Epoxy Resins. I. The Stability of The Epoxy–Trimethoxyboroxine System

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Synopsis

The useful life of a material depends on its environmental exposure. The diglycidyl ether of bisphenol A (DGEBA) cured with trimethoxyboroxine (TMB) was evaluated under various aging conditions. For isothermal aging, the main factor controlling weight loss appeared to be related to the diffusion of the degradation products ($E_{act} = 22.1$ kcal/mole). Chemical decomposition kinetic parameters were obtained using vacuum thermogravimetric analysis (TGA) on powder samples. The thermal decomposition activation energy and the reaction order of cured DGEBA were 37.5 kcal/mole and 1.05, respectively. The hydrolytic aging of this material was also kinetically analyzed, and it was concluded that the weight change was controlled by both water diffusion into the sample and diffusion of hydrolysis products from the sample. During hydrolytic aging below the glass transition temperature, the specimens gained weight up to 0.05 g based on 1-g unaged cured resin and then leveled off. At higher temperatures, the specimens initially gained weight and then began to lose weight, reaching a constant weight gain. The activation energies for water diffusion into the cured resin are 19.5 kcal/mole at temperatures above T_g and 21.5 kcal/mole at temperatures below T_g. The main hydrolysis product was boric acid from reaction of the boroxine ring with water. The time–temperature superposition principle was used for the weight loss study on isothermal and isothermal hydrolytic aging. The scale factor in this approach was found to be the ratio of the diffusion coefficient at the temperature of interest to that at a reference temperature.

INTRODUCTION

Polymers of reasonably good stability and mechanical properties useful in various materials of construction are based on the epoxy resins of the diglycidyl ether of bisphenol A (DGEBA). The properties of a cured epoxy resin are dependent on the type and the amount of curing agent used. Trimethoxyboroxine (TMB) is a Lewis acid and has three active sites, which should give a highly crosslinked, stable polymer with good mechanical properties if the epoxide groups are completely cured with this curing agent.

Brunner and Waghorn[1] first used TMB to cure DGEBA-based liquid polyepoxide and obtained a hard coating. Lee and Neville[2] investigated this epoxy curing agent and concluded that TMB is an anhydride-type curing agent and can be used as a primary curing agent or as a cocuring agent for epoxy resins. In a study of various boron-containing compounds as curing agents for epoxy resins, for the purpose of increasing the thermal stability of the result polymers, Haworth and Pollnow[3] concluded that the boroxine–amine complex showed considerable promise as a homogeneous curing agent. This latent curing agent gave cured epoxy resins with heat deflection temperatures ranging from 80 to 120°C.

TMB was also used in the preparation of epoxy resin foams. Chen and Nixon[4,5] used a primary polyamine and TMB to obtain a highly crosslinked polymer which remained rigid at temperatures up to 300°C. The addition of

Journal of Applied Polymer Science, Vol. 23, 3355–3374 (1979)
0021-8995/79/0023-3355$01.00

a mixture of boric acid and sodium borate improved the self-extinguishing properties of the epoxy–boroxine–amine system due to boron oxide formation which is assumed to form a glasslike coating on the burning mass while hindering the access of oxygen and the egress of volatile gases. Shepard[6] prepared epoxy resin foams with high closed cell content by curing a polyepoxide at room temperature with a TMB–BF_3–$EtNH_2$ complex curing agent. Lee[7] used TMB as the epoxy curing agent in the presence of a liquid hydrocarbon, halogenated hydrocarbon, or borate ester foaming agent to obtain rigid foams showing good hydrolytic resistance with slow-burning and good mechanical properties, all useful for building wall insulation and encapsulating materials.

Parker, Fohlen, and Sawko[8] first used TMB as a curing agent to prepare transparent epoxy panels which had a heat distortion temperature of 110°C. This crosslinked transparent aromatic system was thermomechanically stable up to 400°C, gave a high char yield, and had a high tensile strength. Recently, Lopata, and Riccitiello[9] investigated this epoxy–TMB system by differential thermal analysis (DTA) and noted the occurrence of three exothermic peaks at approximately 390, 430, and 470°C, with the major exotherm at 430°C.

The useful life of a material depends on its environmental exposure. Thus, the stability of a material under environmental use conditions is a very important factor related to its ultimate utility. The studies were primarily concentrated on the curing of the epoxy resin or epoxy resin foam preparation using TMB as a primary curing agent or as a cocuring agent and on the curing reactions between epoxide and TMB. No information about the stabilities of TMB-cured epoxy exposed environmentally have been studied, since TMB was found to be useful in the preparation of cured epoxy resins. In this study, the epoxy–TMB system was evaluated under various aging conditions, and the factors which control the aging were also investigated.

The stability of an epoxy resin system was determined by the structure of the resin itself, the curing agent, and the amount of the curing agent.[10,11] Two approaches used for evaluating a new polymeric material for its application at elevated temperature were dynamic thermal analysis and isothermal aging. The first gives the highest temperature at which the polymer can be expected to maintain its structure during a relatively short time period. The second is a more reliable approach to determine the useful life of a polymeric material under specified service conditions. The weight loss is useful as an initial screening test, and then if a polymer seems promising, the more detailed evaluations including physical properties are measured.[12]

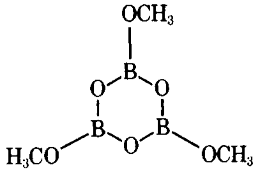
The ether linkage in the simple organic molecule has much greater hydrolytic resistance than the corresponding ester, acetal, or amide links. Thus, it may be expected that the polyether should have high resistance to hydrolysis. Murray and Stein[13] studied the absorption–decomposition characteristics of DGEBA resin cured by *m*-phenylenediamine, $BF_3 \cdot NH_2CH_2CH_2OH$, and chlorendic anhydride under various exposure media including deionized water, acid aqueous solution, and alkali aqueous solutions. The samples gained weight and leveled off after 1% weight gain in the aqueous media and contained small air bubbles observed under a microscope. They concluded that the samples were stable chemically under the conditions employed and that a physical structure change probably occurred during aging. In this study, the hydrolytic aging of the DGEBA–TMB system was carried out at several temperatures in order to determine the factors affecting the deterioration of the polymeric material.

Due to the broad scatter of data and the irregular decay process, it is very difficult to predict the useful life of a polymeric material in the exposure environment. Doyle[14] applied the superposition principle to the study of aging effects on polymeric materials. By means of the superposition principle, it is possible to select one temperature as a reference and to shift or to superposition the data points for all the other aging temperatures along the time axis to times that are equivalent at the reference temperature. Thus, all of the data points are employed to define a single master curve which more clearly illustrates the variation in properties. In this study the superposition principle was also applied to treat the results from isothermal and isothermal hydrolytic aging. Furthermore, the shift factor or the scale factor was investigated.

EXPERIMENTAL

Sample Preparation

The material used in this study was prepared by casting the mixture of Shell Epon-825 (epoxy number of 192 g per eq. of epoxide group, determined by titrating the epoxy resin in a chloroform and chlorobenzene mixture with a solution of hydrogen bromide in acetic acid)[15] mixed with 5 phr of the curing agent, trimethoxyboroxine (Aldrich), between two Mylar films at 80°C for 3 hrs. The Mylar films were removed and the resins cured completely at 135 and 180°C for 3 and 2.5 hr, respectively.[8,9] The cured epoxy sheet, about 1.2 mm thick, was cut into 19 × 19 mm^2 samples for weight change studies during isothermal aging and isothermal hydrolytic aging.



Trimethoxyboroxine

Isothermal Aging

In the case of the isothermal aging, the specimens were put into an isothermal air circulating oven (Fisher Isotemp Oven, Senior Model) and kept at a specified temperature. The temperatures used in this study were 175.3, 189.9, 211.1, and 220.0°C. The samples were weighed before and after aging. The surface morphology of aged and unaged samples was obtained from scanning electron microscopy.

Isothermal Hydrolytic Aging

For isothermal hydrolytic aging studies, the specimens were immersed in water and held at constant temperature in a flask. The temperatures in this study were 44.4, 53.4, 62.1, 74.5, 81.7, and 100°C. The samples were removed from water, wiped free of surface moisture, and weighed immediately. To obtain the weights of the samples after aging, the specimens were put in a vacuum desiccator until each of them showed a constant dry weight.

Effects of Acid and Base on Hydrolytic Aging

The effects of acid and base on hydrolytic aging were determined at a constant temperature of 89.5°C. Aqueous solutions of sulfuric acid with concentrations of $1.279M$ and $0.535M$ and aqueous solutions of sodium hydroxide with concentrations of $1.480M$ and $0.750M$ were used for this study. The gravimetric analysis followed the same procedures as for the neutral hydrolytic aging.

Analysis of Hydrolytic Product

After 405 hr of hydrolysis of the cured samples in boiling water, the aqueous solution was collected and then evaporated to dryness. The dried product was reacted with methanol and then distilled at 65°C. The distillate was collected for gravimetric analysis as boric acid.[16] The infrared spectrometer (Perkin–Elmer Model 521) was also employed to identify the hydrolytic products.

Scanning electron microscopy was used to observe the surface morphology changes that occurred during hydrolytic aging.

RESULTS AND DISCUSSION

Isothermal Aging

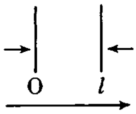
The specimens during isothermal aging changed from clear to yellow, to brown, to very dark, and from transparent to opaque. The rate of color change was dependent on the exposure temperature and time.

In the case of the weight change study during isothermal aging, it can be observed that the weight of the specimen decreased with aging, and the rate of its change increased as the temperature was raised. From a mass transfer point of view, the solid–gas reaction can be considered to consist of the following steps[17]; (1) diffusion of gas reactants across the "fluid film" surrounding the solid, (2) diffusion of the gas reactants through the solid layer, (3) adsorption of the "fluid" reactants at solid reactant surface, (4) chemical reaction with the solid surface, and (5) diffusion of the gas product away from the reaction surface through the solid media and through the "fluid film" surrounding the solid. The slowest step will be rate determining.

If the rate-determining step is assumed to be the diffusion of volatile product through the solid to the surrounding gas, Fick's second law can be applied to the quantitative study of this system:

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

where C is the concentration of diffusing material at time t and at position x. By using the semiinfinite slab approach,[18] this equation is solved with the boundary conditions of $C = C_0$ at $t = 0, x > 0$; $C = C_\infty$ at $t = t_\infty, x > 0$; $C = C_\infty$ at $x = 0, l, t > 0$; $\partial C/\partial x = 0$ at $x = \frac{1}{2}l$



to give the solution

$$\frac{W - W_0}{W_\infty - W_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-[(2n+1)\pi/l]^2 Dt\}}{(2n+1)^2} \tag{2}$$

where W_0, W, and W_∞ are the weights of the specimen at exposure times equal to 0, t, and ∞, respectively; D is the diffusion coefficient of volatile degradation product; l is the thickness of the sheet sample; and n is any integer. It was assumed that the diffusion coefficient was independent of the concentration of the diffusing material and the structure changes that occurred in the solid during the reaction.

For long-time diffusion, $t \to \infty$, eq. (2) may be approximated by

$$\frac{W - W_0}{W_\infty - W_0} = 1 - \frac{8}{\pi^2} \exp\left(\frac{-\pi^2 Dt}{l^2}\right) \tag{3}$$

and for short time diffusion, $t \to 0$, the equation becomes

$$\frac{W - W_0}{W_\infty - W_0} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{1/2}$$

or

$$\frac{W_0 - W}{W_0} = \frac{W_0 - W_\infty}{W_0} \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{4}$$

The maximum weight loss for the highest aging temperature is about 12% in this study. It was assumed that eq. (4) can be applied for weight loss analysis with such a low change. In this study the specimen thickness has been controlled so as to be relatively constant. By assuming the final weights of the specimen after infinite aging to be the same for all aging temperatures, eq. (4) may be simplified to the form

$$\frac{W_0 - W}{W_0} = Kt^{1/2} \tag{5}$$

where K was equal to

$$\frac{W_0 - W_\infty}{W_0} \frac{4}{l}\left(\frac{D}{\pi}\right)^{1/2}$$

a constant, dependent only upon temperature.

The variation of weight loss against the square root of exposure time during isothermal aging is shown in Figure 1. The slopes at various temperatures are determined in Table I.

Diffusion may be regarded as a thermally activated process with the relationship between D and T expressed by the Arrhenius equation

$$D = D_0 \exp(-E/RT) \tag{6}$$

Combining eq. (6) and the definition of K, eq. (7) may be obtained:

$$\log K = \log\left(\frac{W_0 - W_\infty}{W_0}\right) \frac{4}{l}\left(\frac{1}{\pi}\right)^{1/2} + \frac{1}{2}(\log D_0) - \frac{E}{2 \times 2.3RT} \tag{7}$$

The activation energy can be obtained from the slope of the curve of log K versus the reciprocal of the temperature in K. The apparent activation energy for this process from Figure 2 is 22.1 kcal/mole.

A good approach for predicting the property change of a material during aging

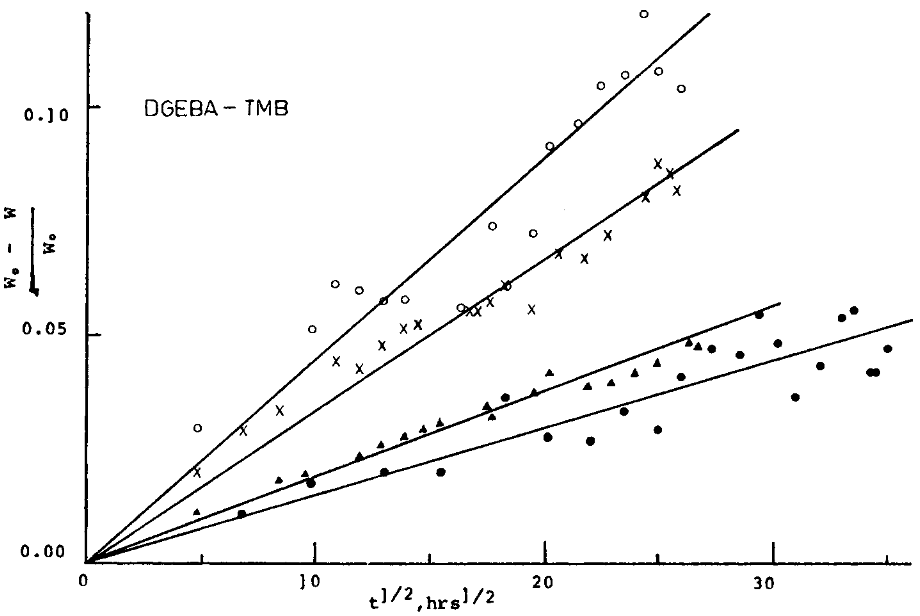


Fig. 1. Weight loss vs square root of time during isothermal aging at various temperatures: (○) 220.0°C; (×) 211.1°C; (▲) 189.9°C; (●) 175.3°C.

TABLE I
Parameters Calculated from the Results of Isothermal Aging at Various Temperatures

T, °C	175.3	189.9	211.1	220.0
$K \times 10^3$, hr$^{-1/2}$	1.47	1.89	3.35	4.40
α_f	0.19	0.32	1.00	1.73

at a normal temperature was to use the time–temperature superposition principle which has been developed and applied to some polymeric material.[14] In this case the weight change during deterioration was proportional to the square root of exposure time. In order to apply the time–temperature superposition toward the degradation effect on the weight change of polymeric material, the scale factor should be obtained from suitable parameters.

Equation (2) was a common expression for the weight change of a material during aging. At any specific value of changed weight W_f $(W_f - W_0)/(W_\infty - W_0)$ becomes a constant at t_f, which was defined as elapsed time. If a particular aging temperature T_r was chosen as a common reference temperature, eq. (8) can be obtained from eq. (2) for expressing the relationship between exposure time and temperature related to the reference temperature at the same degree of deterioration:

$$\sum_{n=0}^{\infty} \frac{\exp\{-[(2n+1)\pi/l]^2 Dt_f\}}{(2n+1)^2}\,_r = \sum_{n=0}^{\infty} \frac{\exp\{-[(2n+1)\pi/l]^2 D_r t_{fr}\}}{(2n+1)^2} \tag{8}$$

The real solution of eq. (9) was

$$\exp[-(\pi/l)^2 Dt_f] = \exp[-(\pi/l)^2 D_r t_{fr}] \tag{9}$$

which can be simplified as

$$D/D_r = t_{fr}/t_f = \alpha_t \tag{10}$$

where α_t is a scale factor or shift factor.

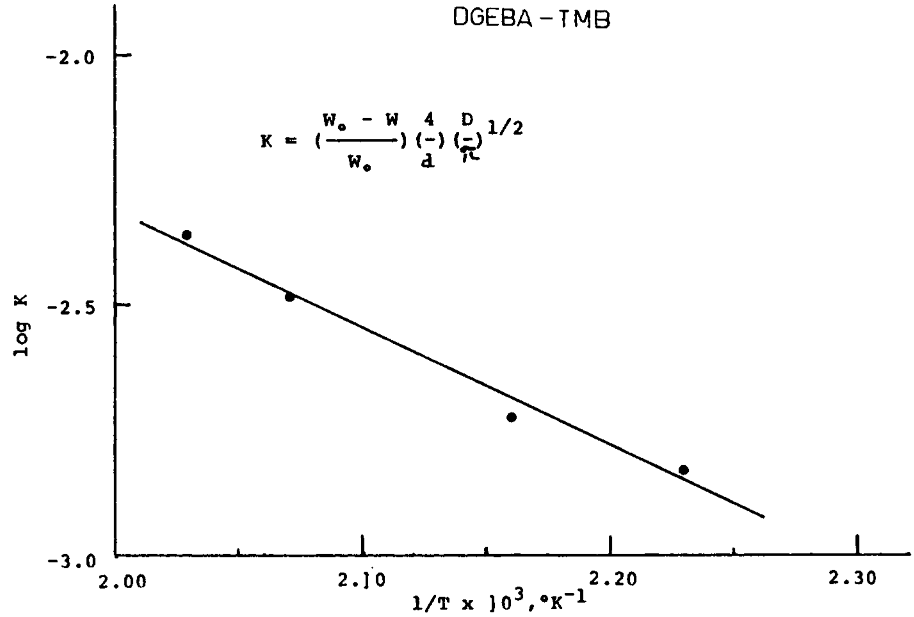


Fig. 2. Evaluation of the diffusion activation energy of the volatile products formed during isothermal aging.

By applying the Arrhenius relation, eq. (6), eq. (11) can be obtained:

$$\ln \alpha_t = \frac{E}{R}\left(\frac{1}{T_r} - \frac{1}{T}\right) \qquad (11)$$

From these results it can be observed that the k parameter in the original time–temperature superposition principle was equal to the diffusion coefficient of the diffusing material into or out of the degrading sample.

Figure 3 shows the weight variation of isothermally aged specimens as a function of exposure time after treatment with the time–temperature superposition principle. The scale or shift factors for various aging temperatures are shown in Table I. A master curve calculated from the diffusion coefficient of the volatile product as a result of aging at a temperature, 211.1°C, is also shown in Figure 3 as compared with the experimental results. It can be observed that the theoretical calculation was in agreement with the experimental results. From this, it can be confirmed that the degradation effect on the weight change of a bulk material is controlled by the diffusion of the volatile degradation products.

Figure 4(a) is a scanning electron microscopic photograph of sample aged at 211.1°C for 480 hr. From this, crazing phenomenon can be observed by comparing it with that of the unaged specimen, Figure 4(b). The crazing may be caused by the stress induced from the shrinkage of the sample after releasing the degradation product and from the char formation which weakened the structure of the degrading surface.

As discussed above, the weight loss of a polymeric material during degradation was controlled by the diffusion of the degradation product through the material. The rate of diffusion was dependent primarily on the physical structure of the material. To understand the kinetic aspects of a decomposition reaction,

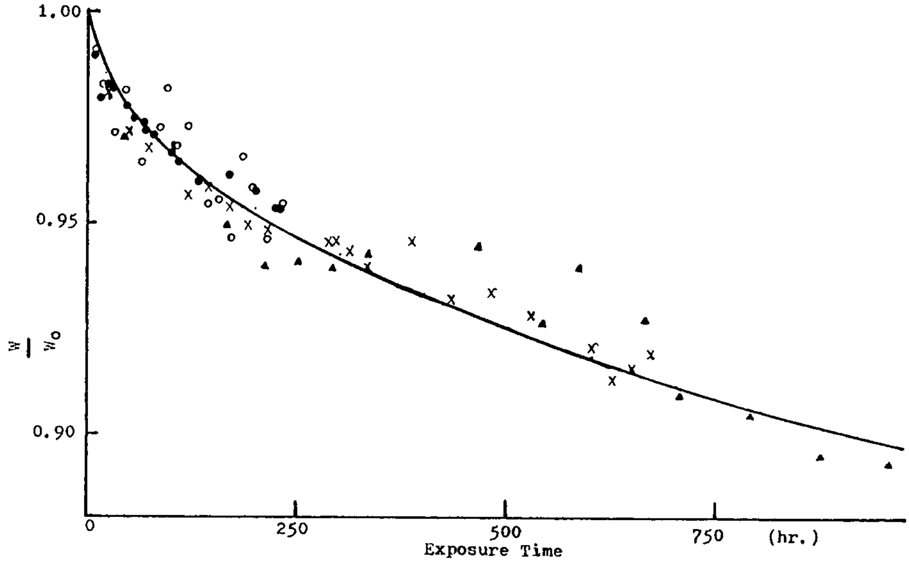


Fig. 3. Relationship between residue weight of isothermally aged specimens (based on 1-g unaged sample) and exposure time after treating with time–temperature superposition principle. Solid line is obtained from theoretical calculation for reference temperature, 211.1°C: (▲) 220°C; α_f = 1.73; (×) 211.1°C, α_f = 1.00; (●) 189.9°C, α_f = 0.32; (○) 175.3°C, α_f = 0.19.

thermogravimetric analysis (TGA) turns out to be a useful tool. Under vacuum condition, the decomposition product can be forced out of the degrading material and the rate-controlling step for the weight loss can also shift from a diffusion process to a chemical process. Freeman and Carroll[19] first applied both techniques and derived the equation, eq. (12), to calculate kinetic parameters for nonreversible reactions

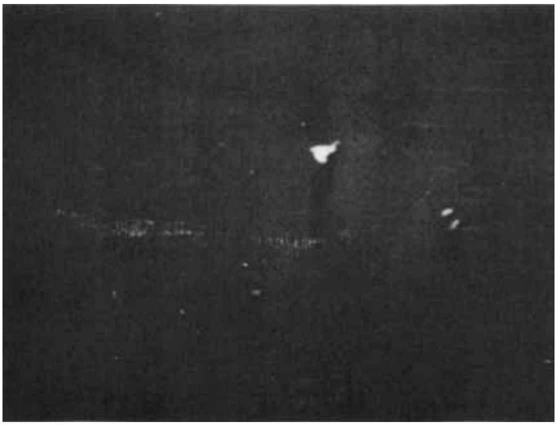
$$\Delta \log (dw/dt) = n\, \Delta \log W_r - (E/2.3R)\, \Delta(T^{-1}) \qquad (12)$$

where $W_r = w_c - w$, n is reaction order, w_c is weight loss at completion of reaction, E is activation energy, w is total weight loss up to time t, R is ideal gas constant, and T is absolute temperature. Figure 5 resulted from calculations from the TGA thermogram for the DGEBA–TMB cured system (Fig. 6). The activation energy and reaction order for the degradation reaction of DGEBA–TMB cured system in this study are 37 kcal/mole and 1.05, respectively. Anderson[20,21] also studied the pyrolysis of the DGEBA hardened with maleic anhydride (E = 34 kcal/mole and n = 1.07), and with m-phenylenediamine (E = 31 kcal/mole and n = 1.03).

Isothermal Hydrolytic Aging

In the case of isothermal hydrolytic aging in distilled water, there are two different phenomena, Figures 7 and 8, that have been observed: (1) at aging temperatures lower than 62.1°C, the samples gained weight and leveled off at about 5% weight gain; and (2) at aging temperatures higher than 74.5°C, the samples gained weight initially up to a maximum weight gain of about 6% to 8% and then started to lose weight and leveled off at about 3% of weight gain. This latter phenomenon is different from that of other curing systems,[13] which showed the former phenomenon only.

(a)



(b)

Fig. 4. Scanning electron microscopic pictures: (a) sample aged at 211.1°C for 480 hr (2000×); (b) unaged sample (1000×).

There are four possible explanations for this phenomenon. The first possibility was cavity formation which was observed in the samples aged at a temperature higher than 74.5°C only. The cavity in the sample was visible and can be detected by (1) annealing the aged sample above its softening temperature whereupon the sample recovered its clarity except for the cavitation sections; (2) the maximum weight gain for high-temperature aging which is higher than that from low-temperature aging (8% vs 5%); and (3) observing the rough surface and hole formation in the high-temperature-aged sample by use of the scanning electron microscope, Figures 9(a), 9(b), and 9(c). The cavity formation may be due to the high local vapor pressure in the sample from the high evaporation rate of absorbed water at high temperature and the inhomogeneity of the structure of cured epoxy resins previously noted by others.[22-26] As described by others, the cured epoxy consisted of moderate molecular weight agglomerates and a low molecular weight surrounding matrix. The inhomogeneity of the structure may induce an inhomogeneous distribution of absorbed water, swell the aging specimen, develop local vapor pressure, and stress the material. Figure 9 shows small

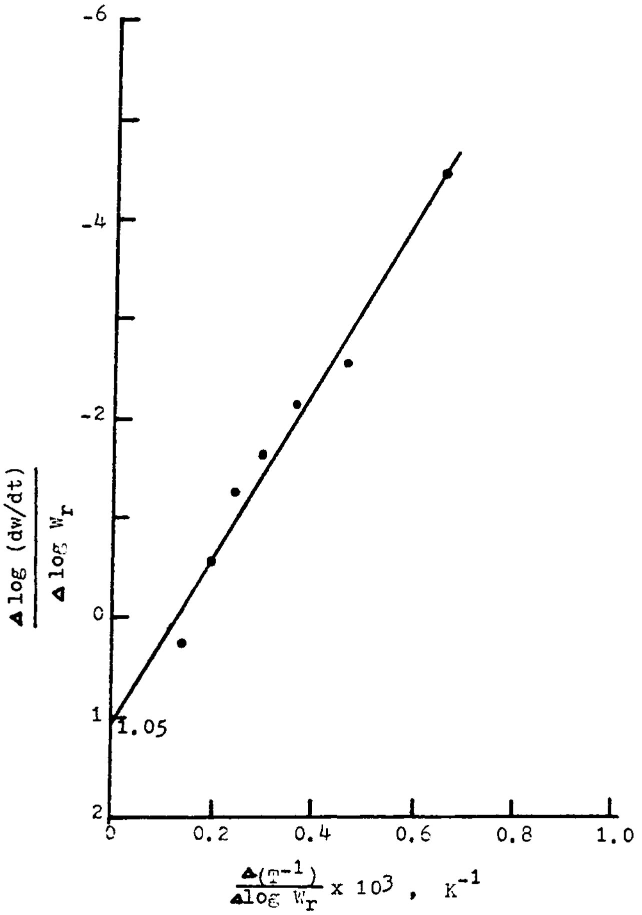


Fig. 5. Calculation for kinetic parameters of DGEBA–TMB thermal degradation from TGA results in vacuum. $E = 37$ kcal/mole.

holes formed on the sample surface which may be due to stress development as a result of molecular relaxation and nonhomogeneous swelling of the material at this temperature. This phenomenon could also increase the water absorption, and this in turn can reduce intermolecular interactions. The reaction of the boroxine group with water may also create the active sites for developing cavities.

Specimens were placed in water at 89.5°C for 112 hr to obtain an 8% maximum weight gain. Cavities developed in the sample and were then immersed 55.5°C water. The results indicated no observable weight change. This indicated that cavity formation alone cannot account for the weight loss which occurred during high temperature aging.

The other possibility is related to the softening of the specimen at high temperature. After water diffused into the sample, it could act as a plasticizer and thus decreased the glass transition temperature. The samples were in a rubbery state after saturation with hot water. This explanation was suitable for interpreting the weight loss during high temperature aging.

From a phenomenologic view, the diffusion coefficients are quite different

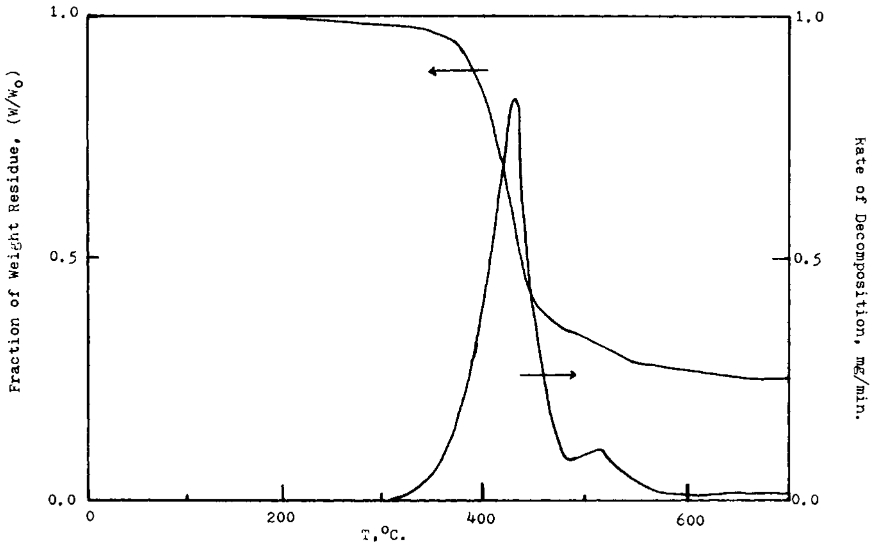


Fig. 6. TGA thermogram of the DGEBA-TMB system in vacuum.

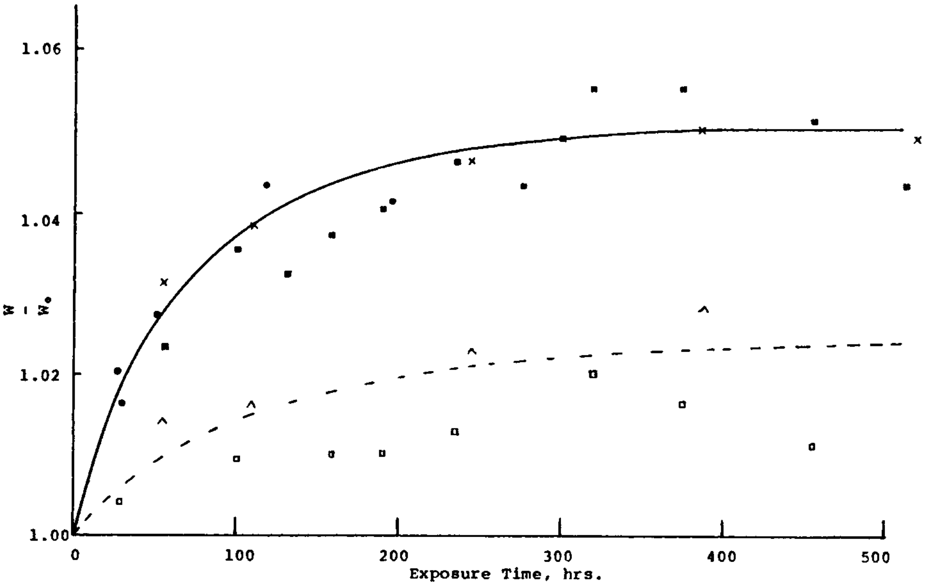


Fig. 7. Weight variation of the specimens (based on 1-g unaged sample) during isothermal hydrolytic aging at temperatures below 62.1°C as function of exposure time. All results were treated with time-temperature superposition principle. (- - -) Theoretical result calculated from diffusion coefficient of water at 53.4°C. Wet sample: (×) 62.1°C; (●) 53.4°C; (■) 44.4°C. Dry sample: (Λ) 62.1°C; (□) 44.4°C.

below and above the transition temperature.[27] In this study it was observed that the energy of activations for water diffusion coefficients below and above the glass transition temperature were 23.4 and 19.1 kcal/mole, respectively, and that for the hydrolytic product above the glass transition temperature was 21.5 kcal/mole. The third possibility was related to the low solubility of boric acid (major hydrolytic product) in water at low temperature. The solubility of boric

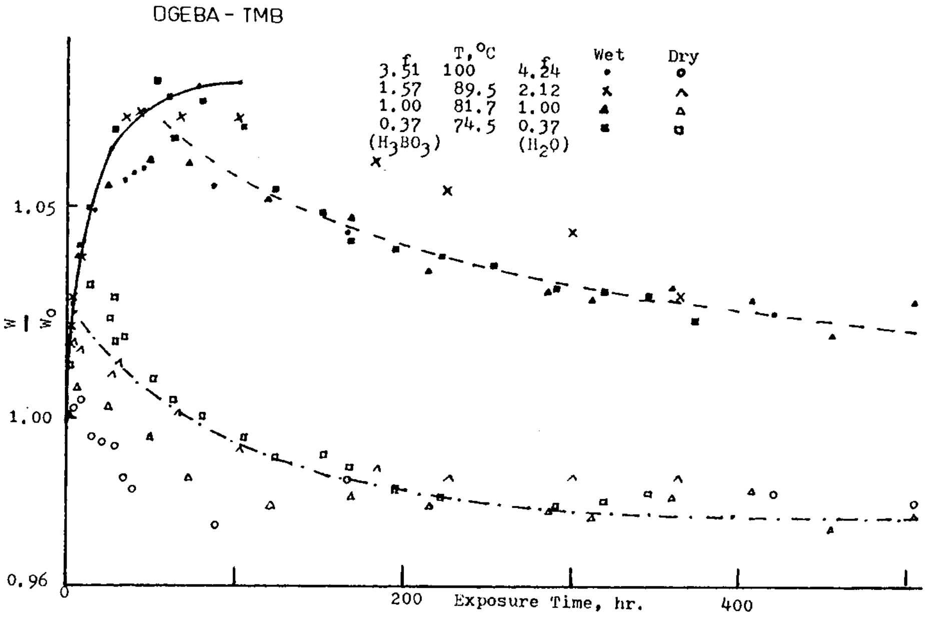
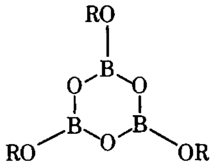


Fig. 8. Weight variation of the specimens (based on 1 g unaged sample) during isothermal hydrolytic aging at various temperature after treating with time–temperature superposition principle. (---) Theoretical calculation of water diffusion into sample; (- -) and (- · -) master curves for wet and dry sample, respectively.

acid[28] was 29.6 g/100 ml water at 100°C and only 6.35 g/100 ml water at 30°C. Because the sample absorbed less than 5% of water based on 1 g unaged sample, only a small amount of boric acid dissolved in the absorbed water at low temperature. Weight loss was not observed (Fig. 8) in low-temperature aging throughout the entire study period, and thus it appears that the solubility of boric acid may not play an important role related to weight loss.

Another possibility is that the hydrolysis rate was very low at low temperatures. However, the samples hydrolytically aged at low temperature also showed weight gain after drying as shown in Figure 8. The maximum weight gain for hydrolytically aged dried samples was about 3%, which was equivalent to the stoichiometric result, 2.9%. This indicated that the low hydrolysis rate was not suitable to account for the weight loss phenomenon during high-temperature hydrolytic aging.

The weight increase was due to water absorption, while the weight decrease was due to hydrolysis and leaching of fragments from the cured epoxy. The dried weight of the aged sample also leveled off after a certain aging period. This indicated that only part of the material can be reacted with water and diffuse out of the sample. From these and the previous wet specimens, the water absorption can be obtained. A possible explanation related to boric acid formation during hydrolysis is indicated in eq. (13):



$$+ 6H_2O \longrightarrow 3H_3BO_3 + 3ROH \qquad (13)$$

In support of this assumption, it is known that TMB, which has —B—O—C bonds analogous to the cured epoxy, reacted very rapidly with water to form methanol and boric acid.[29]

The weight of the wet sample (W_{wet}) and the dried sample (W_{dry}) after leveling off, of water absorption ($W_{\mathrm{H_2O}}$), of the extrapolated weight gain at $t = 0$ (W_{ext}) of the residue (W_{ROH}) after drying and of boric acid ($W_{\mathrm{H_3BO_3}}$) are summarized in Table II.

Table II showed that the experimental results were coincident with stoichiometric calculations from eq. (13). The DSC thermogram and the infrared spectrum of the dried hydrolytic product were the same as those for boric acid. This supported the assumption that the weight loss was due to boric acid formation. Gravimetric analysis indicated 92% conversion to boric acid after 405 exposure hours at 100°C water.

Diffusion theory can also be applied to hydrolytic aging. Combining the diffusion phenomenon and the hydrolytic reaction, eq. (13), eq. (14) can be obtained if the diffusion coefficient is assumed to be concentration independent:

$$\frac{\partial C_{\mathrm{H_2O}}(x,t)}{\partial t} = D_{\mathrm{H_2O}} \left[\frac{\partial^2 C_{\mathrm{H_2O}}(x,t)}{\partial x^2} \right] - R_{\mathrm{H_2O}} \tag{14}$$

where $C_{\mathrm{H_2O}}(x,t)$ is the concentration of water in the sample at position x and time t and $R_{\mathrm{H_2O}}$ is the reaction rate. Only one diffusion direction is considered, because a square sheet is used in the study. The boundary conditions were the same as in the isothermal aging analysis.

From the stoichiometry, the relation of the reaction rates for each component was

$$-6R_{\mathrm{epoxy}} = -R_{\mathrm{H_2O}} = 2R_{\mathrm{H_3BO_3}} = 2R_{\mathrm{ROH}} \tag{15}$$

For the case of high-temperature hydrolytic aging, the weight loss is mainly due to boric acid formation, and the concentration rate change of boric acid will be

$$\frac{\partial C_{\mathrm{H_3BO_3}}}{\partial t} = R_{\mathrm{H_3BO_3}} - D_{\mathrm{H_3BO_3}} \frac{\partial^2 C_{\mathrm{H_3BO_3}}}{\partial x^2} \tag{16}$$

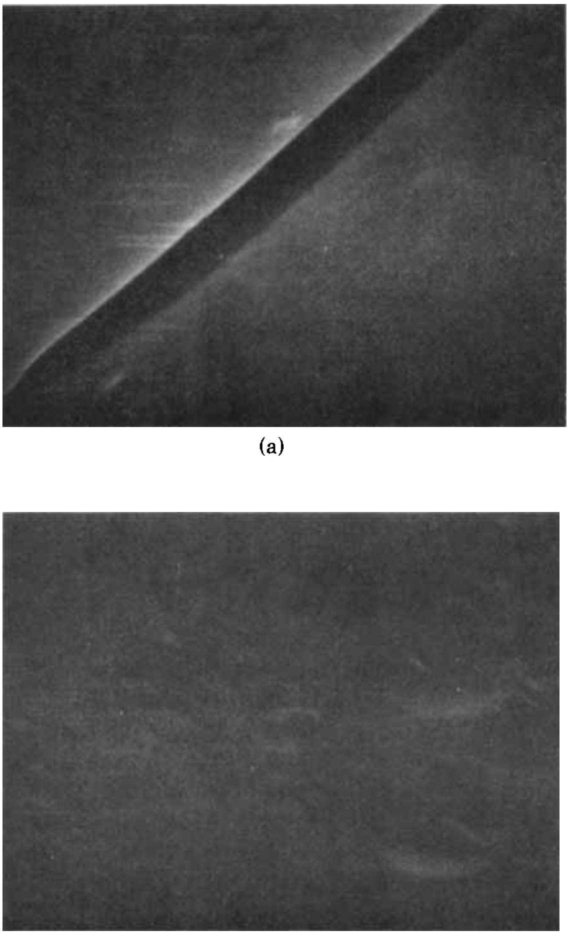
Therefore

$$\frac{\partial C_{\mathrm{H_3BO_3}}}{\partial t} = -\frac{1}{2} R_{\mathrm{H_2O}} - D_{\mathrm{H_3BO_3}} \frac{\partial^2 C_{\mathrm{H_3BO_3}}}{\partial x^2} \tag{17}$$

Based on the mass balance, the mass accumulation was equal to the mass input minus the mass output. The overall weight change rate for the entire system should then be

$$\frac{\partial W}{\partial t} = M_{\mathrm{H_2O}} \frac{\partial C_{\mathrm{H_2O}}}{\partial t} + M_{\mathrm{H_3BO_3}} \frac{\partial C_{\mathrm{H_3BO_3}}}{\partial t} + M_{\mathrm{ROH}} R_{\mathrm{ROH}} + M_{\mathrm{epoxy}} R_{\mathrm{epoxy}} \tag{18}$$

where M is the molecular weight of the various components, and $\partial W/\partial t$ is the total weight change per unit volume at position x and time t. Combining eqs. (14), (16), (17), and (18), eq. (19) may be obtained:



(a)

(b)

Fig. 9. Scanning electron microscopic photograph of hydrolytically aged samples: (a) and (b) 80°C for 24.1 hr; (c) at 100°C for 624 hr (5000×).

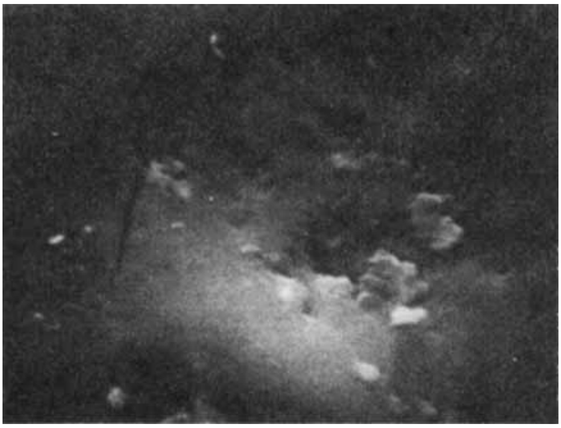
$$\frac{\partial W}{\partial t} = M_{H_2O}D_{H_2O}\frac{\partial^2 C_{H_2O}}{\partial x^2} - M_{H_3BO_3}D_{H_3BO_3}\frac{\partial^2 C_{H_3BO_3}}{\partial x^2} - \left(M_{H_2O} + \frac{1}{6}M_{\text{epoxy}} - \frac{1}{2}M_{H_3BO_3} - \frac{1}{2}M_{\text{ROH}}\right)R_{M_2O} \quad (19)$$

The results shown in Figures 7 and 8 indicated that the dry sample gained weight very rapidly, indicating that the reaction was very fast. The weight change was determined by a diffusion process. However, as the aging time approaches zero, the weight change was initially only attributed to the water absorption. Thus, eq. (19) can be simplified to

$$\left(\frac{\partial W}{\partial t}\right)_{t=0} = M_{H_2O}D_{H_2O}\frac{\partial^2 C_{H_2O}}{\partial x^2} \quad (20)$$

The solution of this equation was the same as that of eq. (2). Therefore, eq. (5) may be applied in this case to obtain the diffusion coefficients of water at various temperatures.

The variations of $(W - W_0)/W_0$ against $t^{1/2}$ are shown in Figure 10, and the



(c)

Fig. 9. (*Continued from previous page.*)

TABLE II

The Weight of Sample after Leveling Off and the Weight of Hydrolysis Products During Hydrolytic Aging[a]

T, °C	100	81.7	74.5	62.1	44.4
W_{wet}, g	1.016	1.025	1.027	1.050	1.050
W_{dry}, g	0.979	0.977	0.980	1.030	1.020
W_{H_2O}, g	0.037	0.048	0.047	0.020	0.030
W_{ext}					
g	1.067	1.077	1.080	1.050	1.050
Calcd.	0.050	0.050	0.050	0.050	0.050
$W_{H_3BO_3}$					
Expt.	0.051	0.052	0.053	0.051	0.041
Calcd.	0.979	0.979	0.979	0.979	0.979
W_{ROH}, expt.	0.979	0.977	0.980	—	—

[a] All are based on 1-g unaged dry sample. T, Temperature; W_{wet}, weight of wet sample; W_{dry}, weight of dried aged sample; W_{H_2O}, water absorption; W_{ext}, extrapolated weight at $t = 0$; $W_{H_3BO_3}$, weight of boric acid formation; W_{ROH}, sample weight after long-term hydrolytic aging.

TABLE III

Parameters Calculated from the Results of Isothermal Hydrolytic Aging at Various Temperatures

T, °C	44.4	53.4	62.1	74.5	81.7	89.5	100
$K \times 10^3$, hr$^{-1/2}$	2.37	3.87	6.39	10.9	13.5	19.7	27.8
$(W_\infty - W_0)/W_0$	0.05	0.05	0.05	0.08	0.08	0.08	0.08
$D \times 10^5$, cm^2/hr^2	0.64	1.69	4.62	5.25	8.05	17.1	34.1
$\alpha_f(H_2O)$	0.61[a]	1.00[a]	2.73[a]	0.65[b]	1.00[b]	2.12[b]	4.24[b]
$\alpha_f(H_3BO_3)$	—	—	—	0.37[b]	1.00[b]	1.57[b]	3.51[b]

[a] The result was calculated by using 53.4°C as reference temperature.

[b] The result was calculated by using 81.7°C as reference temperature.

slopes at $t = 0$ at various temperatures were obtained. By assuming that the maximum water absorption of the samples under low-temperature and high-temperature aqueous conditions was 0.05 and 0.08 g, respectively, and based on 1 g unaged sample, the diffusion coefficient can be obtained from the definition of the K value. The results are shown in Table III.

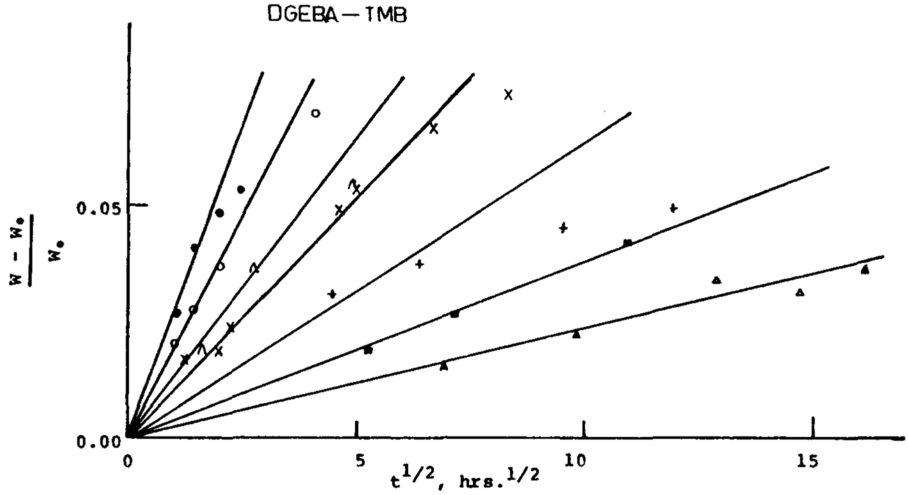


Fig. 10. Weight gain during isothermal hydrolytic aging at various temperatures vs square root of exposure time: (●) 100°C; (○) 89.5°C; (Λ) 81.7°C; (×) 74.5°C; (+) 62.1°C; (■) 53.4°C; (▲) 44.4°C.

The activation energy of water diffusion into the cured epoxy resin was obtained from Figure 11 by applying the Arrhenius equation. There are two activation energies observed. Under low-temperature hydrolytic aging this activation energy was 19.1 kcal/mole instead of 23.4 kcal/mole for the high-temperature hydrolytic aging. Hefty[30] used the time–temperature superposition principle for isothermal humidity aging and obtained an activation energy of 16 kcal/mole.

Owing to the diffusion of water into the sample, boric acid formation and the diffusion of boric acid out of the sample occurring simultaneously, the hydrolytic product diffusing out of the sample can be analyzed in the same manner as water diffusion into the sample. But the scale factor at various aging temperatures can be obtained from the exposure time as shown in eq. (10). The activation energy for the hydrolytic product diffusing out the sample can be obtained from eq. (11) and scale factors (Table III) as shown in Figure 11. The activation energy hydrolytic product to diffuse out of the sample was 21.5 kcal/mole at temperatures above 74.5°C.

Figures 7 and 8 showed the experimental and theoretical results for the weight change due to hydrolytic aging as a function of exposure time. All results have been treated with the time–temperature superposition principle. The results were in agreement with the experimental data.

During the isothermal hydrolytic aging, all specimens changed from transparent to white, opaque samples. Transparency reappeared after annealing these samples at a temperature higher than their glass transition temperature.

Hydrolytic aging in different concentrations of aqueous solutions of sulfuric acid and sodium hydroxide at 89.5°C are shown in Figures 12 and 13. In both cases the weight change was only slightly dependent on the concentration of acid or alkali solution. The initial weight gain versus the square root of aging time for both cases are shown in Figures 14 and 15. These results indicated that isothermal hydrolytic aging in distilled water appeared to give slightly higher

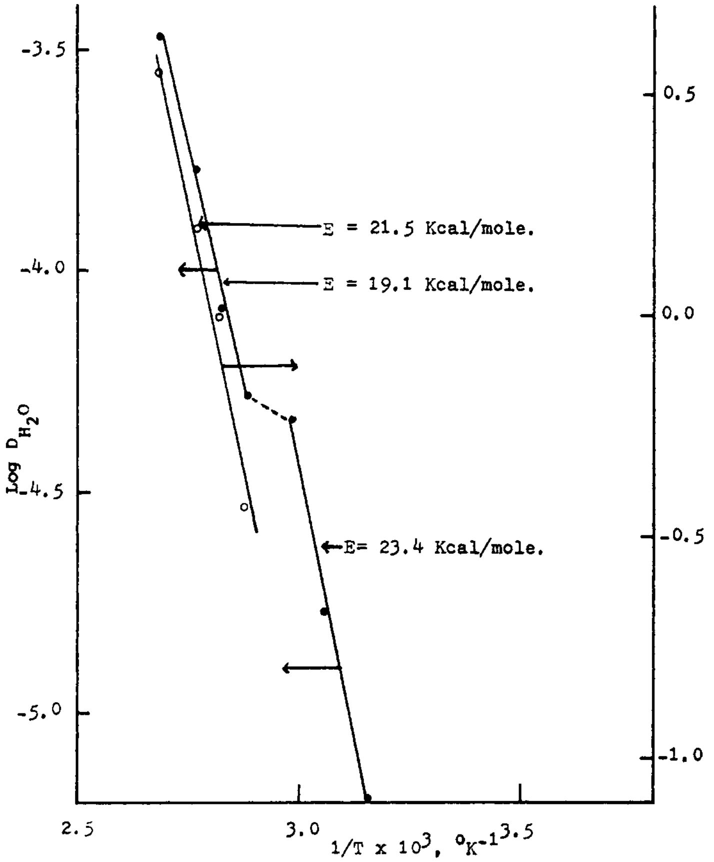


Fig. 11. Arrhenius plots of water diffusion coefficient and of the scale factor for the hydrolytic products.

water uptake than the others. If this was correct, it indicated that the hydrolysis was catalyzed by both acid and alkali, thus accounting for the differences in these observations. However, experimental uncertainties allow us to only hypothesize this.

CONCLUSIONS

The purpose of this study on the diglycidyl ether of bisphenol A (DGEBA) cured by trimethoxyboroxine (TMB) was to investigate the factors controlling the stability of this cured epoxy system.

Color changes occurred from transparent water white to black opaque during isothermal aging. During isothermal aging, the main factor controlling weight loss appeared to be related to the diffusion of the degradation products. The activation energy for diffusion of these isothermal degradation products in this cured epoxy–boroxine system was 22.1 kcal/mole.

Visible thermal crazing occurred after 300 hr at 211°C and after 150 hr at 220°C and was not seen after 900 hr at 189.9°C and after 1200 hr at 175.3°C. The thermal decomposition activation energy was 37.5 kcal/mole, and the reaction order was equal to 1.05 obtained from TGA results under vacuum where the diffusion control of weight loss can be minimized.

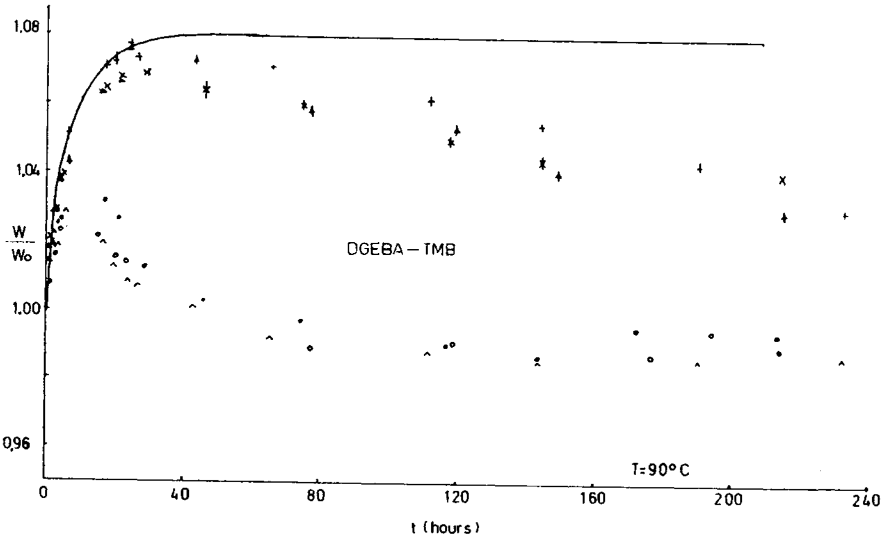


Fig. 12. Weight change of the specimens (based on 1-g unaged sample) during isothermal hydrolytic aging at 90°C in various concentrations of the H_2SO_4 aqueous solution. Wet sample: $[H^+] = 0.000M$ (+); $[H^+] = 0.535M$ (†); $[H^+] = 1.279M$ (*). Dry sample: $[H^+] = 0.000M$ (Λ); $[H^+] = 0.535M$ (o); $[H^+] = 1.279M$ (●).

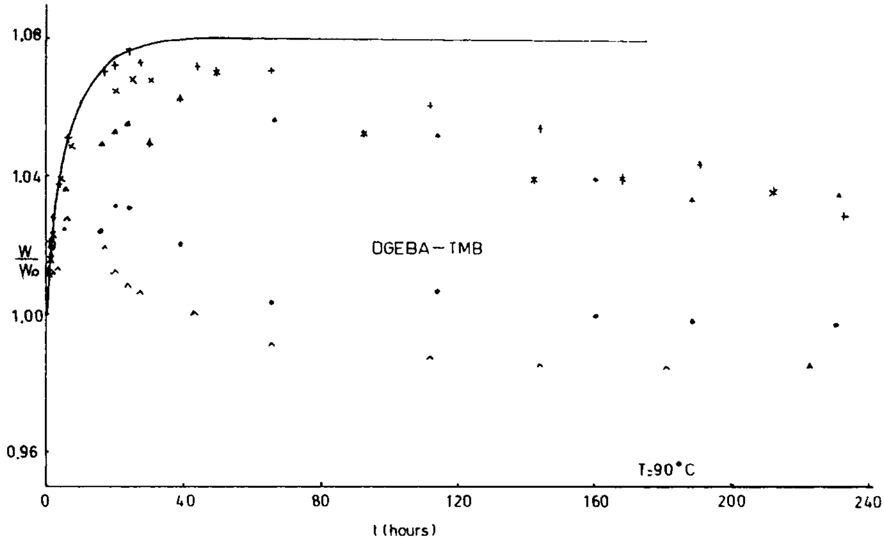


Fig. 13. Weight change of the specimens (based on 1-g unaged sample) during isothermal hydrolytic aging at 90°C in various concentrations of NaOH aqueous solution. Wet sample: $[OH^-] = 0.000M$ (+); $[OH^-] = 0.750M$ (*); $[OH^-] = 1.489M$ (†). Dry sample: $[OH^-] = 0.000M$ (Λ); $[OH^-] = 0.750M$ (o); $[OH^-] = 1.489M$ (●).

The main product from the hydrolysis of DGEBA–TMB cured system was boric acid (92 wt-% of the product). The remaining product (8 wt-%) was epoxy resin. In isothermal hydrolytic aging, the weight change was controlled by water diffusion into the samples and by diffusion of the hydrolysis products out of the samples. The activation energy for water diffusion into the epoxy resin was 19.1

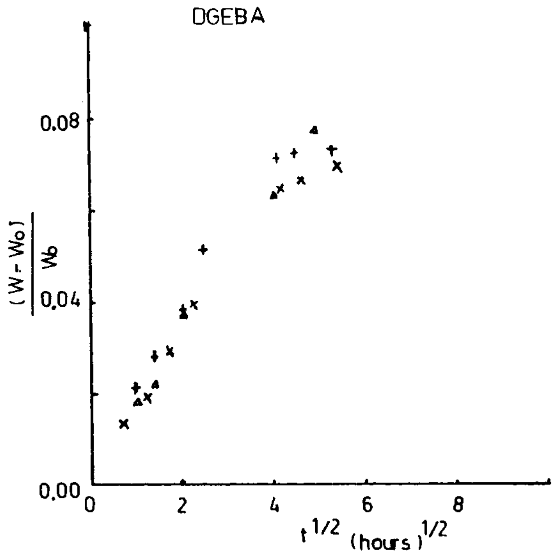


Fig. 14. Initial weight change of the specimens (based on 1-g unaged sample) during isothermal hydrolytic aging at 90°C in various concentrations of H_2SO_4 as function of square root of exposure time: $(H^+) = 0.000M$ (+); $(H^+) = 0.535M$ (▵); $(H^+) = 1.279M$ (×).

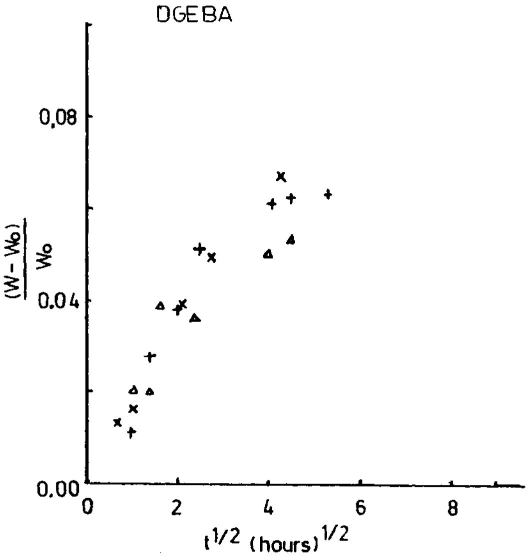


Fig. 15. Initial weight change of the specimens (based on 1-g unaged sample) during isothermal hydrolytic aging at 90°C in various concentrations of NaOH as function of square root of exposure time: $(OH^-) = 0.000M$ (+); $(OH^-) = 0.750M$ (×); $(OH^-) = 1.489M$ (▵).

kcal/mole at a temperature above 74.5°C and 23.4 kcal/mole at a temperature below 62.1°C. During isothermal hydrolytic aging at temperatures higher than 74.5°C the specimens gained weight up to 1.06 to 1.08 based on 1-g unaged cured epoxy resin and then started to lose weight, finally reaching a plateau at 1.02. At temperatures lower than 62.1°C, the specimens absorbed water up to 1.05 and then leveled off. The samples formed cavities during isothermal hydrolytic aging at temperatures higher than 74.5°C.

The time–temperature superposition principle was successfully applied to the aging effects on weight change during either isothermal or isothermal hydrolytic aging. The scale factor for the time–temperature principle turned out to be the ratio of diffusion coefficients at the temperature concerned and that at a reference temperature, i.e., $\alpha_f = D/D_r$.

The activation energy for the hydrolysis product diffusion out of the specimen was 21.5 kcal/mol at temperatures above 74.5°C. Isothermal hydrolytic aging of DGEBA–TMB cured system did not appear to be catalyzed by acid or alkali aqueous solution.

The authors acknowledge the helpful discussions and contributions of S. R. Riccitiello of the NASA–Ames Research Center and of the NASA–Ames Research Center for the scanning electron microscopy studies and financial support of this program under Grant No. NSG-2182.

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Received August 1, 1978