position  $x$ , and  $C_{eq}$  is the concentration in the resin after infinite time.

The kinetics of absorption are obtained by integrating the concentration with respect to space within the resin:

$$\frac{M_{\infty} - M_t}{M_{\infty}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\left(-\frac{(2n+1)^2\pi^2}{4l^2} Dt\right) \quad (5)$$

where  $M_t$  is the total amount of water which has entered the resin at time  $t$ , and  $M_{\infty}$  is the corresponding amount after infinite time.

#### Desorption

A uniform concentration of water through the resin is obtained when the equilibrium absorption is attained. The rate of loss of water by evaporation from the surface is expressed by:

$$-D \cdot \frac{\partial C}{\partial x} = F_o(C_s - C_{ext}) \quad (6)$$

where  $F_o$  is the rate of evaporation of pure water under the same conditions,  $C_s$  is the actual concentration of water on the surface, and  $C_{ext}$  is the concentration on the surface which is at equilibrium with the surrounding atmosphere. The gradient of concentration is calculated on the surface. Under these conditions, the solution is:

$$\frac{C_{eq} - C_{xt}}{C_{eq} - C_{in}} = \sum_{n=1}^{\infty} \frac{2L \cos(\beta_n x/l)}{(\beta_n^2 + L^2 + L) \cdot \cos \beta_n} \cdot \exp\left(-\frac{\beta_n^2}{l^2} Dt\right) \quad (7)$$

where the  $\beta_n$ s are the positive roots of

$$\beta \cdot \tan \beta = L \quad (8)$$

and  $L$  is a dimensionless number:

$$L = \frac{l \cdot F_o}{D} \quad (9)$$

The total amount of water  $M_t$  leaving the sheet up to time  $t$  is expressed as a fraction of  $M_{\infty}$ , the corresponding quantity after infinite time, by:

$$\frac{M_{\infty} - M_t}{M_{\infty}} = \sum_{n=1}^{\infty} \frac{2L^2}{\beta_n^2(\beta_n^2 + L^2 + L)} \exp\left(-\frac{\beta_n^2}{l^2} Dt\right) \quad (10)$$

#### Numerical model

A numerical model with finite differences is helpful when the initial concentration of water in the coating is not uniform, and when the diffusivity is concentration-dependent.

As shown in Fig. 1, the thickness of the coating is divided into equal slices of thickness  $\Delta x$ . The balance of the water entering and leaving the slice at position  $n$  during the increment of time  $\Delta t$  enables one to express the new concentration  $CN_n$  after the elapse of time  $\Delta t$  in terms of the previous concentration:

$$CN_n = \frac{1}{M} [C_{n-1} + (M-2) \cdot C_n + C_{n+1}] \quad (11)$$

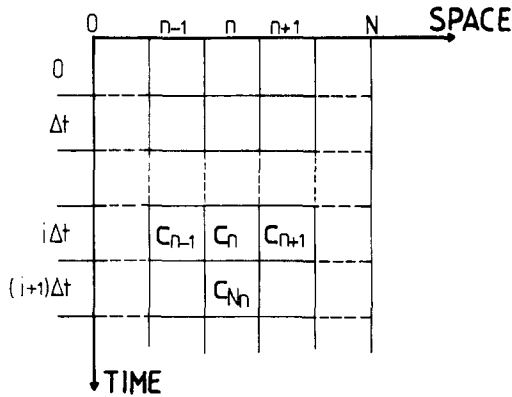


Fig. 1. Space-time diagram for numerical analysis.

where  $C_n$  is the concentration of water in the slice  $n$  at time  $t$ , and  $C_{Nn}$  is the value of this concentration at time  $(t + \Delta t)$ .

Equation (11) can be used for the water transport within the coating during either the absorption or the desorption.

**Absorption.** On the surface of the coating, following assumption (ii), the concentration is at equilibrium as soon as the process starts.

$$C_s = C_{eq}. \quad (12)$$

**Desorption.** The matter balance is calculated in the slice in contact with the surface (Fig. 1) by considering the diffusion of water from the inside of the coating and the evaporation from the surface. The new concentration on the surface is thus expressed by:

$$CN_0 = \frac{1}{M} \left[ \frac{1}{2} C_2 + (M - \frac{1}{2} - N) \cdot C_0 + N \cdot C_{ext} \right] \quad (13)$$

where  $C_0$  and  $C_{N0}$  are the concentration on the surface at time  $t$  and  $(t + \Delta t)$ , respectively and  $C_{ext}$  is the concentration of water on the surface which is at equilibrium with the surrounding atmosphere and the dimensionless numbers.

$$M = \frac{(\Delta x)^2}{\Delta t} \cdot \frac{1}{D} \quad (14)$$

$$N = \frac{F_0 \cdot \Delta x}{\rho D} \quad (15)$$

## RESULTS

Two types of results are of interest: one is concerned with the data, such as the diffusivity, the amount of water absorbed and desorbed, and the rate of evaporation, the other with the validity of the model, and the kinetics of absorption and desorption, as well as the profiles of concentration of water developed through the thickness of the coating.

### (1) Data for the absorption and desorption

**Absorption.** The kinetics of absorption of water at  $80^\circ$  are shown in Fig. 2. After a high rate of absorption expressed by the vertical tangent at time zero, the rate decrease regularly with time, and an asymptotic value is reached for times exceeding 80 hr.

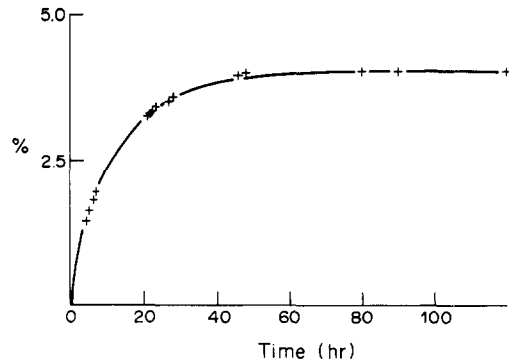


Fig. 2. Kinetics of absorption of water by the coating at  $80^\circ$ . Thickness = 0.09 cm,  $D = 1.6 \times 10^{-8}$  (cm<sup>2</sup>/sec),  $M_i = 0.7564$  g.  $M_\infty = 4.045\%$ . +, Experiments; —, models.

By plotting the amount of water absorbed vs (time)<sup>1/2</sup>, a straight line is obtained for times < 10 hr, and the diffusivity is calculated by using the well-known equation:

$$\frac{M_t}{M_\infty} = \frac{4}{2l} \left( \frac{D \cdot t}{\pi} \right)^{0.5}. \quad (16)$$

The diffusivity and the maximum value of the water absorbed are shown below. Data for the absorption of water are:

$$D = 1.6 \times 10^{-8} \text{ (cm}^2\text{/sec)}$$

$$M_\infty = 4.045\%$$

where  $M_\infty$  is the amount of water in 100 g of the initial resin.

**Desorption.** When the sample of coating previously saturated of water is exposed to air at  $20^\circ$ , only part of the water in the coating evaporates. After various drying steps at higher temperature, e.g. 80 and  $100^\circ$ , complete dryness of the coating is not achieved (Fig. 3).

The diffusivity is calculated by using equation (10) for long times, when only the first term of the series need be considered:

$$\ln \frac{M_\infty - M_t}{M_\infty} = \frac{\beta_p^2}{l^2} Dt + \ln \frac{2L^2}{\beta_p^2(\beta_n^2 + L^2 + L)}. \quad (17)$$

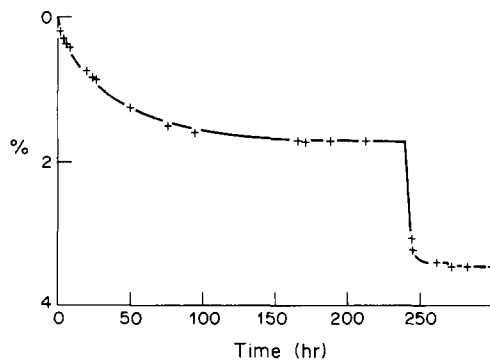


Fig. 3. Kinetics of desorption of water from the coating, successively at 20, 80 and  $100^\circ$ .  $M_i = 0.7564$  g,  $M$  desorbed = 3.463%.

Table 1. Data for the two-step desorption of water at 20° and 80°.

	Temperature (°C)		Amount of water remaining
	20	80	
$D \times 10^8$ (cm <sup>2</sup> /sec)	0.52	8.9	
$F_0 \cdot 10^6$ (g/cm <sup>2</sup> ·sec)	2.86	1860	
$M$ evaporated (%)	1.718	1.692	0.635

Table 2. Data for the desorption of water at 80°

$D = 7.3 \times 10^{-8}$ (cm <sup>2</sup> /sec) - $F_0 = 1.86 \times 10^{-3}$ (g/cm <sup>2</sup> ·sec)
$M$ absorbed = 4.09%
$M$ evaporated = 3.44%
$M$ remaining = 0.65%

The rate of evaporation is obtained from experiments with pure water at room temperatures. The values at other temperature are easily calculated, as the rate of evaporation is proportional to the vapour pressure (Tables 1 and 2).

### (2) Validity of the model

The validity of the mathematical model and of the numerical model is tested by comparing the kinetics obtained by experiment with those by calculation. As shown in Fig. 2 in the case of absorption at 80° and in Fig. 4 (first step of desorption at 20°) and Fig. 5 (second step of desorption at 80°), good agreement is obtained for the absorption and for the two step desorption. Good agreement is also obtained for the kinetics of drying at 80°.

### (3) Profiles of concentration of water

The profiles of concentration of water can be calculated with the help of equations (7) and (11), as they are developed through the coating as a function of time. It is difficult to determine these profiles by experiment, as indicated in previous studies [12, 13]. However, there is proof of the validity of these profiles, as the kinetics are obtained by integrating the concentration of water in the coating with respect to space.

The profiles calculated during the process of absorption (Fig. 6) show that a steep gradient of concentration of water is developed next to the surface at the beginning of the immersion. When the absorption equilibrium is reached, a uniform concen-

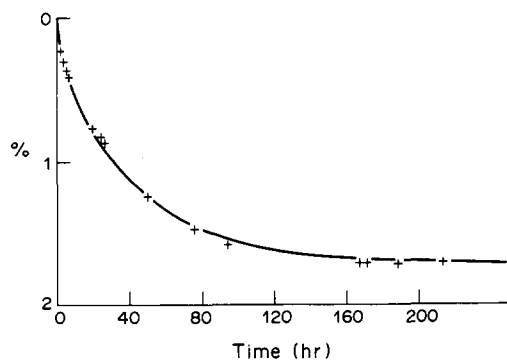


Fig. 4. Kinetics of desorption of water from the coating at 20°, thickness = 0.09 cm,  $D = 0.52 \times 10^{-8}$  (cm<sup>2</sup>/sec),  $F_0 = 2.86 \times 10^{-6}$  (g/cm<sup>2</sup>·sec),  $M_i = 0.7564$ ,  $M$  desorbed = 1.718%.

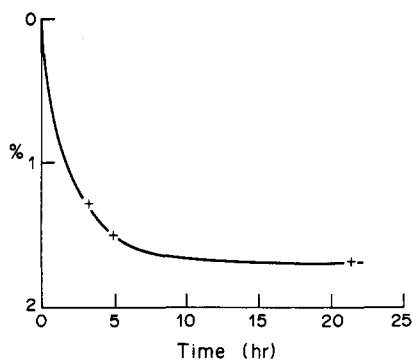


Fig. 5. Kinetics of desorption of water from the coating at 80°, thickness = 0.09 cm,  $M_i = 0.7564$  g,  $D = 8.9 \times 10^{-8}$  (cm<sup>2</sup>/sec);  $F_0 = 1.86 \times 10^{-3}$  (g/cm<sup>2</sup>·sec),  $M$  desorbed = 1.69%,  $M_{\text{remaining}} = 0.635\%$ .

tration of water through the thickness of the coating is obtained.

The same profiles of concentration of water are calculated during the two-step desorption first at 20° (Fig. 7) and then at 80° (Fig. 8).

The following conclusions are drawn from these curves:

- the concentration of water on the surface of the coating decreases regularly during the desorption at 20°, because the rate of evaporation is not very high and at 80°, this concentration drops very quickly, the rate of evaporation being considerably higher;
- at the equilibrium of desorption attained at 20 and 80°, there is uniform concentration of water in the coating.

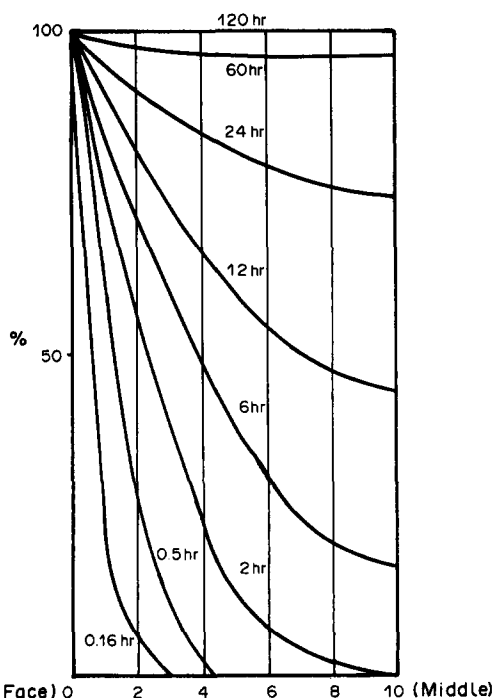


Fig. 6. Profiles of concentration of water developed through the thickness of the coating, during absorption at 80°.

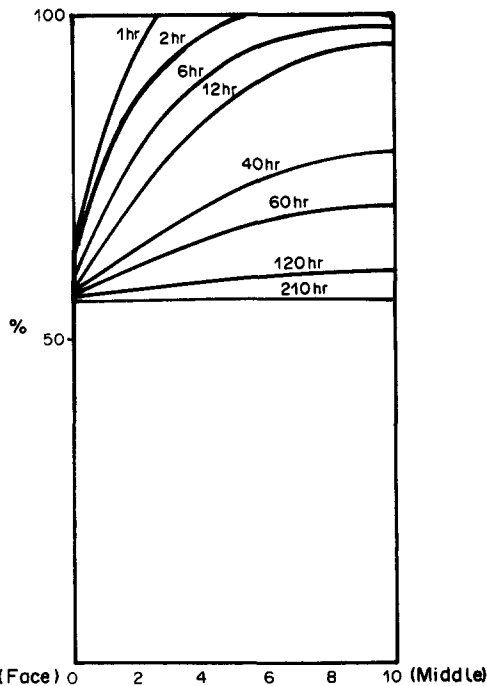


Fig. 7. Profiles of concentration of water developed through the thickness of the coating, during desorption at 20°.

The second conclusion is of interest, because it shows not only that an equilibrium of desorption is attained for each temperature but also that a flat gradient of concentration is obtained under these conditions. The water located in the solid is in part bound to the hydrophilic part of the resin, and high temperatures are necessary to evaporate this water.

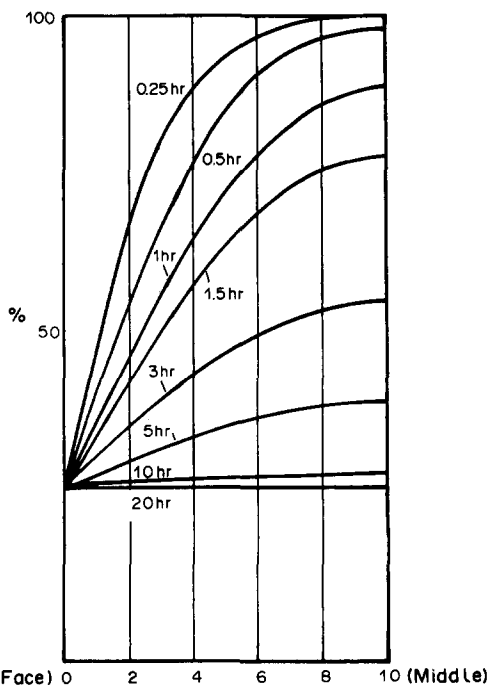


Fig. 8. Profiles of concentration of water developed through the thickness of the coating, during desorption at 80°.

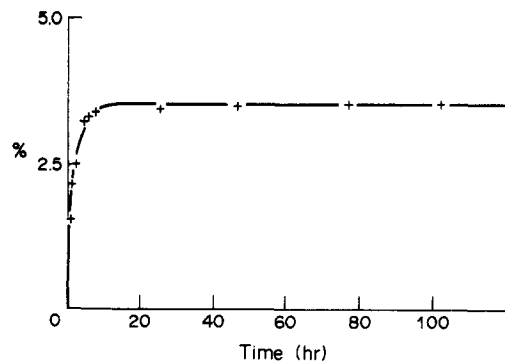


Fig. 9. Kinetics of absorption of water at 80° by the coating previously saturated with water and then dried at 80°.  $D = 9.3 \times 10^{-8} \text{ cm}^2/\text{sec}$ ,  $M_{\text{absorbed}} = 3.543\%$ , + experiments, —, models.

#### (4) Kinetics of re-immersion of the pre-treated sample

The sample previously immersed in water at 80° and dried to constant weight at 80° in air, is thus soaked again in water at 80°. The kinetics for the second absorption are also described by the model (Fig. 9). Two facts are worth noting:

- (i) the diffusivity is higher for the second absorption than that calculated in the first absorption. Following this fact, a higher rate of absorption is observed at the beginning of the process;
- (ii) the total amount of water absorbed, resulting from the water remaining after the first drying and from the further addition during the second absorption, is about the same as the amount absorbed at the end of the first absorption (Table 3).

Table 3. Data for the second absorption

$D = 9.3 \times 10^{-8} \text{ (cm}^2/\text{sec)}$	$M_{\text{abs}} = 3.543\%$
$M = 4.125\%$	

#### CONCLUSIONS

When coatings made of epoxy resin are in contact with water at 80°, absorption occurs. The process is controlled by transient diffusion with a constant diffusivity and around 4% by weight of water is absorbed at equilibrium.

The coating previously saturated is then dried in the surrounding atmosphere under various conditions. Only 42% of the water located in the resin is evaporated at room temperature; after further drying at 80°, ca 16% of the initial amount of water remains in the sample. The process of drying is described by transient diffusion through the resin and evaporation from the surface, with a constant diffusivity.

The coating dried at 80°, when immersed in water for a second time, exhibits a higher rate of absorption with a higher diffusivity; absorption occurs to about the same extent as in the first absorption.

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