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# KINETICS OF ABSORPTION OF TOLUENE BY COATINGS MADE OF EPOXY RESIN; MODELLING AND EXPERIMENTS

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**Abstract**—When a coating made of epoxy resin is in contact with toluene at room temperature, a matter transport may take place, with approximately linear kinetics. The process of this matter transfer is described by considering the diffusion of the liquid within the coating with concentration-dependent diffusivity. The concentration of the liquid on the coating surface increases with time by following an exponential law. A numerical model with finite differences is capable of describing the kinetics of absorption, following these two assumptions.

## INTRODUCTION

Epoxy resins are materials of high performance, and in some applications they are in contact with aggressive liquids. This point is especially true for the coatings of the tanks in ships used for the transport of crude oil, which are thus in contact either with crude oils of various kinds or with sea water.

When a thermoset is in contact with a liquid, a liquid transport may take place within the resin, and this fact is responsible for a modification in the physical and mechanical properties of the solid [1]. In the case of a polymer, above the transition temperature $T_g$, the solid is said to be in the elastomeric state, and the liquid transport is controlled by diffusion with constant or concentration-dependent diffusivity [2–5]. When the thermosetting polymer is in the glassy state, below $T_g$, the problem of liquid transport may be more complex for two reasons at least:

(i) the behaviour of a polymer toward a liquid differs notably whether it is below or above its transition temperature;
(ii) the liquid which has entered the thermoset can act as a plasticizer, and thus a solid initially in the glassy state may turn into an elastomeric state [6, 7].

The first objective in this paper is to experiment the behaviour of a coating made of epoxy resin when it is in contact with a very aggressive liquid such as toluene [8]. The other main purpose is to build a numerical model able to describe the process of the liquid transport. The kinetics of absorption of toluene is particular in the sense that the amount of the liquid absorbed varies about proportionally with time and not proportionally with the square root of time, as is usual when the transport of liquid is assumed to be controlled by transient diffusion [1, 9]. A numerical model, based on a method with finite differences, takes into account the following facts:

(i) the concentration of the liquid on the surface of the thermoset increases with time following an exponential law;
(ii) the transport of liquid within the solid is controlled by diffusion with a concentration-dependent diffusivity.

## EXPERIMENTAL PROCEDURES

### *Materials*

The resin was obtained by mixing the epoxy resin (Lopox 200, from CDF-Chimie) and the hardener containing an anhydride of MeTHP (D 2605, CDF-Chimie), with an accelerator containing 0.75% of an aromatic amine (type A, 105, CDF-Chimie). The binary mixture was prepared at room temperature with continuous stirring. The composition in weight percent was: epoxy resin 56, hardener 44.

### *Preparation of the coating*

The mixture was deposited on steel sheets, the coating having a thickness of around 1 mm. After a cure of 44 hr at 50°, a part of the coating was studied by calorimetry, showing that the state of cure (SOC) had reached 90% under these conditions [10].

### *Studies of liquid transport*

The coating was removed from the steel plate, and then immersed in toluene at room temperature. The kinetics of absorption of liquid were followed by weighing the sample at intervals.

After immersion in toluene for 580 min, the coating was removed from the liquid and dried in air at room temperature. For longer times of soaking, e.g. 1000 min, some cracks appeared on the surface, preceding disintegration of the resin.

The thickness and the area of the sample were: 0.09 cm and 3.8 $cm^2$. The initial weight of the sheet was: MI = 0.23 g. The amount of absorbed liquid at the end of the immersion (580 min) was: 0.0654 g or 28.44% of MI.

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## THEORETICAL

### *Assumptions*

The following assumptions are made:

(i) The sample is a sheet so thin that the effect of the edges is negligible, and the transport of liquid is perpendicular to the sheet surfaces.
(ii) The dimensions of the sheet do not vary during the absorption.
(iii) The process of absorption is controlled by one-dimensional diffusion under transient conditions, with a concentration-dependent diffusivity.
(iv) The concentration of the liquid on the surfaces varies with time following an exponential law from a given low value to a given higher value.

### *Mathematical treatment*

The equation for the one-dimensional diffusion is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \cdot \frac{\partial C}{\partial x}\right) \tag{1}$$

with a concentration-dependent diffusivity.

The initial condition is:

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

and the boundary condition is:

$$t > 0 \quad C_{0,t} = C_{0,0} + (C_e - C_{0,0}) \cdot (1 - e^{-b \cdot t}) \tag{3}$$

where $C_{0,0}$ is the liquid concentration on the surface as soon as the sample is immersed in the liquid, $C_e$ is the highest concentration of liquid at the final equilibrium and $b$ is a constant characterizing the rate of increase in concentration on the surface.

It is assumed that the diffusivity varies with the concentration of the liquid according to the following relationship as found in previous studies [1, 6, 7].

$$D(x, t) = DA \cdot \exp\left(-\frac{B}{C(x, t)}\right) \tag{4}$$

where $DA$ and $B$ are two constants to be determined. The main interest of this equation is that the diffusivity is zero when the concentration is zero.

### *Numerical analysis*

As the diffusivity is concentration-dependent, there is no analytical solution for the problem, and a numerical model based on finite differences must be used.

The thickness of the sheet $L$ is divided into $2N$ equal finite slices of thickness $\Delta x = L/2N$ (Fig. 1). The abscissae axis is perpendicular to the sheet, and the sheet occupies the space $0 \leqslant x \leqslant L$. For each integer $j$ such that $0 \leqslant j \leqslant N$, the concentration at the abscissa $j \cdot \Delta x$ and at time $t$ or $(t + \Delta t)$ are noted $C(j)$ or $CN(j)$, respectively.

For each integer $j$ such that $1 \leqslant j \leqslant N$ we consider the slice defined by: $(j - 0.5)\,\Delta x \leqslant x \leqslant (j + 0.5)\,\Delta x$. The matter balance in this slice during the interval of time $(t, t + \Delta t)$ gives

$$CN(j) = C(j) + \frac{\Delta t}{\Delta x^2} \cdot \{D(j + 0.5) \cdot [C(j + 1) - C(j)] - D(j - 0.5) \cdot [C(j) - C(j - 1)]\}. \tag{5}$$

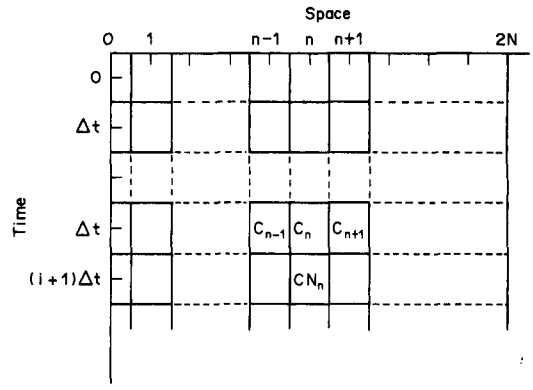


Fig. 1. Diagram for numerical analysis.

The diffusivity $D(j - 0.5)$ is obtained with equation (4) with linear interpolation for $C(j - 0.5)$:

$$D(j - 0.5) = DA \cdot \exp\frac{-2B}{C(j - 1) + C(j)}. \tag{6}$$

Then, on putting the function $G$

$$G(j) = [C(j) - C(j - 1)] \cdot \exp\frac{-2B}{C(j) + C(j - 1)} \tag{7}$$

for

$$1 \leqslant j \leqslant N + 1$$

the following is obtained:

$$CN(j) = C(j) + \frac{\Delta t \cdot DA}{\Delta x^2} \cdot [G(j + 1) - G(j)]. \tag{8}$$

The amount of liquid absorbed by the coating is calculated by integrating the liquid concentration with respect to space.

## RESULTS

Two types of results are of interest:
—the validity of the model;
—the profiles of concentration of the liquid developed through the thickness of the coating.

### *Validity of the model*

The validity of the model is tested by comparing the kinetics of absorption of toluene obtained either by experiment or by calculation. We have taken $N = 40$, $\Delta t = 10$ sec. The parameters shown in Table 1 are determined so that the calculated kinetics fit well the experimental curves, except for the value of $C_e$ which is chosen beyond the maximum amount of liquid absorbed by the sheet during the immersion.

As shown in Fig. 2, good agreement is observed between the kinetics of absorption of liquid obtained by experiment or by calculation, proving the validity of the model as well as accuracy of the data.

Table 1. Values of the parameters

| | | |
|---|---|---|
| $DA = 16.6 \times 10^{-8}$ (cm²/sec) | | $B = 0.365$ (concentration) |
| $C_{0,0} = 0.19$ | $C_e = 0.374$ | $b = 0.01$/sec |

The concentration is expressed in gram of absorbed liquid per gram of initial material.

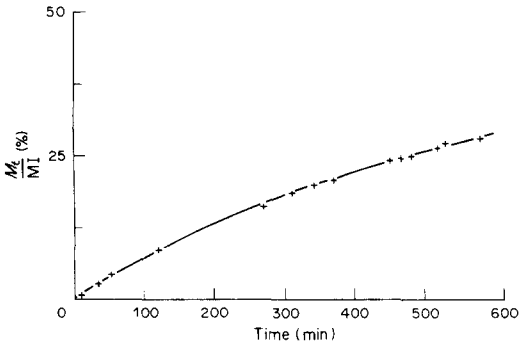


Fig. 2. Kinetics of the liquid absorbed (toluene) by the coating of epoxy resin, obtained by experiment and calculation.

*Profiles of concentration of liquid through the thickness*

The profiles of concentration of liquid developed through the thickness of the coating are drawn in Fig. 3 for various times, as obtained with the model. Some results are worth noting from the curves in Figs 2 and 3.

(i) The kinetics obtained for the absorption of toluene by the coating are not usual. The amount of the liquid absorbed varies approximately linearly with time, up to 580 min.
(ii) The kinetics of absorption obtained by experiment and calculation are about the same.
(iii) As long as the liquid has not reached the middle of the sheet, the profiles of concentration of the liquid are perpendicular to the abscissae axis.

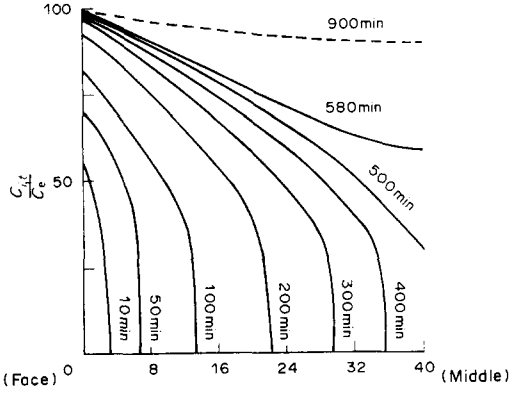


Fig. 3. Profiles of concentration of liquid developed through the thickness of the coating at various times.

(iv) The liquid progresses through the thickness of the coating as shown in Fig. 3. The liquid has reached the midplane of the coating at about 450 min.

## CONCLUSION

The difficult problem of the absorption of a liquid by a thermosetting polymer in the glassy state is studied either by experiments or by building a numerical model able to describe the process.

The kinetics for the liquid (toluene) absorbed by an epoxy resin coating are obtained; the rate is nearly constant. In order to obtain such a result, a numerical model is built by considering the following facts:

—The concentration of the liquid on the surface of the coating increases with time from a given value at the beginning of the immersion to another given value after a long time:
—the transport of liquid within the coating is controlled by transient diffusion with concentration-dependent diffusivity. The diffusivity is zero when the concentration is zero.

The numerical model is successfully tested as well as the data, as the kinetics of the liquid absorbed obtained from experiments and calculation are in good agreement. Moreover, the profiles of concentration of the liquid are developed within the sample during the process, giving a further insight on the process.

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