Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Porowska, Engelina and Tokarzewska, Maria(1979) 'Use of p,p'-Phenolphthalein-bis(trimellitic) Dianhydride for Hardening Low Molecular Weight Epoxy Resins', Journal of Macromolecular Science, Part A, 13: 7, 909 — 921

To link to this Article: DOI: 10.1080/00222337908066617

URL: http://dx.doi.org/10.1080/00222337908066617

J. MACROMOL. SCI.–CHEM., A13(7), pp. 909-921 (1979)

Use of p,p′-Phenolphthalein-bis(trimellitic) Dianhydride for Hardening Low Molecular Weight Epoxy Resins

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ABSTRACT

Hardening of a low molecular epoxy resin with p,p′-phenolphthalein-bis(trimellitic) dianhydride has been studied by using differential scanning calorimetry. The relationships of glass transition temperature of the systems being examined versus time, temperature of hardening, and dianhydride content in the compositions have been determined. The activation energy of crosslinking reactions in systems containing 50% of the stoichiometric amount of dianhydride has been evaluated. The value of activation energy obtained indicates a high reactivity of dianhydride in the examined reactions. The hardened epoxy composition exhibits excellent thermal stability, good hardness, and good resistance to acid solutions.

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During research on soluble, regularly alternating polyesterimides, a synthesis of p,p'-phenolphthalein-bis(trimellitic) dianhydride was carried out and thus a new compound obtained [1]. The presence in the molecule of this new compound of four functional groups capable of reacting with epoxy groups and good solubility in organic solvents and low molecular epoxy resins suggested the use of this compound as a hardening agent for liquid resins. Examinations of the hardening process were conducted by using a low molecular epoxy resin (Beckopox 37-140) which is equivalent to Epidiane 5 and Epikote 828.

EXPERIMENTAL

Materials

p,p'-Phenolphthalein-bis(trimellitic) dianhydride had a melting point of 135-138°C and a free carboxy group content of 0.73%.

Beckopox 37-140 epoxy resin (Reichhold-Albert-Chemie AG, FRG) had a molecular weight of about 380, an epoxy equivalent of 185-195, and an epoxy number of 0.51-0.54 g - equiv/100 g.

Preparation of Epoxy Compositions

The quantity of dianhydride for hardening was calculated by the equation [2]

$$A = fEM/n \tag{1}$$

where: A is the amount of acid dianhydride (g), E is the resin epoxy number, (g-equiv/100 g), M is the molecular weight of the acid dianhydride, n is the number of anhydride groups in the acid dianhydride, and f is a coefficient considering lower dianhydride content than calculated by stoichiometric equations.

In the tested compositions the values of the coefficient f were 0.85, 0.5, and 0.3. Compositions were prepared by mixing the calculated amounts of epoxy resin and dianhydride at a room temperature; they were designated ETMF-0.85, ETMF-0.5, and ETMF-0.3, where the numerals refer to the f coefficient value. Ready to use epoxy compositions could be used within 1-1.5 hr.

RESULTS

Hardening of Epoxy Compositions

The hardening of epoxy compositions was studied by differential scanning calorimetry [3-11]. This method enables one to observe the changes in properties during the whole hardening process. Differential scanning calorimetry (DSC) was carried out under nitrogen with a Perkin-Elmer DSC-IB differential microcalorimeter.

Weighed amounts of compositions prepared for DSC thermal analysis were placed in aluminum dishes, then heated at a predetermined temperature. After a given period of time the DSC curves were recorded, with a rate of temperature increase of 16 and 32°C/min and a sensitivity of 4 mcal/sec. The samples weighed 12 to 15 mg.

Glass transition temperatures of the hardened compositions were read directly from the DSC curves. In cases, when change of state of aggregation was recorded as a DSC curve inflection, the glass transition temperature was read at the initial curve deflection close to the inflection point.

Glass transition temperatures of poorly hardened compositions were determined from the maxima of endothermic peaks. The DSC curves of unhardened compositions are shown in Figs. 1 and 2. The relations of glass transition temperatures to hardening temperature and to hardening time are shown in Figs. 3 and 4. Figure 5 shows the effect of dianhydride content in the composition on glass transition temperature.

Heat and Activation Energy of the Hardening Reaction

The total heat of hardening reaction was calculated from the exothermic deviation surface of the DSC curve. The deviation surface between DSC curve and the baseline was measured by means of a planimeter. A sample with a known heat of fusion, i. e., 6.8 cal/g, was used as a standard sample. The heat of reaction of hardening of the compositions examined are presented in Table 1. The activation energy of the hardening reaction was determined by the method given by Westwood [12], as previously described by Rogers and Smith [13]. Assuming that the quantity of heat emitted during a hardening process is directly proportional to the degree of reaction, the equation describing reaction kinetics may be written in the form (2):

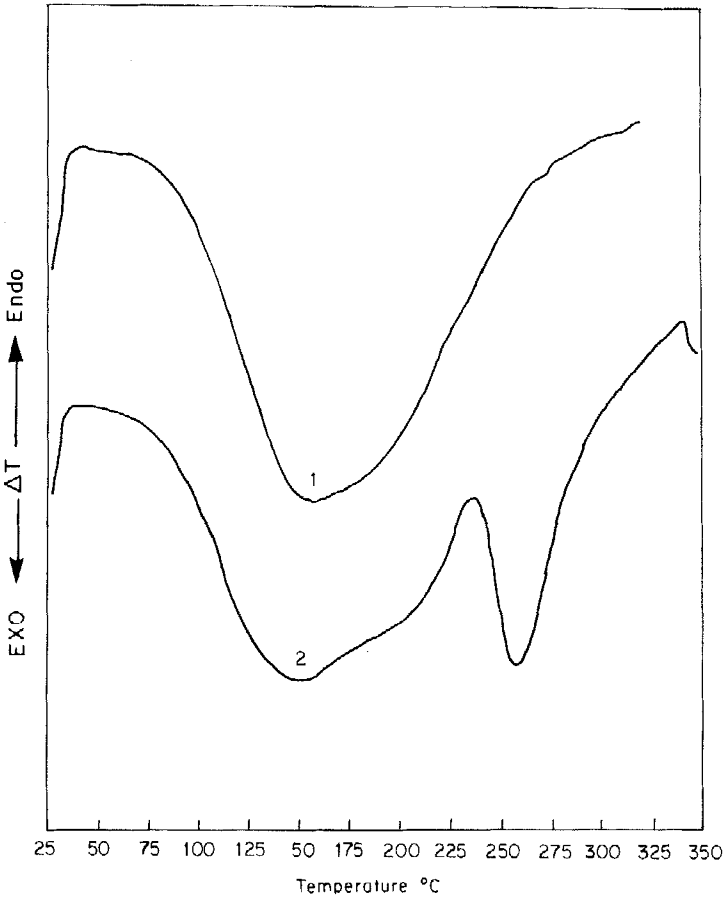

FIG. 1. DSC curves of (1) unhardened ETMF-0.5 and (2) ETMF-0.3 epoxy compositions. Recorded at a rate of heating of 32°C/min.

$$\frac{d}{dt}\left(\frac{H}{H_T}\right) = Ae^{-[E/RT]}\left(1 - \frac{H}{H_T}\right)^n \qquad (2)$$

where H/H_T is the degree of reaction progress, H is the deviation surface of the DSC curve before reaching temperature T, H_T is the total deviation surface of the DSC curve, t is time, A is the Arrhenius

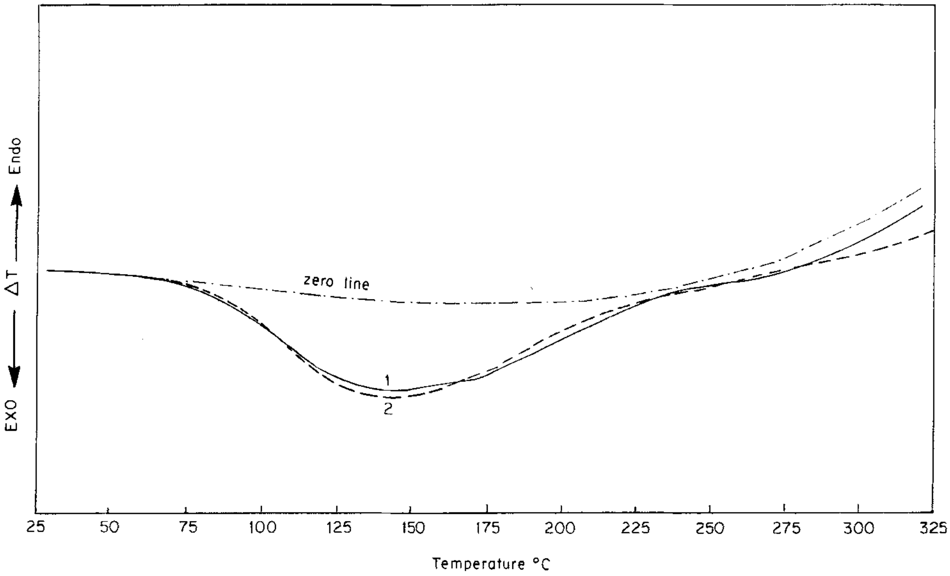

FIG. 2. DSC curves of (1) unhardened ETMF-0.5 and (2) ETMF-0.85 epoxy compositions. Recorded at a rate of heating of 16° C/min.

constant, E is activation energy, R is the gas constant, T is absolute temperature, and n is the order of reaction.

On differentiating Eq. (2) versus time and eliminating the Arrhenius constant from the equation and expressing the dT/dt constant value the predetermined temperature increase rate by β, the Eq. (2) may be rewritten:

$$\frac{\frac{d}{dt}\left(\frac{dH}{dt}\right)\left(1 - \frac{H}{H_T}\right)}{(dH/dt)^2} = \frac{\beta E\left(1 - \frac{H}{H_T}\right)}{RT^2(dH/dt)} - \frac{n}{H_T} \qquad (3)$$

On assuming that the hardening reaction in this case proceeds in accordance with the Arrhenius Law, the expression (3) may be represented by a straight line described by the equation:

$$y = mx - c$$

where $m = E/R$ and $c = n/HT$.

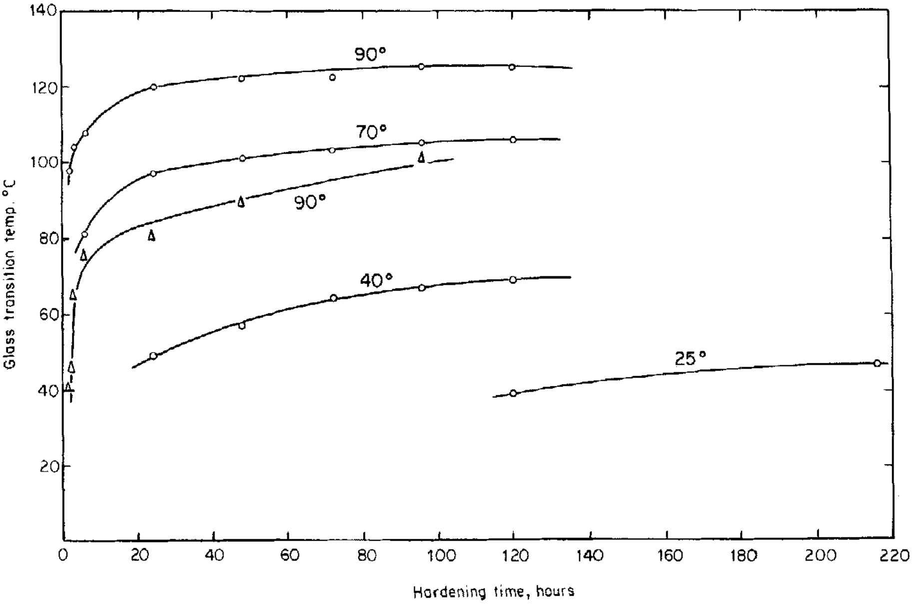

FIG. 3. Relationship of glass transition temperature of epoxy compositions versus hardening time at various temperatures of hardening: (△) 0.3 ETMF; (○) 0.5 ETMF.

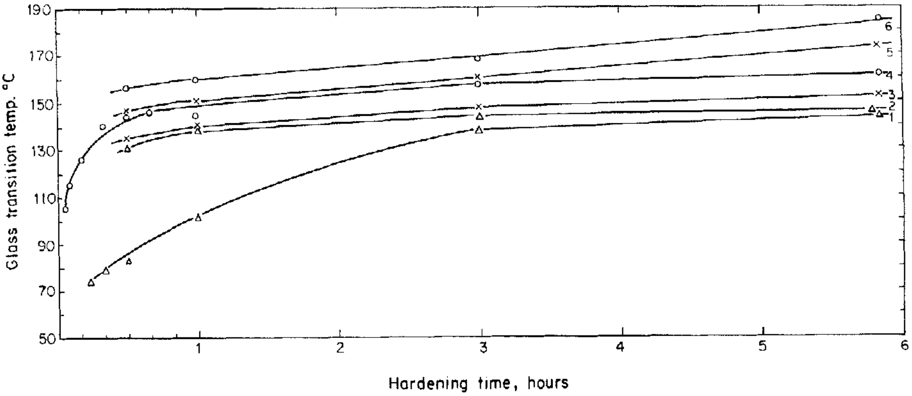

FIG. 4. Relationship of glass transition temperature of epoxy compositions versus hardening time (1, 3, 4) at 150°C and (2, 5, 6) at 170°C: (△) 0.3 ETMF; (○) 0.5 ETMF; (×) 0.85 ETMF.

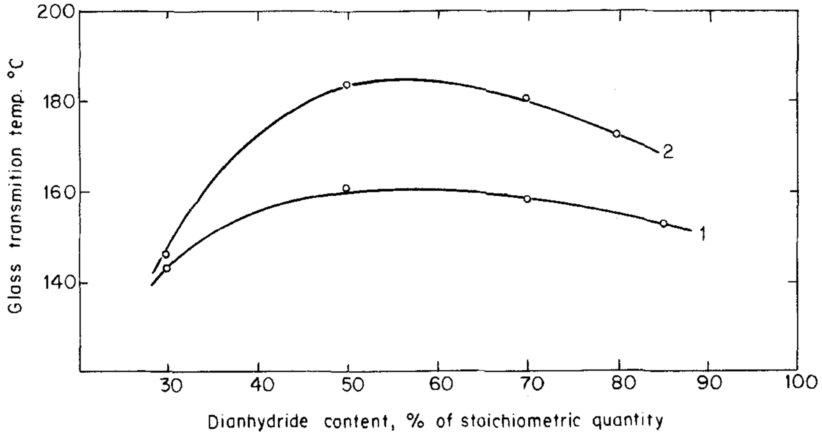

FIG. 5. Relationship of glass transition temperature vs. p,p'-phenolphthalein-bis(trimellitic) dianhydride content in the composition: (1) hardening at 150°C for 6 hr; (2) hardening at 170°C for 6 hr.

TABLE 1. Heat of Reaction of Hardening of Compositions

	Heat of hardening process, cal/g	
Composition	Calculated for 1 g composition	Calculated for 1 g epoxy resin
ETMF-0.3[a]	48.9	73.5
ETMF-0.5	56.8	101.0
ETMF-0.85	55.6	134.0

[a] Heat of hardening process covered by first exothermic effect. The heat of hardening associated with the second exothermic effect is 9.3 cal/g of composition (13.9 cal/g resin).

To draw a straight line it is necessary to know the values of H, H_T, dH/dt, and d(dH/dt)/dt. These values can be obtained from the DSC curve recorded at linear temperature increase rate. A method of plotting these parameters is explained in Fig. 6.

The parameters H, dH/dt, and d(dt/dH)dt were determined for

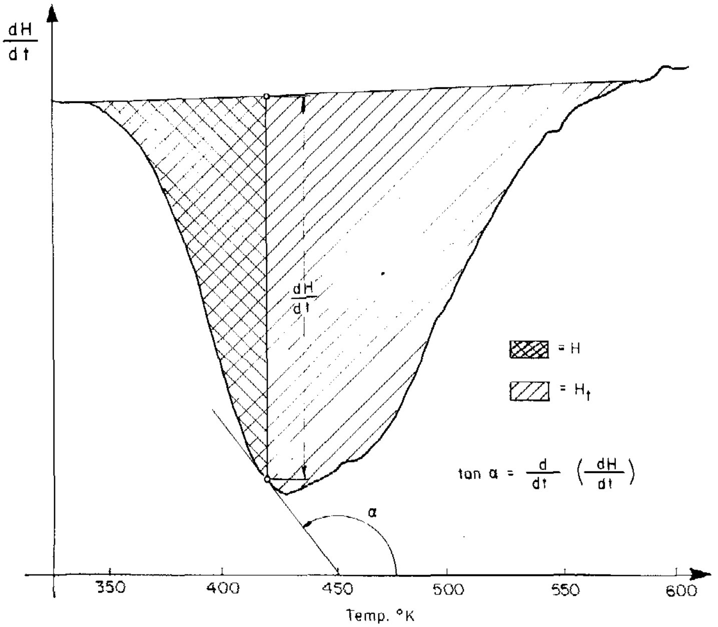

FIG. 6. Determination of the quantities in Eq. (3) from the DSC curve of ETMF-0.5 composition recorded at a rate of heating of 32°C/min.

points on the DSC curve at every 10°C increase. Approximately a straight line was drawn after substituting the determined parameters into the Eq. (3) and calculating the x and y coordinates.

From the slope of the straight line, the activation energy was calculated, and from a knowledge of the intercept c the order of reaction was determined. These procedures are explained in Fig. 7.

Properties of the Hardened ETMF-0.5 Composition

The thermal resistance of the hardened composition (150°C/1 hr) was examined by using the derivatograph (MOM-Budapest, HDR) in air at a rate of temperature increase of 80°C/min. The mechanical properties were examined on coatings 50 μm in thickness. The results are given in Table 2.

The chemical resistance of the hardened composition was tested according to ASTM standard - Method D-543-60T, except that a

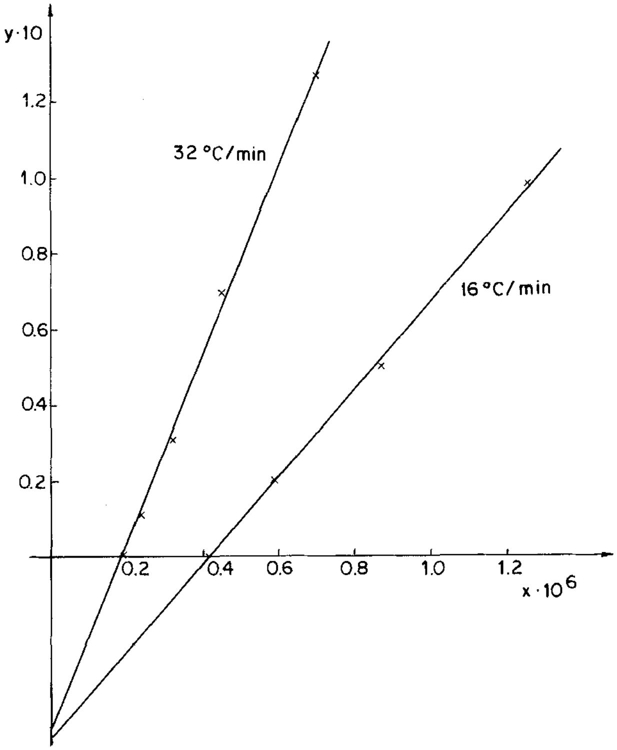

FIG. 7. Straight lines approximating the transition according to Eq. (3) for DSC curves of DTMF-0.5 composition at heating rates of 16°C/min and 32°C/min. At β = 16°C/min, h_t = 54 cal/g, E = 14.5 kcal/mole, and n = 2.54; at β = 32°C/min, h_t = 59.7 cal/g, E = 15.1 kcal/mole, and n = 2.6.

somewhat different procedure of drying the coatings was used. The coatings were dried in a vacuum oven at 40°C to obtain a constant mass instead of drying with a blotting-paper as given in the standard. The thickness of the hardened coatings averaged 120-140 μm. The results are presented in Table 3.

DISCUSSION OF RESULTS AND CONCLUSIONS

From the DSC curves (Figs. 1 and 2) of unhardened epoxy compositions containing 0.5 and 0.85 of the stoichiometric amount of dianhydride, it may be concluded that the hardening process is characterized

TABLE 2. Properties of Hardened ETMF-0.5 Composition

	Results
Thermal resistance	
Temperature of initial thermal decomposition (°C)	ca. 310
Weight loss under heating to 350°C (%)	about 5
Mechanical properties	
Flexibility, mm	$> 20^a$
(Polish Standard PN-69/C-81528-B)	
Impact resistance, (kg-cm)	10
(Polish Standard PN-54/C-81526)	
Relative hardness	0.90
(Polish Standard PN-73/C-81530)	

[a] Free coating 100 μm thick bends without cracking on a mandrel 15 mm in diameter.

TABLE 3. Chemical Resistance of Coatings from Hardened ETMF-0.5 Composition

	Loss in weight of coating (%)[a]	
Solutions	7 days	28 days
10% NaCl	0.17	0.33
10% NaOH	2.5	2.9
3% H_2SO_4	0.71	0.82
CH_3COCH_3	0.67	0.73

[a] Loss in weight of coating after immersion in corrosive chemicals for times stated.

by only one exothermic effect having its maximum in the temperature range 150-160°C at heating rate of 32°C/min or in the range of 135-145°C at a rate of 16°C/min.

In the hardening of the epoxy composition comprising 0.3 of a stoichiometric amount of dianhydride, two exothermic effects occur (Fig. 1).

The first exothermic effect occurs in the range of temperatures close to those of compositions having a larger dianhydride content, whereas the second one occurs at much higher temperatures having its maximum in the range of 266-270°C at a heating rate of 32°C/min. It may be assumed that the epoxy resin compositions containing 0.5 and 0.85 of stoichiometric amount of dianhydride, hardens mainly by reactions of the functional groups of the resin with dianhydride. According to the mechanism of hardening of epoxy resins with acid anhydrides proposed by Fisch and Hofmann [14], these are reactions of anhydride groups with resin hydroxyl groups and of carboxy groups formed by their successive reaction with resin epoxy groups. A lack of exothermic deviation in the DSC curve at higher temperatures does not prove that all the epoxy groups reacted completely. It suggests rather that the crosslinked spacial structure formed interferes with further reactions.

If the dianhydride content in a composition is only 0.3 of the stoichiometric amount, then the reactions of resin functional groups with dianhydride occur with the largest thermal effect in the range of 150-160°C, as in the case of compositions with greater dianhydride content. These reactions result in a loosely crosslinked resin. The remained unreacted functional groups take part in reactions occurring at higher temperatures giving the second exothermic effect. The formation of a crosslinked structure hindering further reaction of functional groups in the resin with larger amounts of dianhydride is proved by comparison of the heat of hardening values presented in Table 1.

The heat of reaction calculated per gram of epoxy resin depends on the number of functional groups taking part in the hardening reaction. The heat of hardening of combinations being tested increases, however, much more slowly than expected from the greater weight ratio of dianhydride to resin in a given composition. At a low dianhydride content varying from 0.3 to 0.5 of stoichiometric amount, the mean ratio of the increase in heat of reaction per gram of resin to increase of added amount of dianhydride averages 33 cal/g dianhydride, whereas at higher dianhydride content, e. g., in the range from 0.5 to 0.85 of stoichiometric amount, this ratio averages only 22.7 cal/g dianhydride.

The glass transition temperature of a composition characterizes the state of its crosslinking. With prolonged crosslinking, the glass transition temperatures of the compositions being examined tend to a certain limiting value characteristic for a given temperature of hardening (Fig. 3).

From the relationship of the glass transition temperatures of compositions tested versus time of hardening at 150°C and 170°C (Fig. 4), it is shown that composition ETMF-0.3 has much lower glass transition temperatures than ETMF-0.5 and ETMF-0.85 under the same conditions. In case of ETMF-0.3, an increase in hardening temperature from 150°C to 170°C does not influence the increase of glass transition temperature of the hardened composition, but merely accelerates the process of hardening in its initial period. For other compositions, the increase of glass transition temperatures is observable.

From the relationship of glass transition temperature versus dianhydride content in the composition shown in Fig. 5, it is evident that the highest glass transition temperature is obtainable at a determined dianhydride content and its variation to lower or higher content results in the decrease of glass transition temperature.

The ETMF-0.5 composition, examined in detail, lies in the range of optimum dianhydride content. The activation energy of hardening determined from the exothermic effect related mainly to a reaction between functional groups in the resin with dianhydride averages 14.5-15.1 kcal/mole. The low value of activation energy indicates high reactivity of the examined epoxy resin-p,p'-phenolphthalein-bis(trimellitic) dianhydride system. For comparison, it can be mentioned that according to Fava [9] the activation energy of hardening of DOW DER 332/LC diane resin with a molecular weight of about 340 and epoxy equivalent of 170-175 hardened with hexahydrophthalic anhydride in the presence of 2,4,6-tri(dimethylaminomethyl)phenol as an accelerator averages 17.8 kcal/mole. The small scatter of points determined from the DSC curve in relation to the approximating straight line (Fig. 7) confirms the assumption that hardening of the epoxy resin with the dianhydride proceeds in accordance with the Arrhenius Law and is probably a reaction of higher order.

The ETMF-0.5 composition is characterized, after its hardening, by high hardness and excellent resistance to sulfuric acid and acetic acid. However, it is much less resistant to alkalis and has a relatively low impact resistance. It also resists heating to 310°C in air.

The advantageous properties of the compositions discussed and their easy processing resulting from good solubility of the hardener offer a new prospect of practical applications of p,p'-phenolphthalein-bis(trimellitic) dianhydride for hardening the low molecular weight epoxy resins.

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Accepted by editor December 7, 1978
Received for publication December 11, 1978