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# Epoxy Resins IV: The Stability of the Epoxy-Triethanolamine Borate System

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The diglycidyl ethers of bisphenol-A, phenolphthalein, and bisphenol-fluorenone were cured with triethanolamine borate to give transparent resins. Curing studies at 160° were made. Comparative properties of the respective epoxy resin systems including  $T_g$ , hydrolysis resistance, thermal degradation and oxygen index flammability data are reported.

## INTRODUCTION

Upon examination of epoxy-trimethoxy boroxine [epoxy-(TMB)] systems the following disadvantages were found:<sup>1</sup> (1) Degassing has to be carried out due to volatile chemical (possibly methanol) formation in the curing process; (2) TMB is very sensitive towards water, as is the cured epoxy resin at temperatures higher than the glass transition temperature; (3) a rippled surface is formed when the epoxy is cured in an open mold and (4) due to the low boiling (130°C) and decomposition (150°C) temperature of TMB, the curing process at high temperature does not give high crosslinking density when used with the diglycidylether of phenolphthalein (DGEPP) and 9, 9-bis (4 hydroxyphenyl) fluorene (DGEBF) systems. In an attempt to overcome these disadvantages and retain the good properties of these systems such as transparency, heat resistance, and laser resistance<sup>2</sup> triethanolamine borate (TEAB) which has a melting point at 235.5°C and decomposes at 260°C and should perform the same role as TMB was used. TEAB has been used as an additive to increase

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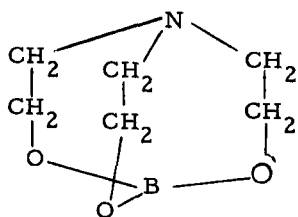
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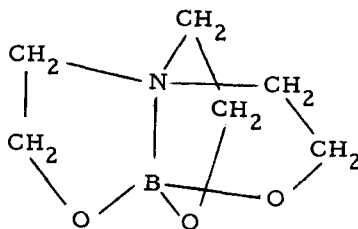
the crystallization or solidification rate and reduce the "sticky" properties of polyamide.<sup>3</sup> Ludwig<sup>4</sup> used it to improve the antistatic and flame resistance of polyethylene. Polyphenylene ethers treated with  $(\text{Me}_2\text{N})_3\text{PO}$ , TEAB and  $\text{AcNH-NH}\phi$  as stabilizers have good heat stability, light stability, flame resistance and drip resistance, as shown in flammability tests.<sup>5</sup>

TEAB was first used along or with a cocatalyst metal chelate compound as a curing agent for epoxy resins by Elbling and Langer.<sup>6,7,8</sup> They found that the TEAB-epoxy systems have a very long pot life and good physical properties. It was also found that TEAB does not promote the gelling of polyepoxides at  $120^\circ\text{C}$  and can be used as a hardening accelerator for epoxy resins.<sup>9</sup>

TEAB was postulated to have two structures, a cage structure (I) and a transannular structure (II).<sup>10</sup>



I



II

Both are in equilibrium in either case. The partial dative bonding between B and N atoms in a transannular structure has a distance of  $1.647 \text{ \AA}$ <sup>11</sup> and was employed to interpret the hydrolytic stability based on a low reaction rate constant with methyl iodide<sup>12</sup> and  $\text{B}^n$  NMR study.<sup>13</sup> In solid TEAB, structure II may be the only structure present in the crystal. The  $\text{B} \leftarrow \text{N}$  bonding was also used to explain the long tank life of epoxy TEAB systems.<sup>6</sup>

It was the purpose of this study to use TEAB as a curing agent for DGEBA, DGEPP and DGEBF maintaining the epoxy-curing agent ratio constant (18.2 epoxy equivalent/l mol TEAB) thus enabling us to compare these systems with TMB systems. In order to characterize the epoxy TEAB systems, the primary aims of this work are:

- 1) To find the best curing conditions: time, by thermomechanical analysis (TMA) and temperature by differential scanning calorimetry (DSC).
- 2) To evaluate its thermal resistance by thermogravimetric analysis (TGA) and oxygen index (OI).
- 3) To study the kinetics of the thermal decomposition by TGA and differential thermogravimetric analysis (DGA) in vacuum.

- 4) To perform isothermal aging at constant temperature in order to compare the different stabilities of these materials.
- 5) To carry out isothermal aging at different temperatures with one epoxy (DGEBA) and be able to predict the lifetime at desired service temperatures.
- 6) To perform hydrolytic aging at 100°C in distilled water to calculate the water diffusion coefficient for these epoxy materials.

## EXPERIMENTAL

### Epoxy equivalent weight determination

ASTM method D.1652-73<sup>14</sup> was used to determine the epoxy resins. The resins were dissolved in chlorobenzene-chloroform (50:50) and 0.1% of crystal violet solution in glacial acetic acid was used as the indicator. The resins solution was titrated with 0.1 N hydrogen bromide in acetic acid to a blue-green end point. The data obtained were:

DGEBA	192 gr/Eq
DGEPP	260 gr/Eq
DGEBF	305 gr/Eq

*Determination of the best curing temperature* In order to determine the best curing condition for epoxy resins cured with TEAB, the DSC thermal analyzer (900 DSC Dupont) was employed to investigate the initial curing temperature.

Figure 1 shows the DSC thermograms of DGEBA, DGEPP, and DGEBF after curing with TEAB.

It can be observed that the mixture of DGEBA and TEAB starts to release heat at 150°C and reaches a maximum at 190°C, that DGEPP mixture starts at 170°C and gives a maximum at 220°C and the DGEBF mixture starts at 180°C and reaches a maximum at 207°C.

Figure 2 shows the DSC thermograms of TEAB. It is possible to observe two peaks one at approximately 210°C, and another at 235°C. The later peak is the melting point, but the first peak may be a phase transition between the sp<sup>3</sup> and sp<sup>2</sup> configurations (transannular structure to cage structure).

Only the cage structure can attack the epoxy ring and start the polymerization.

Based upon these results a curing temperature of 160°C was chosen. This temperature is a compromise between curing and decomposition rates.

*Determination of the best curing time* The best curing time was determined by using a thermomechanical analyzer (942 TMA Dupont).<sup>15</sup> In all the cases a program rate of 10°C/min and expansion vs. time mode was used for deter-

mination of  $T_g$  (glass transition temperature). But when the epoxy (DGEBF) was used it was difficult to measure  $T_g$  because the temperature was very close to the distortion point ( $D_T$ ). In this last case  $D_T$  vs. time was plotted to obtain the best curing time (Figure 3).

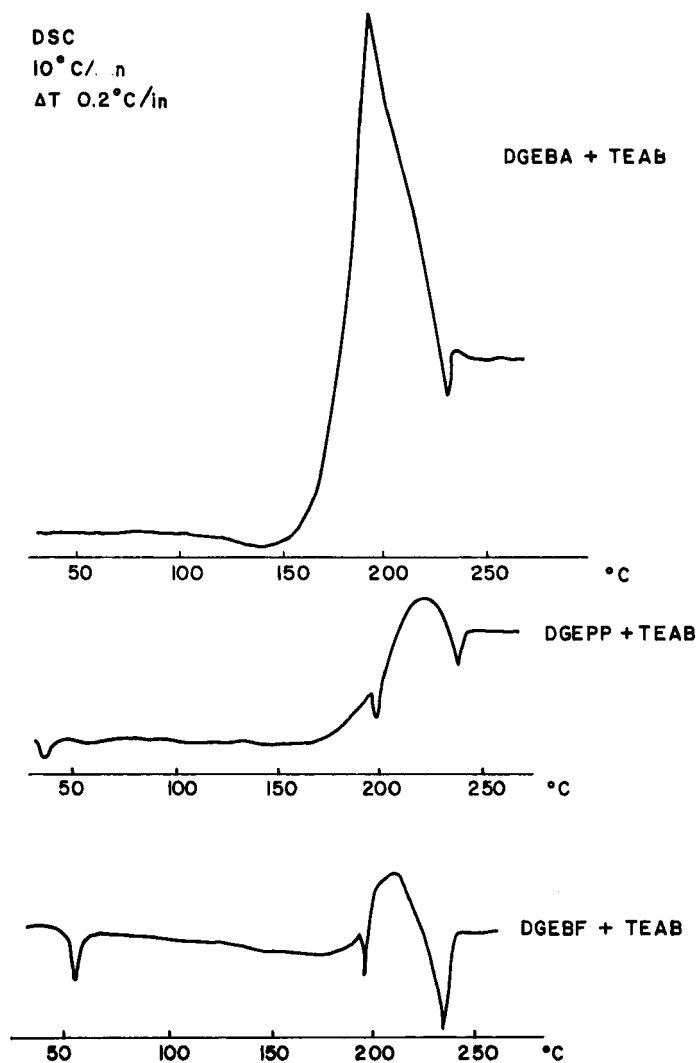


FIGURE 1 DSC thermograms of DGEBA, DGEPP, and DGEBF after curing with TEAB.

DSC  
 $10^{\circ}\text{C}/\text{min}$   
 $\Delta T 0.2^{\circ}\text{C}/\text{in}$

TEAB

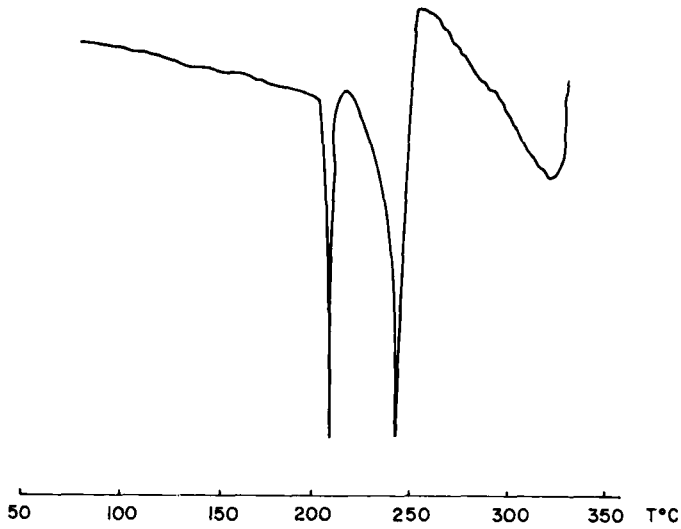
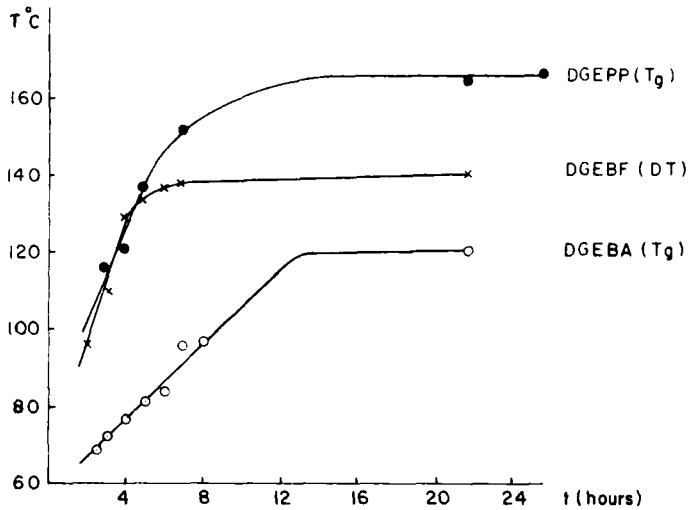


FIGURE 2 DSC thermograms of TEAB.

FIGURE 3 Thermomechanical analysis curves for DGEBA, DGEPP and DGEBF cured with TEAB ( $10^{\circ}\text{C}/\text{min}$ ).

The low  $T_g$  and  $D_T$  observed using DGEBF was attributed to low cross-linking in the cured resin. The residue extracted by THF was 49.4% confirming this idea. It is possible to observe in Figure 3 that the best curing times for DGEBA, DGEPP and DGEBF systems are 22, 12 and 9 hours, respectively.

*Thermogravimetric analyses* The properties of various samples in this study were investigated on a Dupont 950 thermogravimetric analyzer for char residue determination.

All measurements were carried out in  $N_2$  atmosphere at a flow rate of 0.2 liters per minute with a heating rate of  $10^\circ C/min$ .

The values obtained at  $700^\circ C$  were

DGEBA + 4.5 phr TEAB	23.0% char
DGEPP + 3.32 phr TEAB	31.5% char
DGEBF + 2.83 phr TEAB	31.0% char

*Oxygen index measurement* The oxygen indexes (OI) of several samples of DGEBA, DGEPP, and DGEBF systems were measured using the General Electric Model CR 280 KF 11A flammability test kit. The cured resins were molded into sheets (in an open mold) and cut into bars<sup>16</sup> (length  $> 7$  cm,  $A = 3 \times 6.5$  mm<sup>2</sup>). The sample was mounted in the flame chamber and a mixture of oxygen and nitrogen was passed upwards through the chimney at a flow rate of 3 to 5 cm/sec. The test followed the manual procedure.<sup>17</sup> The oxygen index was obtained from this equation.

$$OI = \frac{O_2}{O_2 + N_2}$$

where the unit of gas quantity is volume.

The oxygen indexes obtained are listed in Table I.

TABLE I

Resins	OI
DGEBA	26.6
DGEPP	26.6
DGEBF	32.6

*Kinetics of the thermal degradation of epoxy resins* In this study, the loss in sample weight and its derivative were recorded as a function of temperature using the Dupont 951 Thermogravimetric Analyzer, while the furnace temperature was continuously increased at the rate of  $10^\circ C/min$  from room temperature to  $700^\circ C$  in vacuum (0.1 mm Hg).

The kinetics of reaction was evaluated from the resulting curves by Freeman Carroll's method.<sup>18</sup> In all the cases it is possible to observe two overlapping peaks in the derivative curve and only in the DGEPP systems is it possible to solve the overlapping and calculate the value of  $n$  (order of reaction) and  $E$  (energy of activation) of the degradation reaction.

Figure 4 shows the weight loss and its derivative in the degradation of 7.43 mg of a DGEPP system. The decomposition began at approximately 325°C and was relatively rapid from 325°C to 440°C. From 440°C to 700°C little change occurred. It is possible to observe two peaks, one gives a maximum at 360°C and another at 425°C. The first peak is several times smaller than the second peak. Figure 5 shows the weight loss and its derivative curve for the DGEBA and DGEPP systems. Two overlapped peaks may be observed.

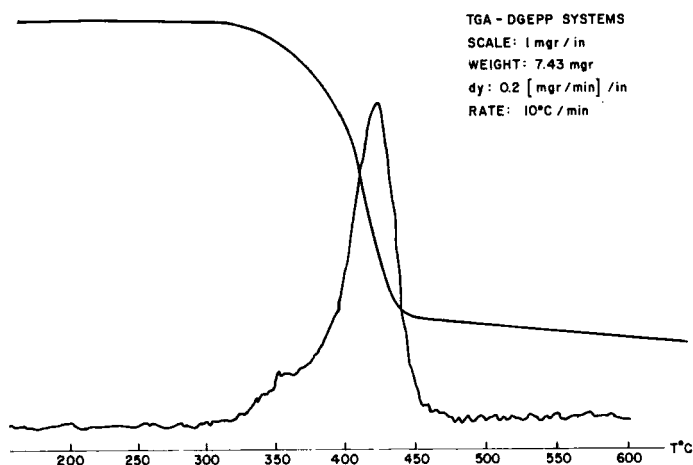


FIGURE 4 Thermogravimetric analysis and derivative curves for DGEPP cured with TEAB (10°C/min).

The kinetics of pyrolysis of DGEPP was evaluated using the following equation<sup>19</sup>

$$\frac{\log(dw/dt)}{\Delta \log wt} = n - \frac{\Delta/2.3R \Delta(1/T)}{\Delta \log wt} \quad (1)$$

$\frac{dw}{dt}$  = rate of loss in weight

$w_t$  = weight loss at completion of reaction minus total weight loss up to the limit  $t$



- $\Delta$  = energy of activation  
 $R$  = gas constant  
 $T$  = absolute temperature ( $^{\circ}\text{K}$ )  
 $n$  = order of reaction

Figure 6 shows the plot of Eq. (1). The values obtained for  $E$  and  $n$  are respectively, 30.5 kcal/mol and 1.2.

*Isothermal aging* It can be noted that during isothermal aging the specimens changed from colorless to dark and from transparent to opaque and the weight decreased. This change is more important for DGEBA systems. The change curve for DGEPP systems is between those for DGEBA and DGEBF (Figure 7) when the temperature was constant at  $200^{\circ}\text{C}$ .

In the DGEBA case, three different temperatures were studied. It was observed that the change in weight increases as the temperature is raised as is seen in Figure 8.

If the rate determining step of the decomposition is assumed to be the diffusion of volatile product through the solid to the surrounding gas,<sup>1</sup> Fick's Second Law can be applied to the quantitative study of these systems.

$$\frac{dc}{\partial t} = \frac{D\partial c^2}{dx^2} \quad (2)$$

For short time diffusion ( $t \rightarrow 0$ ) the solution of this equation becomes<sup>1</sup>

$$\frac{w - w_0}{w_0} = \frac{w_0 - w_{\infty}}{w_0} \frac{4}{l} \left( \frac{Dt}{\pi} \right)^{1/2} \quad (3)$$

- $w$  = weight loss at time  $t$   
 $w_0$  = initial weight  
 $D$  = diffusion coefficient  
 $t$  = time  
 $l$  = thickness

By assuming the final weight of specimen after infinite aging to be the same for all aging temperatures Eq. (3) may be simplified.

$$\frac{w_0 - w}{w_0} = kt^{1/2}$$

where  $k = \left( \frac{w_0 - w_{\infty}}{w_0} \right) \frac{4}{l} \left( \frac{D}{\pi} \right)^{1/2}$  and is constant but dependent upon temperature.

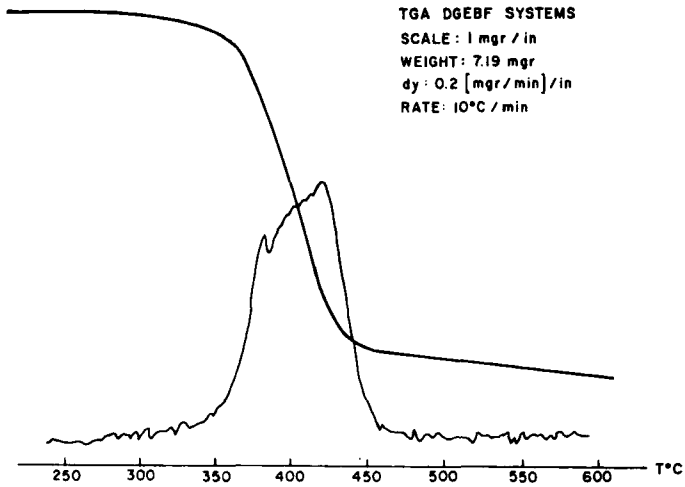


FIGURE 5 Thermogravimetric analysis and derivative curves for DGEBF cured with TEAB 10°C/min).

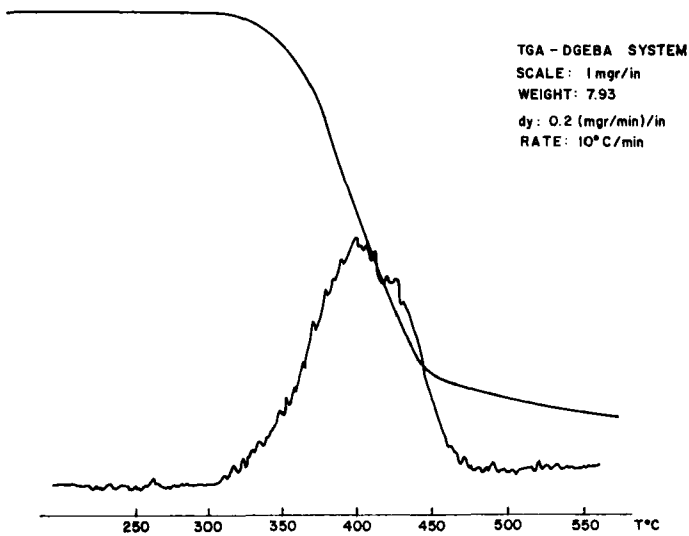


FIGURE 5.1 Thermogravimetric analysis and derivative curves for DGEBA cured with TEA (10°C min).

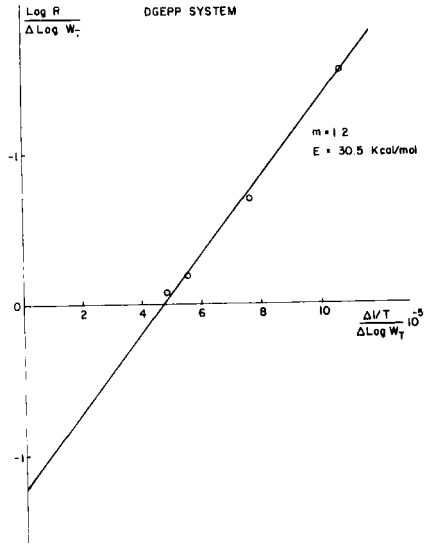


FIGURE 6 Kinetics of pyrolysis: DGEPP cured with TEAB.

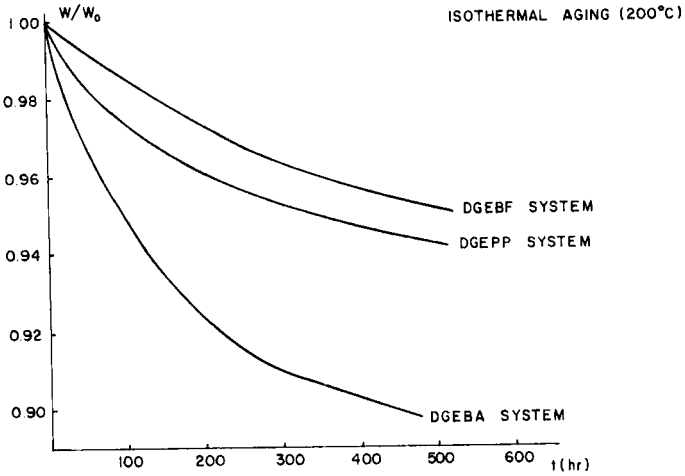


FIGURE 7 Isothermal aging at 200°C for DGEBA, DGEPP and DGEBF cured with TEAB.

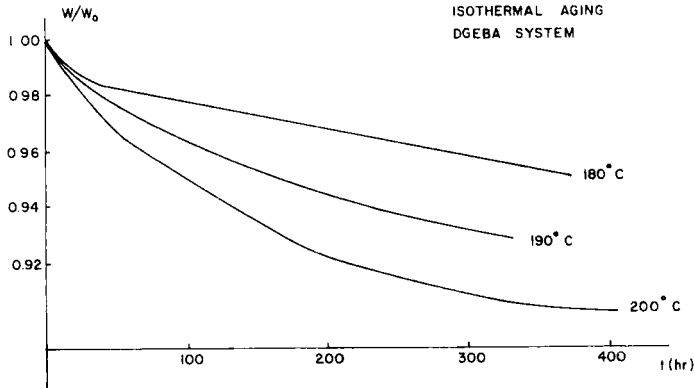


FIGURE 8 Isothermal aging at 180°, 190° and 200° for DGEBA cured with TEAB.

Figure 9 shows the relative weight loss vs. the square root of time for three temperatures (200, 190, 180°C).

If the diffusion may be assumed to be a thermally activated process, it is possible to write the following relation between  $D$  and  $T$ :

$$D = D_0 \exp -E/RT$$

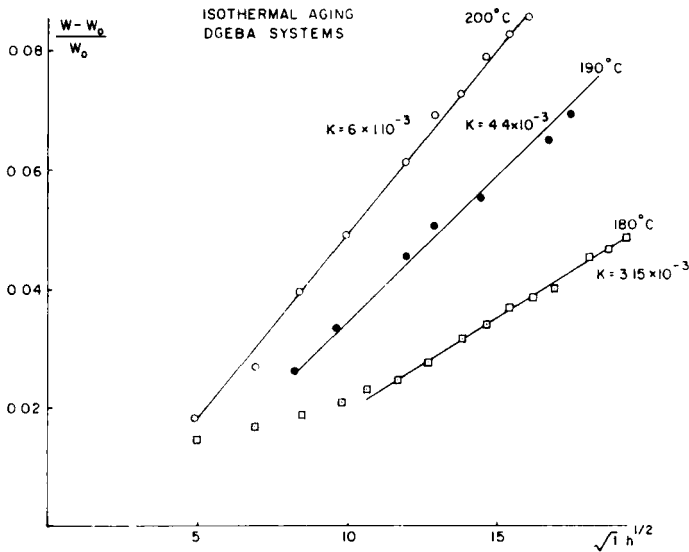


FIGURE 9 Isothermal aging—relative weight loss vs.  $\sqrt{t}$  at 180°, 190°, 200° for DGEBA cured with TEAB.

By incorporating the definition of  $k$  it could be written that:

$$\log k = \log \frac{w_0 - w_\infty}{w_0} \frac{4}{l} + 1/2 \log D_0 - \frac{E}{2 \times 2.3 RT}$$

Figure 10 shows the plot of  $\log k$  vs.  $1/T$  for DGEBA systems. A value of  $E$  equal to 27.3 kcal/mol was calculated from the slope of this plot.

The values of  $k$  for different temperatures are listed in Table II.

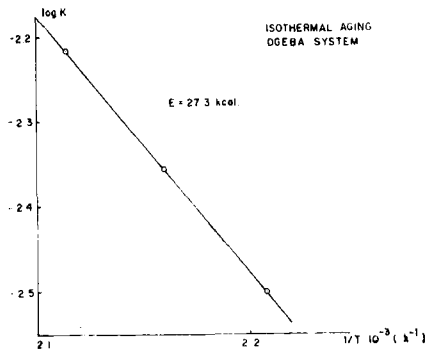


FIGURE 10  $\log K$  vs.  $1/T$  for isothermal aging for DGEBA cured with TEAB.

TABLE II

$T$	$1/T^\circ k 10^{-3}$	$k$	$\log$
180	2.208	$3.15 \cdot 10^{-3}$	-2.502
190	2.160	$6.11 \cdot 10^{-3}$	-2.354
200	2.114	$6.11 \cdot 10^{-3}$	-2.214

*Prediction of the effects of heating on epoxy TEAB systems at a desired service temperature* In order to predict the effect of the heat aging at another temperature it is possible to use the temperature-time superposition principle. It has been described in Ferry's book<sup>20</sup> and has been applied by other investigators.<sup>21,22</sup>

In applying the superposition principle to thermal aging data, one of the actual aging temperatures must be selected to serve as a reference temperature. A temperature of 190°C (middle of experimental range) was chosen in order to reduce error.

It was necessary to derive a set of scale factors  $a_T$  to convert test time at each aging temperature to equivalent times at the central reference temperature.

In order to determine the value of  $\alpha_T$  for each aging temperature, the following must be done:<sup>21</sup>

1) A significant level of change of weight loss is selected so that the chosen amount ( $0.96 = w/w_0$ , Figure 8) can be arbitrary and need not represent a design criterion.

2) The time ( $t_f$ ) is determined on each isothermal curve for the material to undergo the chosen amount of weight loss.

3) The ratio of  $t_f$  at the reference temperature to the time required at another temperature for the same weight loss is the value of  $\alpha_T$  for the other temperature,  $\alpha_T = (t_{fo}/t_{fi})$ ,  $o$  = reference temperature,  $i$  = interest temperature.

See Table III where the times,  $t_f$ , and  $\alpha_T$  values are listed.

TABLE III

$t^\circ\text{C}$	$t_f$ at 0.36	$\alpha_T$
180°C	282	0.44
190°C	124	1
200°C	73	1.70

It is possible to convert actual times to equivalent time at the reference temperature by multiplying each observed time period at each aging temperature by the appropriate scale factor for that aging temperature. In Table IV are listed the values obtained and in Figure 11 was plotted the master curve for the DGEBA systems.

By plotting the values of  $\log \alpha_T$  versus the reciprocal of absolute temperature Arrhenius plot as in Figure 12, the value of  $\alpha_T$  for the desired service condition (170°C) was determined through extrapolation. This value of  $\alpha_T = 1.7 \times 10^{-7}$  must be used to modify the time scale of the master curve to obtain the corresponding scale of time at service condition.

*Isothermal hydrolytic aging* Samples of DGEPP and DGEBA were subjected to hydrolytic aging in distilled water (100°C) as shown in Figure 13. The DGEBA sample shows a rapid weight gain reaching a maximum of up to 7.45% and then starts to lose weight and levels off at 5.75% gain. Figure 14 shows that the sample of DGEPP gained weight slower than DGEBA and leveled off at about 3.85% weight gain. At about 600 hours it was possible to observe the beginning of weight loss. Figure 15 shows that the sample of DGEBF gained weight up to and leveled off at about 4.57% weight gain. DGEBA samples after hydrolytic aging were cloudy but DGEPP samples remained transparent. All the samples maintained their dimensions during

and after the aging and cavities could not be observed. This is attributed to the fact that  $T_g$  (glass transition temperature) remained over  $100^\circ\text{C}$  in the aged sample. The weight loss of the aged sample of DGEBA leveled off after a certain period of aging. This can be due to the fact that only part of the material can react with water and diffuse out of the sample. A possible explanation is related to the boric acid formation during hydrolysis and its late diffusion out.<sup>1</sup>

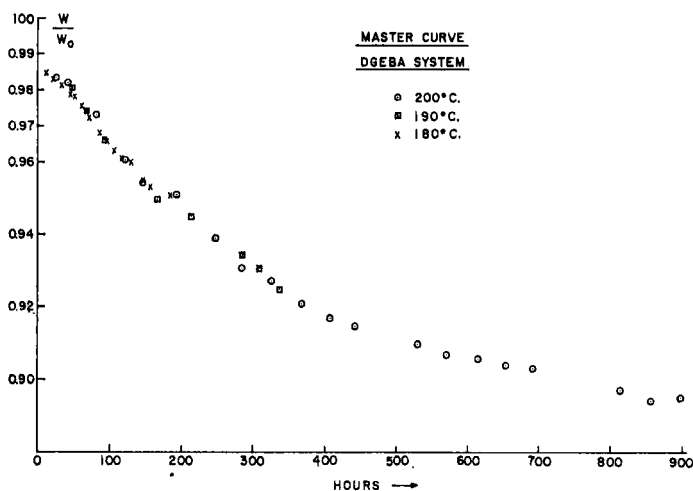


FIGURE 11 Isothermal aging— $w/w_0$  vs. time for DGEBA cured with TEAB.

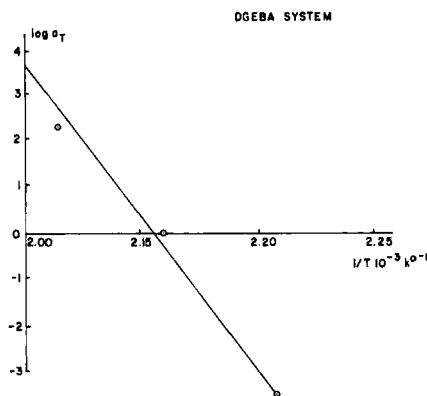


FIGURE 12  $\log a_T$  vs.  $1/T$  for DGEBA cured with TEAB.

TABLE IV

200°C		190°C		180°C	
$t_{\text{shift}}$	$w/w_0$	$t$	$w/w_0$	$t_{\text{shift}}$	$w/w_0$
40.8	0.9818	24	0.9836	10.6	0.9852
81.6	0.9732	48	0.9812	21.1	0.9833
122.4	0.9604	68.5	0.9740	31.7	0.9812
167.5	0.9511	92.5	0.9669	42.2	0.9791
244.8	0.9387	120	0.9611	50.2	0.9769
285.6	0.9310	144.5	0.9546	60.7	0.9755
326.4	0.9274	168	0.9496	71.3	0.9726
367.2	0.9208	212	0.9449	85.1	0.9683
408.0	0.9169	284	0.9353	95.0	0.9660
442.0	0.9150	30.8	0.9308	105.6	0.9633
530.4	0.9100	336	0.9248	116.6	0.9616
571.2	0.9072			126.2	0.9603
612.0	0.9060			145.2	0.9551
652.8	0.9042			155.8	0.9536
691.8	0.9029			165.0	0.9514
814.3	0.8970				
856.8	0.8940				
897.6	0.8955				

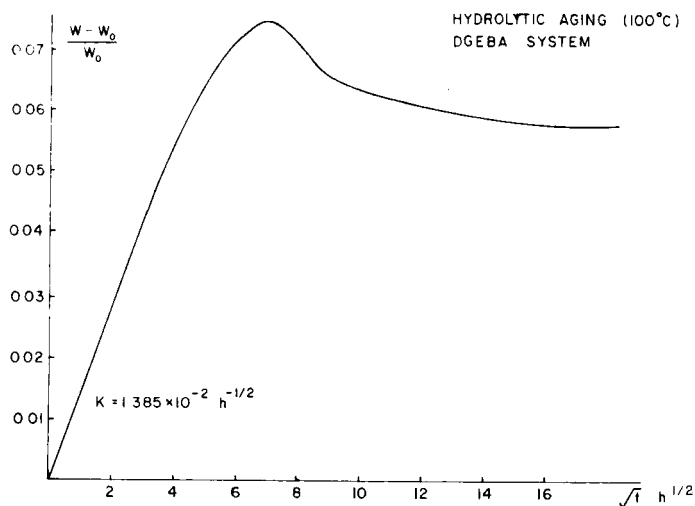
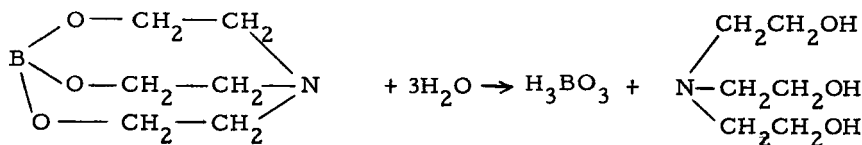


FIGURE 13 Isothermal hydrolytic aging—DGEBA cured with TEAB.



If it is assumed that only  $\text{H}_3\text{BO}_3$  diffuses out of the sample it can be calculated that the difference between the maximum and where the weight levels off



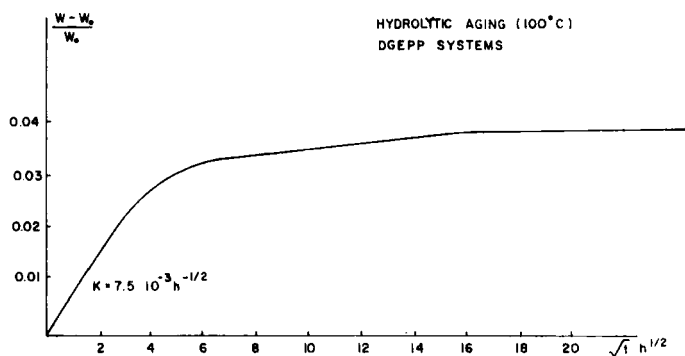


FIGURE 14 Isothermal hydrolytic aging—DGEPP cured with TEAB.

must be 1.77%. This result agrees well with the experimental data of 1.70% (Figure 11).

However, as the aging time approaches zero, it may be assumed that the weight change is determined by the water diffusion process into the polymer network. Then it is possible to write<sup>1</sup>

$$\frac{\partial w}{\partial t} = M_{\text{H}_2\text{O}} D_{\text{H}_2\text{O}} \frac{\partial C_{\text{H}_2\text{O}}}{\partial x^2}$$

$$\frac{\partial w}{\partial t} = \text{rate of weight change}$$

$M_{\text{H}_2\text{O}}$  = water molecular weight

$D_{\text{H}_2\text{O}}$  = water diffusion coefficient

$C_{\text{H}_2\text{O}}$  = water concentration

The solution of this equation is the same as Eq. (2), therefore Eq. (3) may be applied in this case and the diffusion coefficient for water can be calculated from the initial slope of Figures 13, 14 and 15. The values obtained were  $1.7 \cdot 10^{-4} \text{ hr}^{-1} \text{ cm}^2$  (from DGEBA plot),  $2.2 \cdot 10^{-4} \text{ hr}^{-1} \text{ cm}^2$  (from DGEPP plot) and  $1.99 \cdot 10^{-4} \text{ hr}^{-1} \text{ cm}^2$  (from DGEBF plot).

## CONCLUSION

TEAB's high decomposition temperature (260°C) let us use a high curing temperature (160°C) and therefore decreased the viscosity and increased cross-linking in the epoxy resins. It was possible to mold the sample in an open mold without degassing and to obtain a smooth surface and a transparent product (DGEBF systems are somewhat cloudy).

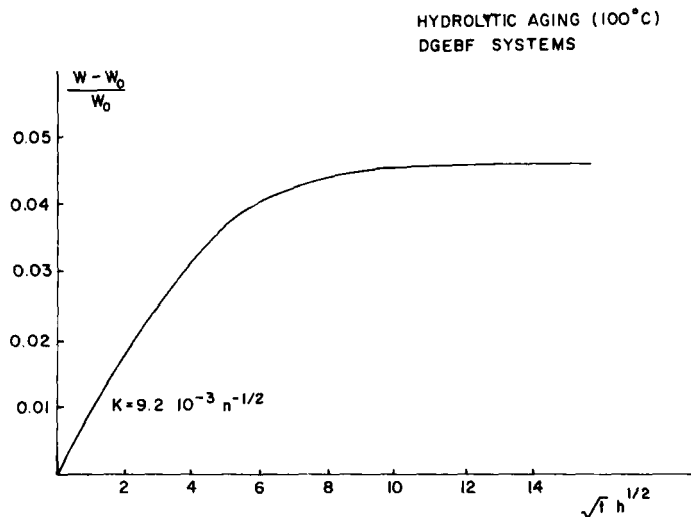


FIGURE 15 Isothermal hydrolytic aging—DGEBF cured with TEAB.

In all the cases the best curing conditions (time and temperature) were found.

The product in the DGEBF system was very brittle, this fact was attributed to the low cross-linking density. It was confirmed by determination of extraction residue in THF (49%).

The use of TEAB as a curing agent for DGEBA, DGEPP, and DGEBF improved the product obtained in several ways in respect to the TMB systems:

- a) The glass transition temperature was increased.
- b) The resistance to hydrolysis was improved (decreasing  $k$  and water weight gained at saturation).
- c) The initial decomposition temperature in a TGA experiment (in vacuum) was increased.
- e) DGEPP systems remained transparent after hydrolytic aging (distilled water 100°C, 700 hours) and it was not possible to observe further weight loss after the weight vs. time curve leveled off.

In other ways, it was possible to calculate the energy of activation and the order of reaction for DGEPP systems' decomposition by TGA and DTGA data. These results agreed very well with the value published by Anderson for epoxy resins with different curing agents.

It was possible to calculate the energy of activation of the decomposition process by isothermal heating in air (27.3 kcal/mol) and then to apply the

time-temperature superposition principle to the isothermal aging data of DGEBA systems and to plot a master curve and predict the behavior at other temperatures.

It is suggested as an aim for further work to study copolymers of these epoxy resins with TEAB as a curing agent in order to maintain the good properties but to lower price and viscosity of the final product.

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