MIGRATION OF ORGANIC SOLUBLE SUBSTANCES FROM EPOXY RESIN INTO SURROUNDING WATER ACCOMPANIED BY A CHEMICAL REACTION

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Soluble substances, such as additives and residual monomers contained in plastics, suffer slow leaching by surrounding liquids during practical applications. This causes contamination of high-purity process fluids in the chemical equipment. Some models for the migration of monomers or additives have been proposed by Reid *et al.*¹⁾ and Till *et al.*,²⁾ postulating the conditions applicable to food containers and film wrapping whereby the situation occurring in the liquid phase affects the migrative behavior of these substances.

The present paper concerns the migration of soluble substances from epoxy resin, accompanied by hydrolysis of uncured substances by penetrating water. It can be regarded as being in a state of infinite dilution of the solute in the leaching bath, and of negligible mass transfer resistance of the diffusant in the liquid film along the surface of the solid.

1. Materials

Commercial epoxy resin (EP4200; epoxide equivalent equal to 182 g/eq.) and hardener (EH530; amine value equal to 596 mg/g), supplied by Asahi Denka Kogyo Inc., were used as raw materials.

Specimens were prepared by molding, and were then sliced to 0.1 mm thickness in order to obtain sufficient surface area for leaching. It was observed by FT-IR spectrometry that the amount of residual epoxy group was ultimately kept to 10% of that of raw resin.

2. Identification of Leachate

Using ¹³C-NMR, ¹H-NMR, and FT-IR, it was detected that the leachate from the raw resin was not a bisphenolic compound but the hydrolyzed product of the reactive diluent—*n*-butyl glycidyl ether.

The leachate from the raw hardener consisted of two portions of soluble and insoluble substances in chloroform, and identification was successful only for

the former. It was identified using ¹H-NMR, ¹³C-NMR and mass spectrometry as *p*-diamino diphenyl methane.

The major component of the leachate from the cured resin of the equimolar and excess resin compositions was identified to be the same as that of raw resin. Unfortunately, identification of the leachate from the cured resin of the excess hardener compositions was unsuccessful, because the expected spectra due to amino group overlapped with that of the others.

3. Leaching Experimentation

Sliced specimens (approx. 2 g) were submitted to batch leaching in conical flasks with 300 ml of distilled water. The amount of leached substance was determined by measuring the total organic carbon (TOC), using a Model 782B (Nippon Jarrell Ash Inc.). Figure 1 is a plot of the amount of leached substance over time. The loss of soluble substance appeared least

Fig. 1. Experimental results of leaching for specimens of various compositions

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in specimens of equimolar composition.

4. Discussion

4.1 Model formulation

The leaching process dealt with in the present paper involves a multicomponent system, making it necessary to consider various accompanying phenomena. Diffusion coefficients defined in the present work are merely proportion constants in the mass flux equations.

The accompanying reaction is assumed to be second-order irreversible, as follows:

It is assumed also that A is slightly soluble and that the magnitude of the diffusion coefficient of C is much less than that of A or B.

The basic differential equations are:

$$\left. \begin{aligned} \frac{\partial C_A}{\partial t} &= D_A \frac{\partial^2 C_A}{\partial x^2} - k C_A C_B \\ \frac{\partial C_B}{\partial t} &= D_B \frac{\partial^2 C_B}{\partial x^2} - k C_A C_B \\ \frac{\partial C_C}{\partial t} &= D_C \frac{\partial^2 C_C}{\partial x^2} + k C_A C_B \end{aligned} \right\} \quad (2)$$

satisfying the conditions,

$$\begin{aligned} C_A &= C_{A0} \text{ and } C_B = C_C = 0, \text{ when } t = 0 \\ \text{and } -l \leq x \leq l, \quad C_A &= C_C = 0 \text{ and } C_B = C_{B0}, \\ \text{when } t > 0 \text{ and } x = \pm l, \text{ and } D_A &= 0, \\ \text{when } C_A &\geq C_B C_{As}. \end{aligned}$$

The amount of migrated substances was evaluated using the sum of the time integrals of the mass flux of A and C across the specimen surface, as follows:

$$Q_T = D_A \int_0^t \left. \frac{\partial C_A}{\partial x} \right|_{x=0} dt + D_C \int_0^t \left. \frac{\partial C_C}{\partial x} \right|_{x=0} dt \quad (3)$$

The solutions were derived numerically using the explicit difference method, with a value of modulus $(\Delta x)^2/D_B \Delta t = 3.0$.

4.2 Comparison of calculated curves with experimental results

An example of calculated migration curves is shown in Fig. 2, wherein Q_T is the sum of the amount of migrated reactant Q_A and that of product Q_C . It is evident that the features of the curve Q_T are sensitive to the values of the parameters C_{A0}/C_{B0} , kl^2C_{B0}/D_B , and D_C/D_B . The authors tried to find pertinent values for the parameters of the above-mentioned model, using the trial-and-error method. Figure 3 shows some examples of superimposed diagrams of the calculated and experimental curves for equimolar and excess

Fig. 2. Example of calculated migration curves for various nondimensional rate constants of hydrolysis when $C_{A0}/C_{B0} = 0.1$, $D_C/D_B = 0.1$, and $C_{As} = 0.1$.

Fig. 3. Example of comparison of calculated curves with experimental results

Table 1. Correlation of parameters of model with composition of specimens

Compo- sition	Specimens		Model			
	H/R	@	$\frac{kl^2C_{B0}}{D_B}$	$\frac{D_C}{D_B}$	C_{As}	$\frac{C_{A0}}{C_{B0}}$
	[-]	[-]	[-]	[-]	[-]	[-]
Equimolar	1.00	0.21	0.2	0.1	0.1	0.03
Excess resin	0.87	0.35	—	—	—	—
	0.71	0.53	0.2	0.1	0.1	0.07
	0.54	0.69	0.2	0.1	0.1	0.2

@ Ratio of residual epoxy group to that of raw resin.

resin compositions. Table 1 summarizes values obtained for the parameters for the preferred fit of the model except for the case of $H/T = 0.87$. It can be seen that the parameter of the model C_{A0}/C_{B0} is correlated within 88% with the fractional amount of the residual epoxy group in the specimens.

Conclusions

The major component of the leachate from the cured resin of equimolar or excess resin compositions was

identified as a hydrolyzed product of the reactive diluent contained in the raw resin. The authors examined a numerical model for migration accompanied by hydrolysis of the reactive diluent by penetrating water. A significant fit with the results of leaching experiments was obtained. The model may be appropriate for the long-term prediction of migrative phenomena.

Nomenclature

C	= concentration	$[\text{mol m}^{-3}]$
D	= apparent diffusion coefficient	$[\text{m}^2 \text{s}^{-1}]$
k	= rate constant of reaction	$[\text{m}^3 \text{mol}^{-1} \text{s}^{-1}]$
l	= half-thickness of slab	$[\text{m}]$
Q	= amount of leached migrant	$[\text{mol m}^{-2}]$
t	= time	$[\text{s}]$
x	= distance from center plane of slab	$[\text{m}]$
H/R	= mole-ratio of hardener to resin	$[-]$

C_{As}	= solubility of A in B	$[\text{mol/mol}]$
$D_B t/l^2$	= nondimensional time	$[-]$
$kl^2 C_{B0}/D_B$	= nondimensional rate constant	$[-]$
$Q/(2lC_{A0})$	= nondimensional amount of leached migrant	$[-]$

<Subscripts>

A	= remaining reactant
B	= penetrating water
C	= hydrolyzed product
T	= sum of A and C
0	= boundary or initial value

Literature Cited

- 1) Reid, R. C., K. R. Sidman, A. D. Schwoppe and D. E. Till: *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 580 (1980).
- 2) Till, D. E., J. E. Ehnthoff, R. C. Reid, P. S. Schwoppe, K. R. Sidman and R. H. Whelan: *Ind. Eng. Chem. Fundam.*, **21**, 163 (1982).