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EFFECT OF TEMPERATURE ON THE TRANSFER BETWEEN EPOXY COATINGS AND WATER

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Abstract—When coatings made of epoxy resin are in contact with water, a matter transfer generally takes place controlled by diffusion. When this pre-saturated coating is exposed to air, part of the water previously absorbed is evaporated; this process of drying is controlled by diffusion within the solid and evaporation from the surface. The effect of temperature, not only on the rate of the absorption and drying but also on the amount of water absorbed and desorbed, is of great importance. The 60–100° temperature range is explored. Numerical models are built in order to describe the process of absorption and desorption. They give kinetics which correlate very well with the results of experiments, and they are able to determine the profiles of concentration of water through the coating.

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_0 = concentration of water on the surface of the coating;
C_{ext} = concentration of water required to maintain equilibrium with the surrounding atmosphere;
D = diffusivity of water in the coating;
Δt = finite increment in time;
Δx = slice thickness of space;
V_0 = rate of evaporation of water;
L = half-thickness of the coating;
Q_t = total amount of water which has been transferred at time t;
Q_∞ = total amount of transferred water after infinite time;
M,N = dimensionless numbers.

INTRODUCTION

Because of their good appearance and high performance, epoxy resins are often used as high-priced coatings [1–8]. Generally, they are used to protect metal sheets against liquids, but some problems arise from the matter transfer which may take place within the resin [2]. As shown in a previous study [3] at 80°, when an expoxy resin coating is in contact with water, water generally enters the solid, the process being controlled by diffusion with a constant diffusivity and a rather low amount absorbed after infinite time. After absorption, the water is desorbed when the pre-saturated coating is exposed to air, this process being controlled by diffusion of water within the solid and evaporation from the surface.

The main purpose of this paper is to determine the effect of temperature on the stages of absorption and desorption, by exploring the 60–100° range. Not only the rate of water transport during these two stages with diffusivities must be considered, but also the amount of water absorbed by the coating and desorbed. As a result, the amount of water which is in contact with the metal could be known, and more generally the concentration–time history for the water in contact with the metal during the stages of absorption and desorption. Another aim in this study is to build numerical models capable of describing the process of absorption–desorption, and thus able to predict the concentration of water in the coating when the coating is alternately placed in contact with water and with air.

EXPERIMENTAL PROCEDURES

Material

The binary mixture of epoxy resin (Lopox 200, CDF Chimie, Orkem) and of hardener (D2605) containing an accelerator with 0.75% of aromatic amine (type 1, 195-Orkem) was prepared at room temperature. The best composition in weight percent was: epoxy resin (56%) and hardener (44%), as shown previously for this resin [4].

Preparation of the coating

The resin mixture was deposited on steel sheets, the coating having an average thickness of 1 mm. After a cure of 44 hr at 50°, part of the coating was studied by calorimetry showing that the state of cure reached 90% under these conditions [5]. The sample was heated in the calorimeter (DSC 111-Setaram) at a constant rate of 5°/min from room temperature to the end of the reaction.

Matter transfer studies

The resin coating was removed from the steel plate, and then immersed in water at constant temperature between 60 and 100°. The kinetics of absorption were followed by weighing the coating sample at intervals. When equilibrium was reached for the absorption of water, the coating sample was dried in air at a constant temperature between 60 and 100°.

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THEORETICAL

Assumptions

The following assumptions are made in order to explain the process:

- (i) As the amount of water is small, the thickness of the coating remains constant during the stages of absorption and desorption.
- (ii) The stage of absorption is controlled by transient diffusion of water through the coating.
- (iii) The stage of desorption is controlled by transient diffusion through the coating and by evaporation from the surface.
- (iv) The rate of evaporation is proportional to the effective concentration of water on the surface of the coating.
- (v) During absorption, the concentration of water on the coating surface reaches equilibrium as soon as the coating is immersed in water.
- (vi) The time necessary for the sample to establish thermal equilibrium is negligible compared with the time of absorption and desorption.

Mathematical treatment

The two stages of absorption and desorption are considered in succession.

The one-dimensional diffusion in the coating of thickness $2L$ is expressed by Fick's law with constant diffusivity.

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} \tag{1}$$

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

Stage of absorption

The initial and boundary conditions are:

$$t = 0 \quad -L < x < L \quad C = 0 \tag{2}$$

$$t > 0 \quad x = \pm L \quad C = C_{eq} \tag{3}$$

The solution of equation (1) with these conditions is [6]:

$$\frac{C_{eq} - C_{x,t}}{C_{eq}} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \frac{(2n+1)\pi x}{2L} \times \exp\left(- \frac{(2n+1)^2 \pi^2}{4L^2} Dt \right) \tag{4}$$

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

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

$$\frac{Q_\infty - Q_t}{Q_\infty} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(- \frac{(2n+1)^2 \pi^2}{4L^2} Dt \right) \tag{5}$$

where Q_t is the amount of water absorbed after time t and Q_∞ the corresponding amount after infinite time.

Stage of desorption

The initial concentration of water within the coating is uniform, as equilibrium is previously reached during absorption.

The rate of loss in weight due to evaporation is expressed by:

$$\left[-D \cdot \frac{\partial C}{\partial x} \right]_{x=L} = V_0 (C_s - C_{exp}) \tag{6}$$

where V_0 is the rate of evaporation of water under these conditions, C_s is the concentration of water on the surface and C_{ext} is the concentration which is at equilibrium with the surrounding atmosphere.

The solution of equation (6) is:

$$\frac{C_{eq} - C_{ext}}{C_{eq} - C_{in}} = \sum_{n=1}^{\infty} \frac{2S \cdot \cos \beta_n \frac{x}{L}}{(\beta_n^2 + S^2 + S) \cos \beta_n} \times \exp\left(- \frac{\beta_n^2}{L^2} Dt \right) \tag{7}$$

where the β_ns are the positive roots of

$$\beta \cdot \tan \beta = S \tag{8}$$

with the dimensionless number S

$$S = \frac{L \cdot V_0}{D}. \tag{9}$$

The total amount of water Q_t leaving the coating after time t is expressed as a fraction of the corresponding quantity after infinite time Q_∞, by:

$$\frac{Q_\infty - Q_t}{Q_\infty} = \sum_{n=1}^{\infty} \frac{2S^2}{\beta_n^2 (\beta_n^2 + S^2 + S)} \times \exp\left(- \frac{\beta_\pi^2}{L^2} Dt \right). \tag{10}$$

We have written a program which calculates the 40 first roots β_n for any value of S, with seven significant figures.

Numerical analysis

The analytical solution is obtained when the diffusivity is constant or when the initial concentration is uniform. In other cases, a numerical model with finite differences is necessary to represent the process.

The thickness of the coating is divided into equal slices of thickness Δx, each slice being characterized by an integer n (Fig. 1). From the balance of water entering and leaving the slice at position n during the increment of time Δy the new concentration of position n after elapse of time Δt is expressed in terms of the previous concentrations:

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

where C_n is the concentration of water at position n and time t, and CN_n the new concentration at time $(t + \Delta t)$, where M is a dimensionless number:

$$M = \frac{(\Delta x)^2}{D \cdot \Delta t} \tag{12}$$

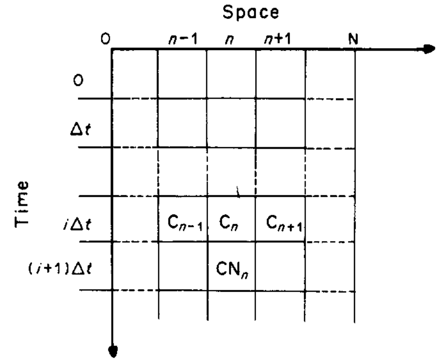

Fig. 1. Space–time diagram for numerical analysis, with integers n and i characterizing position and time.

Equation (11) can be used either for absorption or for desorption.

Absorption

Following assumption v, the concentration at the surface ($n = 0$) reaches equilibrium as soon as the process starts.

$$C_0 = C_{\mathrm{eq}} \tag{13}$$

Desorption

The slice of thickness $\Delta x/2$ next to the surface must be considered, and the water balance is determined during the increment of time Δt by considering the diffusion of water and evaporation from the surface. The new concentration on the surface is thus expressed by [7]:

$$CN_0 = \frac{1}{M}\,[2C_1 + (M - 2 - 2N)C_0 + 2N \cdot C_{\mathrm{ext}}] \tag{14}$$

where C_0 and CN_0 are the concentration on the surface at time t and at time $t + \Delta t$, and C_{ext} the concentration required to maintain equilibrium with the surrounding atmosphere with the dimensionless number N.

$$N = \frac{V_0 \cdot \Delta x}{D} \tag{15}$$

Amount of water located in the coating

The amount of water located in the coating is obtained by integrating the concentration of water with respect to space.

RESULTS

Some parameters must be evaluated from experiments especially performed for this purpose: the diffusivity, and the amount of water absorbed at equilibrium, for the stage of absorption; the diffusivity, and the amount of water which evaporates after infinite time, as well as the rate of evaporation during desorption. These parameters can be used to establish the validity of the model by comparing the kinetics of absorption and of absorption when they are obtained by experiment and from calculation.

The calculation of the profiles of concentration developed throughout the coating during each cycle is capable of giving a fuller insight into the process. Some emphasis is placed upon the effect of temperature not only on the kinetics of absorption and desorption, but also on the amount of water remaining in the coating at the end of each stage of absorption and desorption.

1. Determination of the values of the parameters

Diffusion. During absorption, the concentration of water on the surface of the coating reaches equilibrium as soon as the process starts. It is thus possible to determine the diffusivity from the straight line obtained by plotting the amount of water absorbed as a function of the square root of time, by using the relationship

$$\frac{Q_t}{Q_\infty} = \frac{2}{L}\left(\frac{Dt}{\pi}\right)^{0.5} \quad \text{with} \quad \frac{Q_t}{Q_\infty} < 0.5. \tag{16}$$

During desorption, two parameters play a role: the diffusivity and the rate of evaporation. However it is possible to find a value of the diffusivity by using equation (10) for long times of drying. When $Q_t/Q_\infty > 0.6$, the series in equation (10) converges quickly and the first member of the series can be retained. Equation (10) then becomes:

$$\mathrm{Ln}\frac{Q_\infty - Q_t}{Q_\infty} = \frac{\beta_1^2}{L^2}Dt + \mathrm{Ln}\frac{2S^2}{\beta_1^2(\beta_1^2 + S^2 + S)}. \tag{17}$$

From the slope obtained by plotting the left-hand term as a function of time, the diffusivity can be determined by iteration if the rate of evaporation is known, in spite of the dependence of β_1 on the diffusivity shown in equation (9).

Rate of evaporation. The rate of evaporation is determined from the kinetics of evaporation of the sample, at the beginning of the process when the initial concentration is uniform and well known. The values of the diffusivity and the rate of evaporation are shown in Table 1.

Amount of water absorbed and desorbed at equilibrium. The amounts of water absorbed and desorbed when equilibrium is reached are also given in Table 1. These values are expressed as the fraction of water located in the resin by the weight of the dried resin.

Some conclusions can be drawn from these results:

(i) The amount of water absorbed by the resin decreases with temperature (Fig. 2).
(ii) Only a part of the water previously absorbed can evaporate; the higher the temperature, the greater is the part of the water desorbed. At 60°, only 71% of the water in the resin can evaporate, while all the water previously absorbed can evaporate at 100°.
(iii) The diffusivity for the stages of absorption and desorption varies with temperature, following an Arrhenius law (Fig. 3).
(iv) At each temperature, the diffusivities for absorption and desorption are not the same.

2. Validity of the model

The validity of the mathematical model and of the numerical model can be appreciated by comparing the kinetics of absorption and of desorption obtained from experiment and by calculation for temperatures ranging from 60 to 100° (Figs 4–7). As illustrated in

Table 1. Values of diffusivity and rate of evaporation

Temperature (°C)	ΔQ absorbed (%)	ΔQ desorbed (%)	D abs × 10^8 (cm^2/sec)	D des × 10^8 (cm^2/sec)	V_0 × 10^4 (cm/sec)
60	6.6	4.7	0.27	1.7	0.62
80	4.06	3.6	1.7	8.1	1.4
90	3.9	3.3	7.2	15.8	8.5
100	3.57	3.57	26	16.5	12.4

these curves, good superimposition is obtained between the theoretical and experimental kinetics, proving the validity of these models.

3. *Profiles of concentration*

The profiles of concentration of water expanded within the thickness of the sample can be calculated by using the analytical solutions or the numerical model. No experiments are made to determine the values of these profiles, as these experiments are very time-consuming and destructive of the sample, as shown in previous studies [8, 9]. However, proof of the validity of these profiles of concentration exists, as the kinetics of absorption and desorption are obtained by integration of these profiles.

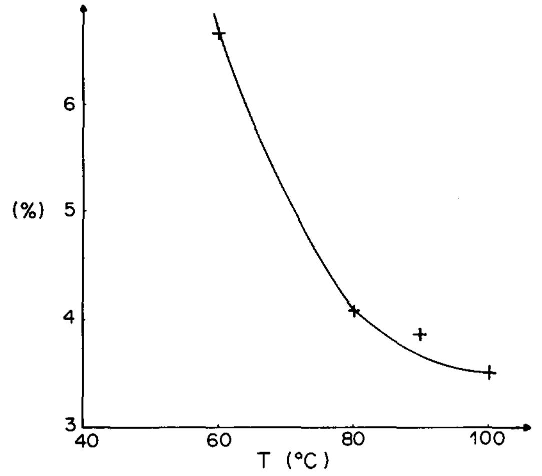

Fig. 2. Variation of the amount of water absorbed with temperature.

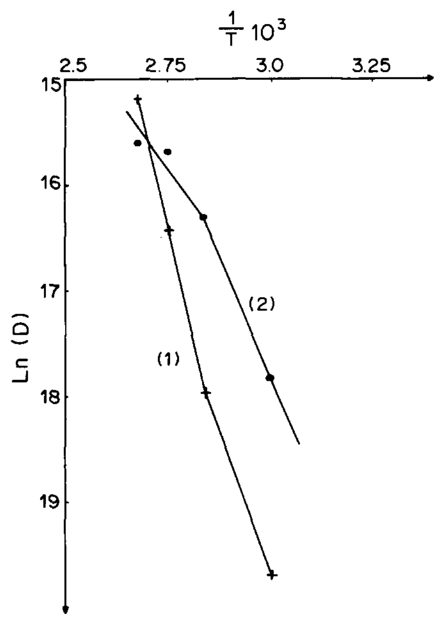

Fig. 3. Temperature-dependence of diffusivities: 1, absorption; 2, desoprtion.

Profiles of concentration are drawn at 60° and 100°, as calculated during the stages of absorption and desorption. The following results are worth noting:

(i) During absorption, the concentration of water on the surface reaches equilibrium as soon as the process starts, following the Vth assumption.

(ii) During desorption, the concentration of water decreases rather quickly. The fact can be observed in Fig. 8 at 60° where short times of desorption are used.

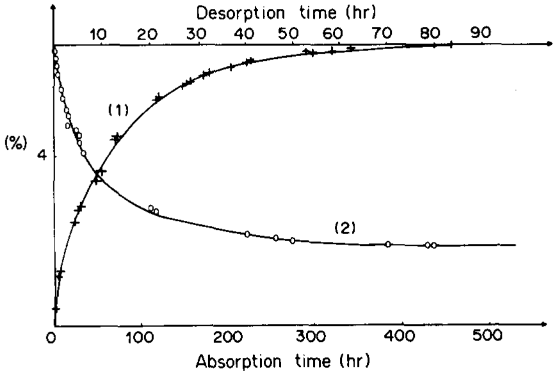

Fig. 4. Validity of the model. Kinetics of absorption and desorption of water at 60° (expressed by the amount of water as a fraction of the weight of the initial coating). 1, Absorption; 2, desorption. +, Experiments; ——, theoretical.

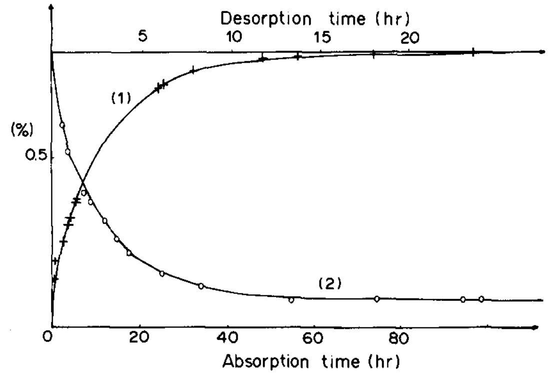

Fig. 5. Validity of the model. Kinetics of absorption and desorption of water at 80° (expressed in the same way as indicated in Fig. 2). 1, Absorption; 2, desorption. +, Experiments; ——, theoretical.

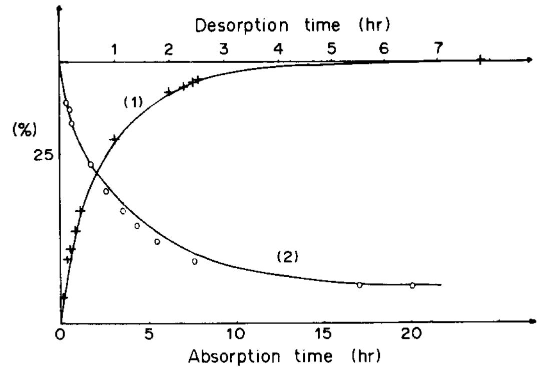

Fig. 6. Validity of the model. Kinetics of absorption and desorption of water at 90°. 1, Absorption; 2, desorption. +, Experiments; ——, theoretical.

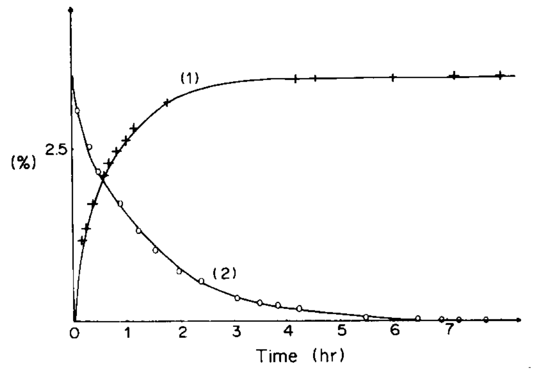

Fig. 7. Validity of the model. Kinetics of absorption and desorption of water at 100°. 1, Absorption; 2, desorption. +, Experiments; ——, theoretical.

- (iii) At the end of the stage of desorption, a flat gradient of concentration is obtained as appears clearly at 60° (Fig. 8) and 100° (Fig. 9). It corresponds with the equilibrium of desorption.
- (iv) The amount of water remaining after each stage of desorption depends on temperature as shown in Fig. 2.

CONCLUSIONS

The absorption of water by coatings made of epoxy resins is studied, as well as the process of desorption. Some emphasis is placed upon the effect of temperature on each process. The absorption is very well described by diffusion with constant diffusivity, and the following stage of evaporation is controlled by diffusion of water within the resin and evaporation out of the surface.

The effect of temperature on the processes of absorption and desorption is of very significance. Temperature plays a role not only on the rate of water transport, but also on the amount of water located in the resin at the end of each stage. The amount of water absorbed by the resin decreases with temperature, while the amount of water desorbed increases. As a result, about 30% of the water absorbed at 60° remains in the resin after evaporation at the same temperature. On the other hand, all the water absorbed at 100° is completely desorbed at 100°.

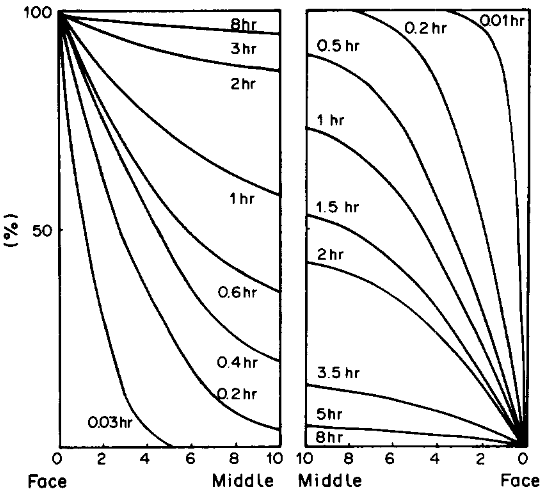

Fig. 8. Profiles of concentration of water developed within the coating at 60°. Left, absorption; right, desorption.

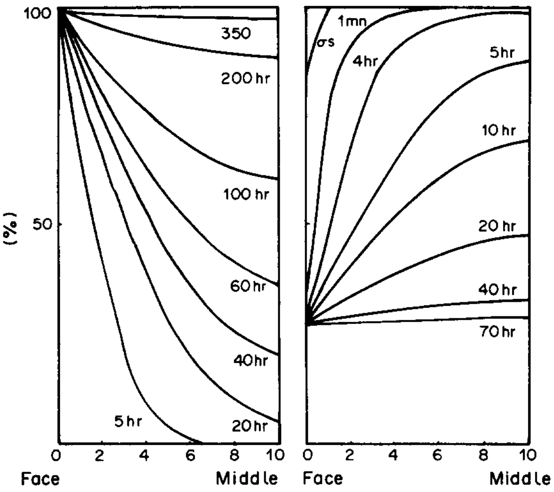

Fig. 9. Profiles of concentration of water developed within the coating at 100°. Left, absorption; right, desorption.

The diffusivities for the stages of absorption and desorption increase with temperature according to an Arrhenius law.

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