

Phosphorus Containing Epoxy for Flame Retardant II: Curing Reaction of Bis-(3-Glycidyoxy) Phenylphosphine Oxide

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SYNOPSIS

The curing reaction of a phosphorus containing epoxide, bis-(3-glycidyoxy) phenylphosphine oxide (BGPPPO), was studied by differential scanning calorimeter (DSC) using dynamic and isothermal methods. Kinetic parameters and activation energy of the BGPPPO cured with diamine or dianhydride curing agents were determined. The dynamic activation energies were significantly larger than the isothermal ones. Via isothermal analysis technique, the activation energies of BGPPPO cured with 4,4'-diaminodiphenylmethane, dicyanodiamide, methyl tetrahydrogen phthalic anhydride, and phthalic anhydride were found to be 69.5, 83.5, 93.6, and 90.6 kJ/mol, respectively. These values were comparable with those of other commercial epoxy curing system. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins, with the characteristics of toughness, low shrinkage on cure, high adhesion to many substrates, good alkali resistance, and versatility in formation, are widely used in adhesive, laminating, coating, and casting application. However, like other organic polymeric materials, epoxy resins' flammability is a major shortcoming in application. To improve the flame resistance of epoxy resin in application, several attempts have been made to impart flame retardance to epoxy resins.¹⁻⁵ In our previous study,⁵ an oxirane compound with phosphorus elements in the backbones, bis-(3-glycidyoxy) phenylphosphine oxide (BGPPPO, Fig. 1), was synthesized. The synthesized phosphorus containing oxirane with a high phosphorus content of 11.5% by weight has been examined to exhibit a high efficiency in enhancing the flame retardance of the epoxy resins.

Curing kinetics, curing rate, variation of rate at various temperature, and activation energy

are useful for epoxy application.^{6,7} These kinetic data provide information for the cure cycles of epoxies. This will ensure that the adequately cured epoxy is able to meet the requirements of its end use. Therefore, the curing reaction of this phosphorus containing epoxy has to be studied in great detail.

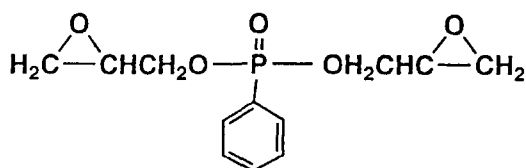
Differential scanning calorimetry (DSC) is often used to characterize the curing behavior of epoxy resins. Apart from that, DSC has been established to optimum curing conditions for epoxy resins.^{8,9} Furthermore, capable of recording the rate and the enthalpies of reaction simultaneously, DSC is also a valuable technique for investigating the kinetic parameters of the curing reaction of epoxy resins.^{6,7,10-15} In general, the cure kinetics can be described by a rate law given by

$$d\alpha/dt = k \cdot f(\alpha)$$

where α is the fractional conversion, k is the rate constant, and $f(\alpha)$ is a function of the fractional conversion. The rate constant k is usually assumed to be of the Arrhenius form

$$k = A \exp(-E_a/RT)$$

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BGPPO

Figure 1 The chemical structure of BGPPO.

where A is a constant, R is the gas constant, E_a is the activation energy, and T is the absolute temperature. It is common in thermal analysis to quote the rate constants. A number studies of reactions using DSC have given values for rate constant and activation energy that are in good agreement with those determined by other methods.¹⁶

Based on the above, both dynamic and isothermal techniques of DSC were used to investigate the curing reactions of BGPPO with several curing agents. The reaction enthalpies, the kinetic parameters, and the activation energies of these reactions were obtained.

EXPERIMENTAL

Materials

BGPPO was synthesized as described previously.⁵ The curing agents of dicyanodiamide (DICY), 4,4'-2diaminodiphenylmethane (DDM), methyl tetrahydrogen phthalic anhydride (MEPHTA), and phthalic anhydride (PA) were used as received.

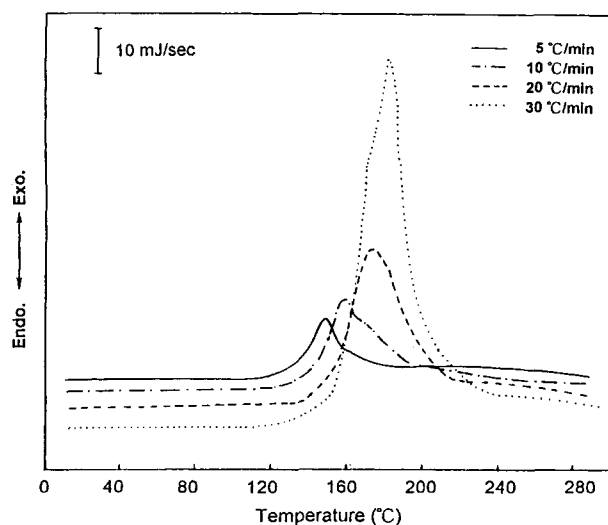


Figure 2 Dynamic DSC curves for the curing of BGPPO/DICY at various heating rates.

Table I Enthalpies of the BGPPO/Curing Agents Curing Reactions

Curing Agent	Heating Rate (°C/min)	Enthalpy (J/g)
DDM	5	245
DDM	10	235
DDM	20	230
DICY	5	406
DICY	10	398
DICY	20	415
MEPHTA	5	159
MEPHTA	10	143
MEPHTA	20	137
PA	5	119
PA	10	104
PA	20	101

DSC Measurements

The reactant compositions were dissolved in acetone. The solvent was then evaporated under vacuum to obtain the reaction mixtures. Samples of 7.0 ± 0.1 mg were used for DSC measurements. The DSC thermograms were recorded under nitrogen atmosphere with a Seiko DSC 5200. In the dynamic analysis, the experiments were carried out at heating rates of 5, 10, and 20°C/min, re-

Table II Rate Constants of BGPPO/DICY Curing Reactions From Dynamic Method I

Heating Rates (°C/min)	Temperature (°C)	Rate Constant $k \cdot 10^3$ (s ⁻¹)
5	135	1.36
5	140	2.73
5	145	5.00
5	155	9.13
5	160	11.12
5	165	14.26
10	145	2.23
10	150	4.24
10	155	8.06
10	160	12.21
10	165	13.45
10	170	16.10
10	175	22.12
20	160	4.92
20	165	9.17
20	170	14.05
20	175	17.36
20	180	22.56
20	185	28.78
20	190	39.52

Table III Rate Constants Calculated by Dynamic Method I at 10°C/min From BGPPPO/Curing Agent Reactions

Curing Agent	Temperature (°C)	Rate Constant $k \cdot 10^3$ (s ⁻¹)
DDM	110	2.06
DDM	120	5.07
DDM	130	11.02
DDM	140	18.10
DICY	150	4.24
DICY	160	12.14
DICY	170	16.04
DICY	175	22.00
MEPHTA	175	3.68
MEPHTA	180	5.09
MEPHTA	190	10.05
MEPHTA	200	17.32
PA	180	4.72
PA	190	9.09
PA	200	17.15
PA	210	36.25

spectively. In the isothermal analysis technique, the samples were placed in the calorimetric cell at room temperature and then heated at 200°C/min up to the desired temperatures for a certain period of time.

Data Analysis Methods

Dynamic Method I

In this method,^{6,10} only one reaction curve is analyzed. As the temperature of the system increases continuously, a series of rate constants at different temperatures can be obtained by

$$k = (dH/dT)/\Delta H \tag{1}$$

where $\Delta H = \Delta H_o - \Delta H_T$, where ΔH_T is the enthalpy read at temperature T and ΔH_o is the total reaction enthalpy of cure reaction. From these rate constants at various temperatures, the activation energy can be determined.

Dynamic Method II

A simple but accurate relationship^{10,11,14,15} among activation energy (E_a), heating rate (ϕ), and temperature of exothermic peak (T_p) as

$$E_a \approx \frac{-R}{1.052} \frac{\Delta \ln \phi}{\Delta(1/T_p)} \tag{2}$$

is used. The method provides an easy calculation of the activation energy.

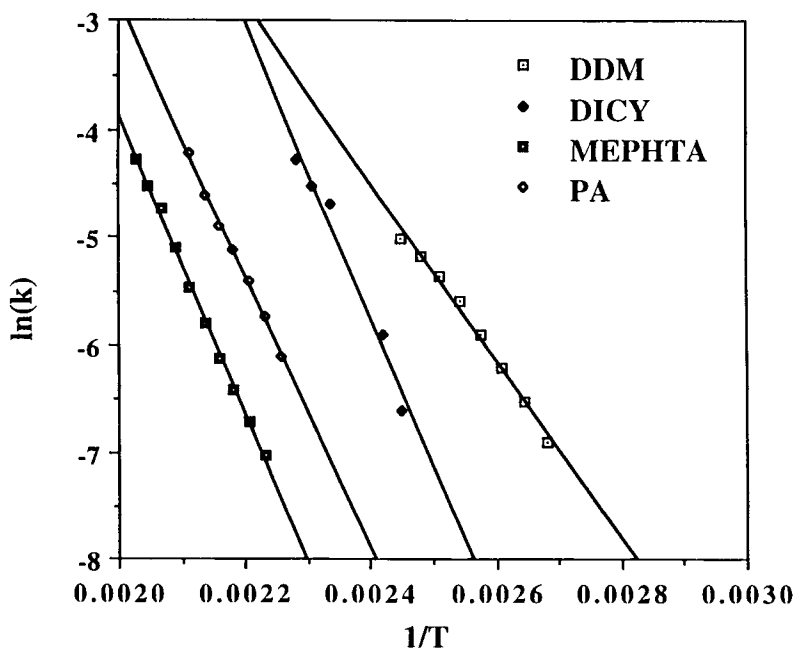


Figure 3 Arrhenius plot from dynamic method I at 10°C/min.

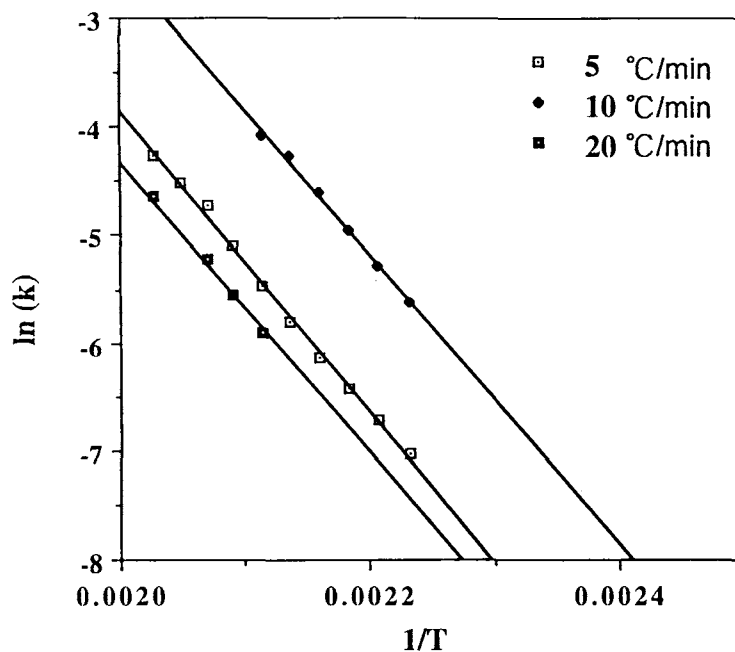


Figure 4 Arrhenius plot from dynamic method I for the curing of BGPPO/PA.

Isothermal Method

The rate of enthalpy evolution is recorded as a function of time.^{6,7,10-13} Consequently, the degree of conversion at a time t could be obtained by

$$\alpha_t = \Delta H_t / \Delta H_o \quad (3)$$

where ΔH_t is the enthalpy read at time t and ΔH_o is the total reaction enthalpy of cure reaction. Subsequently, the rate of reaction is given by $d\alpha/dt$. The rate constant can be determined from these parameters. Furthermore, the activation energy of the reaction can be also obtained from isothermal studies at various temperatures. However, the error in setting the baselines of the isothermal curves is not negligible due to the fact that certain degree of reaction may occur during the initial temperature ramp before the isothermal equilibrium. Because of

that, the correction for this is made according to the literature.^{7,17}

RESULTS AND DISCUSSION

The thermal curing reactions of BGPPO and various curing agents DDM, DICY, MEPHTA, and PA were studied. Figure 2 shows the typical DSC thermograms of rate of heat evolution as a function of temperature. It is noteworthy that an endothermic peak was found in the curing curve of BGPPO/DDM. This endothermic peak at 80°C corresponds to the melting of DDM. Nevertheless, the baseline was straight before the exothermic behavior appeared. For other curing agents, no endothermic peak was found in the curing curves, and the baseline was straight before the exo-

Table IV Activation Energies (kJ/mol) of BGPPO/Curing Reagent Reaction

Curing Agent	Isothermal Method	Dynamic Method I			Dynamic Method II
		5 ^a	10 ^a	20 ^a	
DDM	69.5	100.0	102.7	111.7	64.9
DICY	83.5	114.2	103.6	107.1	86.0
MEPHTA	93.6	115.9	111.3	111.5	107.9
PA	90.6	105.6	118.6	98.7	97.7

^a Heating rate (°C/min).

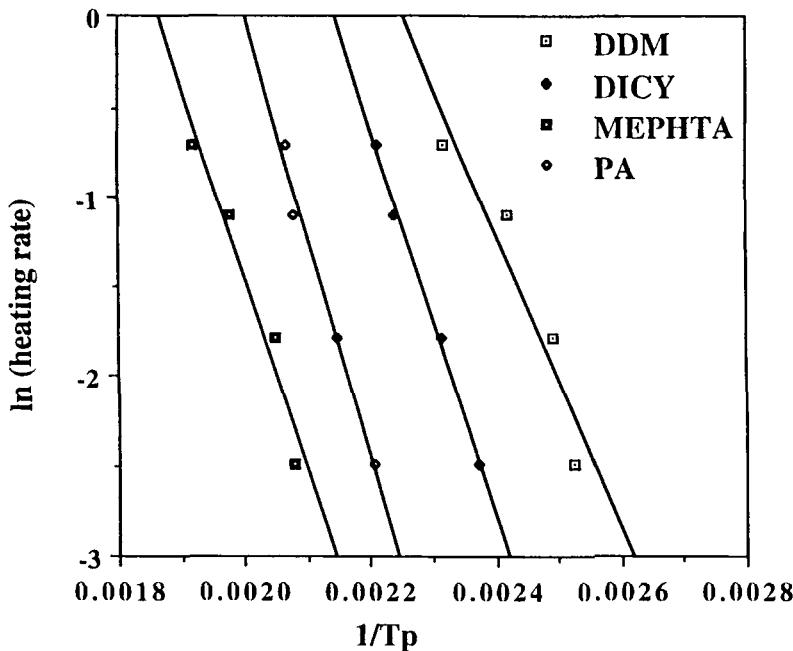


Figure 5 Determination of the activation energy by dynamic method II.

thermic peak appeared. This implies that the enthalpy values are directly applicable for the kinetic parameter calculation.

Dynamic Method I

The enthalpy of complete curing reaction was first obtained from dynamic scan. Values of the enthalpy were obtained at several heating rates. Variation in heating rates did not have significant effect on the value of the complete curing enthalpy (Table I).

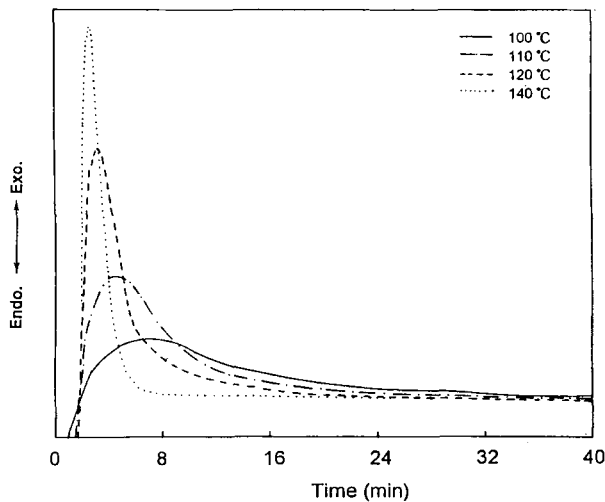


Figure 6 Isothermal DSC curves for the curing of BGPPO/DDM at various temperatures.

The reaction enthalpies were found to be 222, 401, 144, and 104 J/g for BGPPO/DDM, BGPPO/DICY, BGPPO/MEPHTA, and BGPPO/PA, respectively.

For applying eq. (1) to calculate the activation energy, the known reaction order is a prerequisite. Therefore, the curing reaction was assumed to be a first-order reaction in the first place. dH/dT and ΔH were obtained at various temperatures from the DSC thermograms. Table II summarized the values of dH/dT , ΔH , and rate constant k of the curing reaction of BGPPO with DICY at various heating rates. The maximum values of dH/dT increased with the increase of heating rates. On the other hand, the values of rate constant k at a constant temperature decreased with the increase of heating rates. The rate constant of curing reaction of BGPPO with different curing agents were collected in Table III. From the beginning temperatures of the curing reaction, it was revealed that DDM is most reactive toward BGPPO among these curing agents. This was also confirmed by the rate constants of these curing reaction at a certain temperature.

The activation energy was obtained from Arrhenius plots (Figs. 3 and 4). It is important to note that the Arrhenius plots for all curing reactions were linear. This verifies that the assumption of first-order reaction is correct. Moreover, the obtained values of the activation energy were varied with heating rates. However, this variation was not significant. For examples, the values of 100.0–111.7

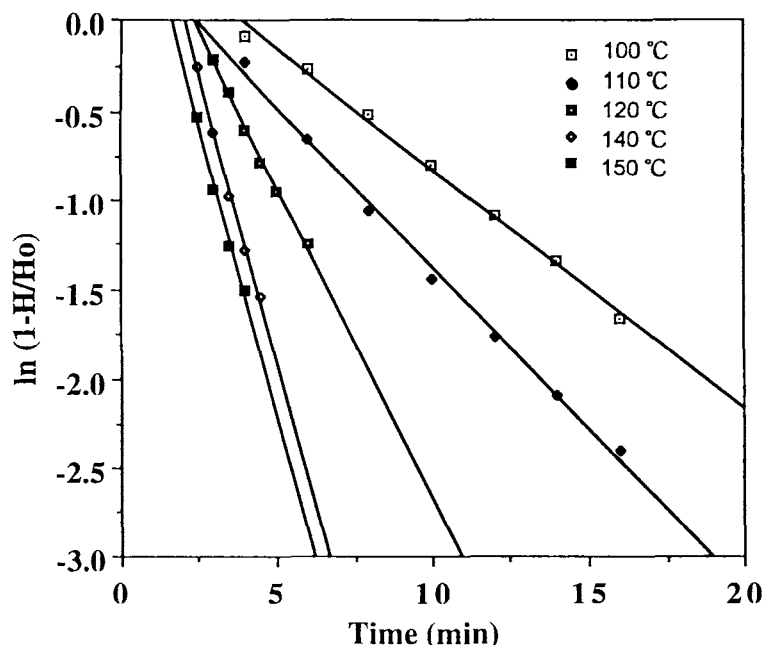


Figure 7 Plot from isothermal method for a first-order curing of BGPPO/DDM.

and 111.5–115.9 kJ/mol for BGPPO/DDM and BGPPO/MEPHTA, respectively, were obtained.

More values of activation energy were summarized in Table IV. The smallest activation energy was obtained for the curing reaction of BGPPO/DDM, whereas the largest activation energy was found for the BGPPO/MEPHTA curing reaction.

Table V Rate Constant k from Isothermal Method

Curing Agent	Temperature (°C)	Rate Constant $k \cdot 10^3$ (s ⁻¹)
DDM	100	2.23
DDM	110	3.02
DDM	120	5.82
DDM	130	11.11
DICY	130	1.68
DICY	140	2.85
DICY	150	5.46
MEPHTA	160	1.79
MEPHTA	170	4.02
MEPHTA	180	4.99
MEPHTA	190	7.32
MEPHTA	210	14.02
PA	150	1.53
PA	160	3.96
PA	170	4.44
PA	180	8.86
PA	190	13.05
PA	200	16.12

Furthermore, the activation energies of BGPPO/amine curing agents were smaller than those of BGPPO/anhydride curing agents.

Dynamic Method II

Dynamic method II provides a convenient way to obtain the activation energy of a curing reaction without resorting to the evaluation of the reaction order and reaction rate constant. The plot based on eq. (2) for determining the activation energy is shown in Figure 5. The activation energies determined by this method were also summarized in Table IV. The activation energies of the curing reactions for BGPPO and various curing agents were found in the order of DDM < DICY < PA < MEPHTA. However, the obtained values from this method were smaller than those from dynamic method I. Somehow, this agrees with the results of the literature.⁷ This is because calculations relying on the variation of peak position with heating rate (dynamic method II) generally show smaller estimates than those on the initial and prepeak portion of the curves (dynamic method I).

Isothermal Method

Although the sample was cured isothermally, the evaluating heat of the reaction was recorded as a function of reaction time (Fig. 6). The rate constant was therefore obtained on the basis of

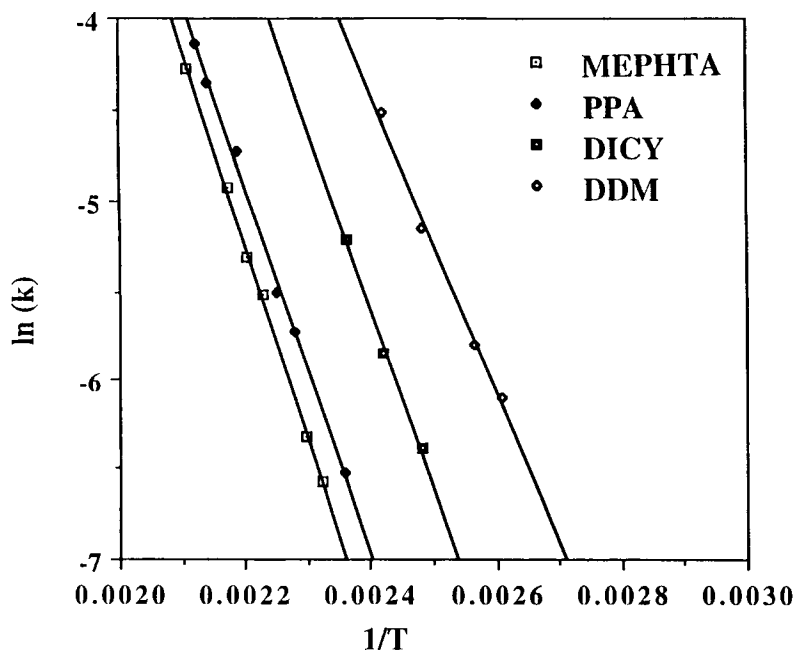


Figure 8 Arrhenius plot from isothermal method.

a first-order curing reaction. For the curing reaction of BGPPO/PPA, Figure 7 shows a typical plot of isothermal method. Not only BGPPO/PPA but other compositions showed linear representation (regression coefficient > 0.99) for all curing temperatures in the plots. This validates the assumption of first-order reaction for all curing reactions.

Table V shows the calculated k values. These k values are not in good agreement with those from dynamic method I. The dynamic rate constants were smaller than the isothermal ones at low temperatures, whereas at high temperatures, it is the other way around. Furthermore, the activation energy was obtained from Arrhenius plot (Fig. 8). All of the activation energy values are smaller than those obtained from dynamic method I (Table III). This phenomenon can be explained by the above mentioned rate constant data. A smaller rate constant at a low temperature for dynamic method I leads to a larger activation energy due to the factor of the activation energy was obtained from Arrhenius plots. This also has been reported in other epoxy curing studies.^{8,11}

For amine-curing agents, the values of activation energy were in agreement with the values from dynamic method II. The activation energy of DDM, 64.9 and 69.5 kJ/mol from dynamic method II and isothermal method, respectively, are com-

parable with the activation energy of other epoxies cured with DDM.¹⁷⁻²⁰ For anhydride curing agents, however, the values of curing activation energy were somewhat smaller than those from dynamic method II. The deviation of activation energy estimation from dynamic method II could be owing to the complex mechanism of the anhydride curing reactions. From DSC thermograms, more than one exothermic peaks were found for anhydride curing reaction. The complex exothermic behavior could be possibly due to the fact that both esterification and etherification reaction take part in the anhydride curing reaction.^{6,21,22} Furthermore, autocatalytic features and diffusion effects also made this curing reaction complicated.¹² This made it difficult to locate the temperature of the exothermic peak. As a result, inaccuracy might occur when the activation energies of the epoxy/anhydride curing reaction were estimated. This also implies that the isothermal DSC data is generally easier to be interpreted than the dynamic DSC data. The reported values of activation energy of anhydride curing epoxy reaction were varied from 60 to 150 kJ/mol.²³⁻²⁶ With baseline correction,^{12,27} the values of activation energy for BGPPO/MEPHTA and BGPPO/PA are found to be 93.6 and 90.6 kJ/mol, respectively. These values are well located in the range of the activation energies for epoxy systems without any phosphorus content.²³⁻²⁶

CONCLUSION

The curing kinetics of the novel phosphorus containing epoxy BGPPO was determined. BGPPO was more reactive toward amine curing agents than toward anhydride types. The curing reaction could be considered as a first-order reaction. From dynamic and isothermal analysis, the activation energy of the BGPPO curing reaction was determined. The activation energy from dynamic method I showed somewhat overestimated than those from isothermal method. Furthermore, activation energies measured by isothermal analysis were in good agreement with those measured by dynamic II method. The activation energies of curing reactions for BGPPO/DDM, BGPPO/DICY, BGPPO/MEPHTA, and BGPPO/PA were found to be comparable to those in literature.²³⁻²⁶

Financial support of this work from National Science Council (NSC-85-0210-D-007-020) is acknowledged.

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Received November 28, 1995

Accepted March 18, 1996