

Diffusion of Acids into Epoxy Resin Compositions

P. KALENDA

Department of Polymers, Institute of Chemical Technology, Pardubice, Czechoslovakia

SYNOPSIS

The study deals with the diffusion of aqueous acid solutions into diethylenetriamine-hardened epoxy resins. The results obtained indicate that the diffusion of acids into epoxy resins is affected heavily by the epoxy resin structure, the epoxide group content in the respective resin, and thus also by the molecular mass of the resin concerned. A straight-line dependence has been found between the diffusion coefficient of acids and the epoxide group contents in the resin.

INTRODUCTION

Epoxy resins belong to the synthetic resins produced in a mass scale all over the world. On their basis various products, such as construction materials and paints, are produced. From the lifetime of such products point of view, it is good to know their resistance to the corrosion due to various aggressive media. The resistance of epoxy resins to the diffusion of solutions was reported earlier for water,¹ sulfuric acid,² hydrochloric acid,² inorganic salt solutions,³ and alkali solutions.³ Comparatively low attention has been devoted to the diffusion of organic acids into epoxy resins.

This work is directed to mapping the diffusion of formic, acetic, and propionic acids into the commercial compositions based on CHS-Epoxy 12, CHS-Epoxy 13, and CHS-Epoxy 15 resins. Further there is followed also the diffusion of sulfuric and hydrochloric acid solutions into these compositions.

Knowledge concerning the diffusion processes enables us to evaluate the appropriateness of applying individual construction materials to various chemically corrosive media, the durabilities of the materials in the media, and thus the potential uses of the materials. The data obtained can be used also for estimating the density and strength of macromolecular network in hardened epoxy resins and for getting appropriate quantitative dependences.

THEORETICAL

The diffusion processes have been treated theoretically by many authors in the past. The mathematical models formulated on the basis of such treatments are covered to a sufficient extent by both the periodic⁴⁻⁶ and (in a critically conceived form) monographic⁷ literature. Almost all such treatments start with Fick's laws.

The diffusion coefficient (D in $\text{mm}^2 \text{s}^{-1}$) is then defined by the Einstein diffusion-mobility relationship reading as follows:

$$D = l_0^2 / \pi t \quad (1)$$

where t = time of diffusion in seconds and l_0 = the depth of diffusion in millimeters.

EXPERIMENTAL

Characteristics of Starting Materials

CHS-Epoxy 12

Manufacturer: Spolek pro chemickou a hutní výrobu, s.p. (Association for the Chemical and Metallurgical Production, State Enterprise), Ústí nad Labem (Czechoslovakia).

Composition: Diane-based epoxy resin of mean molecular mass, without solvent.

Appearance: Semisolid resin.

Density at 20°C: 1.16 g cm^{-3} .

Epoxy equivalent/100 g: 0.3426.

CHS-Epoxy 13

Manufacturer: Spolek pro chemickou a hutní výrobu, s.p., Ústí nad Labem (Czechoslovakia).

Composition: Diane-based epoxy resin of low molecular mass, without solvent.

Appearance: Yellow-brown viscous resin.

Epoxy equivalent/100 g: 0.4308.

CHS-Epoxy 15

Manufacturer: Spolek pro chemickou a hutní výrobu, s.p., Ústí nad Labem (Czechoslovakia).

Composition: Diane-based epoxy resin of low molecular mass, without solvent.

Appearance: Yellow-brown viscous resin.

Viscosity at 20°C: 32.6×10^3 mPa s.

Epoxy equivalent/100 g: 0.5154.

Formic, acetic, propionic, sulfuric, and hydrochloric acids were of analytical-grade quality.

Diethylenetriamine (amine number 1500 mg KOH/1 g).

Preparation of Samples and Measuring Method

The test bodies (sizes 30 by 10 by 4 mm) were prepared by a standard casting procedure comprising homogenizing the solutions composed of 20% dibutyl phthalate and epoxy resin (CHS-Epoxy 12, 13, or 15), adding the diethylenetriamine hardening agent in a necessary amount, and aging at a laboratory temperature for 30 days.

The test bodies were dipped into aqueous 8% formic, 8% acetic, 3% or 8% propionic, 8% sulfuric, or 8% hydrochloric acid solutions. The acid solution volume was always 150 mL per a test body.

The measurements were done in approximately 5-day intervals for about 50 days. Prior to performing the respective measurements, the test bodies were removed from the solutions and dried with a pad of cotton wool, and using a desk microtone the cross-section slices of 10–20 μm in thickness were cut off.

The depth of solution diffusion into the epoxy resins was measured by the indicator microscopic method described earlier.^{5,6,8}

RESULTS AND DISCUSSION

The results obtained have shown that the time of exposure dependences of diffusion depths obtained in the first part (0 to 30 days) of the time interval of interest rise sharply. In the subsequent interval part the rates of diffusion suffer a reduction, the effects being due to the fact that the systems concerned near their energy equilibria. Figures 1 and 2 represent the time dependences of diffusion depths for formic, acetic, propionic, sulfuric, or hydrochloric acids into the CHS-Epoxy 12, CHS-Epoxy 13, or CHS-Epoxy 15 compositions containing the constant amounts of dibutyl phthalate (DBP). The dependences show clearly that there are some differences between individual acids in their diffusion ability. The following order of diffusibility for the acid series investigated has been found:

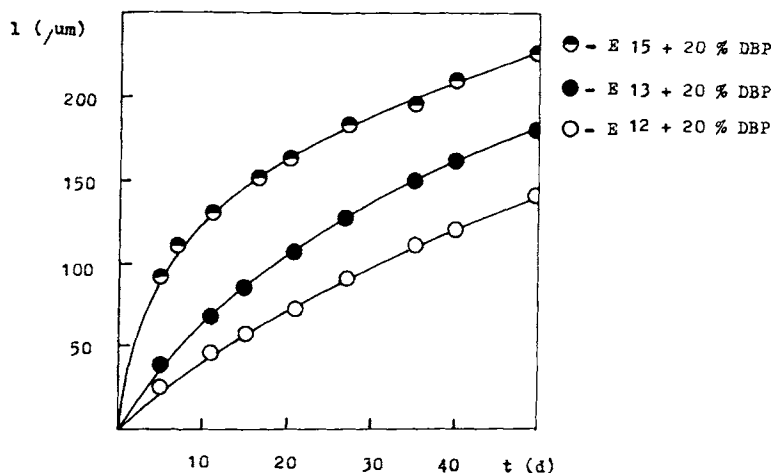
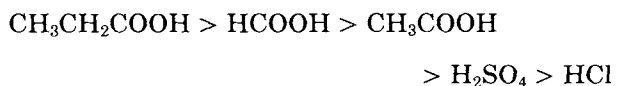


Figure 1 The time of exposure dependence of the depth of diffusion of 8% CH_3COOH solutions into epoxy resins.

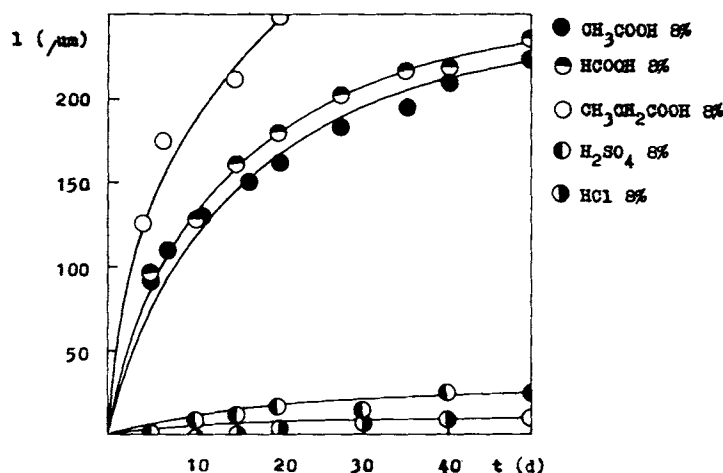
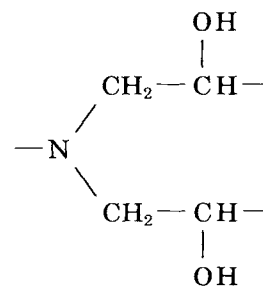


Figure 2 The time of exposure dependence of the depth of diffusion of acid solutions into the epoxy (E 15 + 20% DBP) resin.

Owing to the fact that the propionic acid is really corrosive, the samples of epoxy resins were destroyed in a 10-day exposure to an 8% $\text{CH}_3\text{CH}_2\text{COOH}$ acid solution. Due to this effect propionic acid was used at a concentration as low as 3% in the subsequent experiments. The rapid decomposition of the resin samples reduces namely the accuracy of the measurements, and the reproducibility suffers.

Already in the past there was found⁸ that the differences in diffusibility of individual acids depend on neither the dissociation constants nor the molecular masses. The order of acids found can be explained only by the chemical reactions between the acid and the epoxy resin running parallel with the purely physical processes of diffusion. In such a way the resistance of epoxy resins to the corrosive effects of acids does not depend only on the macromolecular network density but also on the weak places of epoxy resins at the positions that are easily attackable. In

this case the epoxy resins were hardened using diethylenetriamine, which forms the following weak places in the macromolecule on the hardening process:



The Einstein diffusion mobility relationship (1) was used for calculating the D values, which define the diffusion process in a quantitative manner. Table I contains the diffusion coefficients for individual acids and epoxy resin compositions.

Table I Diffusion Coefficients (D) and Their Correlation Parameters (r) for Individual Epoxy Resins and Individual Acid Solutions

Aq. Solns. of Acids	ChS-Epoxy 12		ChS-Epoxy 13		ChS-Epoxy 15	
	$D \times 10^{10}$ ($\text{mm}^2 \text{s}^{-1}$)	r	$D \times 10^{10}$ ($\text{mm}^2 \text{s}^{-1}$)	r	$D \times 10^{10}$ ($\text{mm}^2 \text{s}^{-1}$)	r
HCOOH 8%	44.6	0.989	90.3	0.999	135.9	0.998
CH_3COOH 8%	44.5	0.989	84.5	0.996	121.2	0.998
$\text{CH}_3\text{CH}_2\text{COOH}$ 8% ^a	—	—	—	—	—	—
3%	11.6	0.981	28.9	0.992	48.7	0.989
H_2SO_4 8%	0.2	0.996	0.4	0.994	0.7	0.994
HCl 8%	0.03	0.994	0.05	0.984	0.08	0.982

^a The destruction of samples took place already in a 10-day exposure.

It was found that the dependences of D values on the epoxide equivalents of epoxy resins exhibit a straight-line character. In such a way the epoxide equivalent defines the number of positions in a macromolecule that are easily attackable. In this investigation both the mean-molecular-mass and low-molecular-mass types of epoxy resins were used. The CHS-Epoxy 12 (mean-molecular-mass type) resin has the lowest epoxide equivalent, whereas the CHS-Epoxy 13 (low-molecular-mass type) resin and the CHS-Epoxy 15 (also low-molecular-mass type) resin have the highest number of epoxide groups and, at the same time, the macromolecular network of the highest density.

The results found lead to a conclusion that the diffusion of the acid solutions into the epoxy resins depends on the kind of acid on the one hand and on the type of epoxy resin on the other. Further it was found that the diffusion of acids into epoxy resins is affected more heavily by the chemical processes than by purely physical processes. With the highest probability it can be assumed that the acids react probably with the $-\text{NH}_2$, >NH , and >N- groups contained in the resin after hardening. The following order was found of epoxy resins reflecting their resistance to the acids used: CHS-Epoxy 12 > CHS-Epoxy 13 > CHS-Epoxy 15.

CONCLUSIONS

The results obtained, namely the order of resistances of the individual resins to the penetrations of acid solutions (CHS-Epoxy 12 > CHS-Epoxy 13 > CHS-

Epoxy 15) reflecting the diffusion process as affected by the molecular mass of resin, and the order of diffusibilities of individual acids to the resins ($\text{CH}_3\text{CH}_2\text{CO}_2\text{H} > \text{HCO}_2\text{H} > \text{CH}_3\text{CO}_2\text{H} > \text{H}_2\text{SO}_4 > \text{HCl}$) reflecting the corrosive effects of individual acids, indicate the overwhelming importance of chemical factors compared to the physical factors in the processes involved. The findings outlined help the technologists in gaining orientations when appropriate materials for special applications are sought.

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