

Dynamic DSC Curing Kinetic Study of Epoxy Resin of 1,3-Bis(4-hydroxyphenyl) prop-2-en-1-one Using Aromatic Diamines and Phthalic Anhydride

Pooja P. Adroja, Rizwan Y. Ghumara, Parsotam H. Parsania

Polymer Chemistry Division, Department of Chemistry (UGC-SAP and DST-FIST sponsored), Saurashtra University, Rajkot-360 005, Gujarat, India

Correspondence to: P. H. Parsania (E-mail: phparsania22@gmail.com or phparsania@aol.com)

ABSTRACT: Epoxy resin of 1,3-bis(4-hydroxyphenyl)prop-2-en-1-one has been synthesized and studied its cure kinetics by differential scanning calorimetry at four different heating rates in nitrogen atmosphere and varying proportions of 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulfone and phthalic anhydride. The energy of activation (E_a) and pre-exponential factor (A) has been determined according to Flynn-Wall-Ozawa method at various degrees of cure ranging from 0.1 to 0.9. The derived results are discussed in light of effect of hardeners concentrations, heating rates, degree of cure, and nature of hardeners, etc. The structure of the hardeners and their concentrations affected the cure behavior. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 572–578, 2013

KEYWORDS: differential scanning calorimetry (DSC); kinetics; resins; polycondensation

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INTRODUCTION

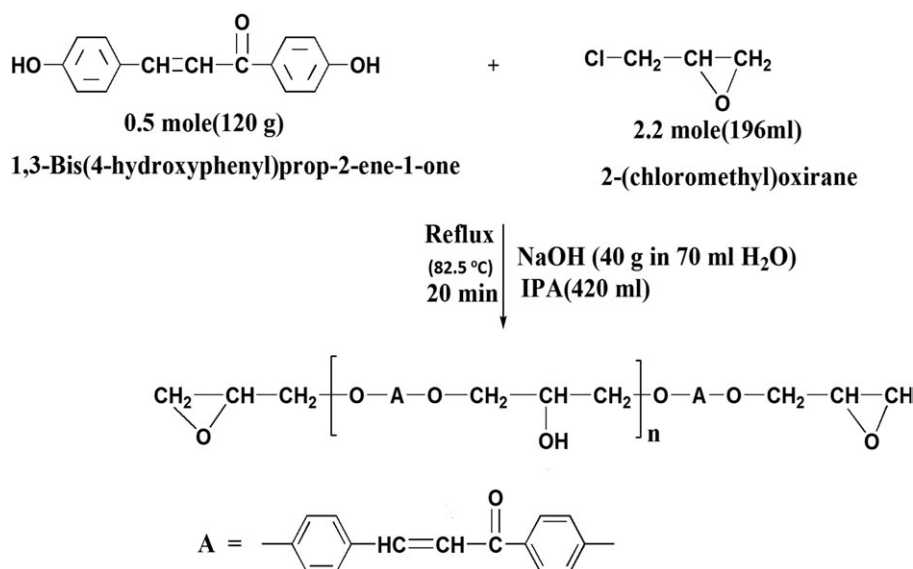
High-performance epoxy resins with improved thermal properties can be synthesized by introducing various aromatic ring systems into epoxy skeletons or by the use of curing agents containing biphenyl, naphthalene, fluorene, heterocyclic ring, etc.^{1–9} Epoxy resins with improved physico-chemical properties such as good thermal stability, low dielectric constant and dissipation factor with low water absorption, low coefficient of thermal expansion, low internal stress, high mechanical strength and low modulus are very useful for advanced technological applications.^{10–13}

Most frequently aromatic diamines are used as curing agents for epoxy resins but bond strength lowers at higher temperatures. The use of modified aromatic diamines and aromatic diamines containing heterocyclic rings are reported in the literature for the improvement of thermal resistance of epoxy resins.^{14–18} Curing kinetics of thermosets is very useful in understanding structure/property/processing relationships for manufacture and utilization of these polymeric materials. Differential scanning calorimetry (DSC) is an important tool for understanding curing kinetics of thermosetting materials, in predicting shelf-life and optimizing processing conditions.^{19–21} Kinetic data of cured epoxy resins such as curing kinetics, curing rate, variation of

rate under various conditions and activation energy, etc. are useful parameters for their advanced applications.

Photosensitive polymers possess a combination of good properties in terms of dielectric constant, thermal stability, and sensitivity. Polymers containing an α , β -unsaturated carbonyl (chalcone) group are used as photoresists in microlithography, printing materials, energy exchange materials, etc.^{21–23} Such polymers can undergo crosslinking upon UV irradiation. The main chain or side chain containing functional groups such as cinnamate, chalcone, coumarine, dibenzalacetone, and their derivatives are used as UV sensitive polymers for above mentioned applications. A considerable amount of work has been reported on the photosensitivity of the chalcone epoxy compound.^{24,25}

To the best of our knowledge no work has been reported on DSC curing kinetics of chalcone moiety containing epoxy resins. In this work we have studied DSC dynamic curing kinetics of chalcone moiety containing epoxy resin (Scheme I) by using 4,4'-diaminodiphenyl ether (DDE), 4,4'-diaminodiphenyl sulfone (DDS) and phthalic anhydride (PA) as hardeners. The structure property relation is studied in terms of effect of hardener concentration and heating rates on curing behavior. An effort has also been made to study autocatalytic and other simultaneous side reactions occurring during dynamic curing reactions.



Scheme 1. Epoxidation reaction of 1,3-bis(4-hydroxyphenyl)prop-2-en-1-one.

EXPERIMENTAL

Materials

Solvents and chemicals used were of laboratory grade and purified prior to their use.²⁶ Epoxy resin of 1,3-bis(4-hydroxyphenyl)prop-2-en-1-one (ECH) used in this investigation was synthesized according to our recent work²⁷ as mentioned in Scheme I and has epoxy equivalent of 264. Hardeners such as 4, 4'-diaminodiphenyl ether (DDE) (Spectrochem, Mumbai), 4,4'-diaminodiphenyl sulfone (DDS) (National Chemicals, Vadodara) and phthalic anhydride (PA) (Allied Chemicals, Mumbai) were used as received.

Dynamic DSC Curing of ECH

Curing kinetics of ECH was studied on a Shimadzu DSC60 at four different heating rates namely 5°, 10°, 15°, and 20°C min⁻¹ in an N₂ atmosphere (20 mL min⁻¹) by using 5–20% 4, 4'-diaminodiphenyl ether (DDE), 4,4'-diaminodiphenyl sulfone

(DDS) and phthalic anhydride (PA) hardeners. The samples were prepared thoroughly by grinding required quantities of ECH and hardeners. Known amounts (1.5 mg) of the samples were sealed with the help of a crimper. Here after samples used for curing study are designated as ECH-DDE, ECH-DDS, and ECH-PA.

RESULTS AND DISCUSSION

DSC thermograms of ECH-DDE, ECH-DDS, and ECH-PA of 5–20 wt % at 20°C min⁻¹ heating rate in an N₂ atmosphere are shown in Figures 1–3, respectively from which information about the nature of the curing reaction such as onset of curing reaction (T_o), peak temperature (T_p), the curing range and heat generated (ΔH) were derived from primary curves and are reported in Table I. From Table I, it is observed that the melting transition of ECH remained practically constant for DDE (102.5–103°C) and DDS (100.7–102.5°C) but it is decreased in case of PA (96.9–81.3°C) with increasing hardener

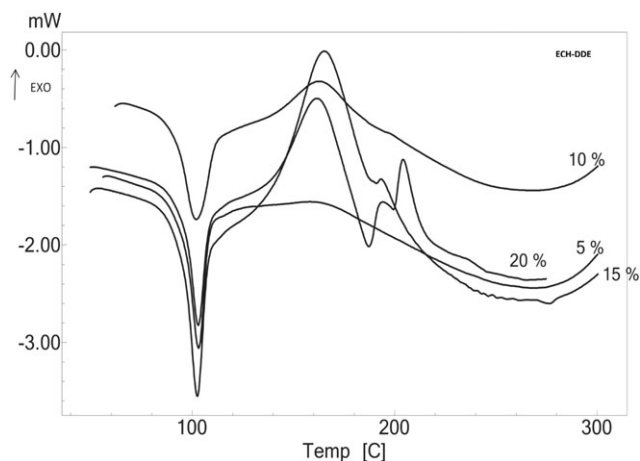


Figure 1. DSC thermograms of ECH resin with varying % of 4, 4' diaminodiphenyl ether as a hardener at the heating rate of 20°C min⁻¹ in N₂ atmosphere.

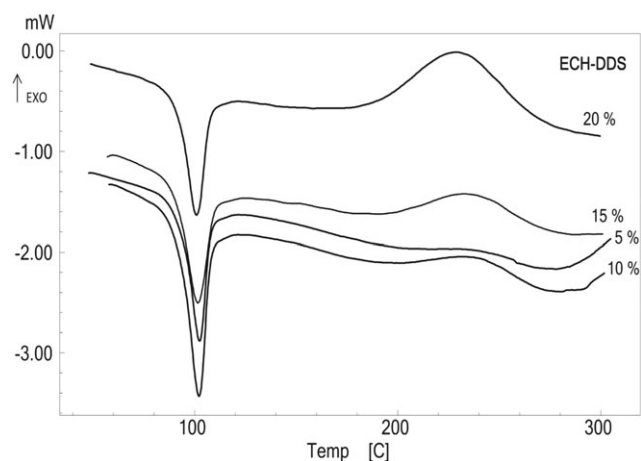


Figure 2. DSC thermograms of ECH resin with varying % of 4, 4' diaminodiphenyl sulfone as a hardener at the heating rate of 20°C min⁻¹ in N₂ atmosphere.

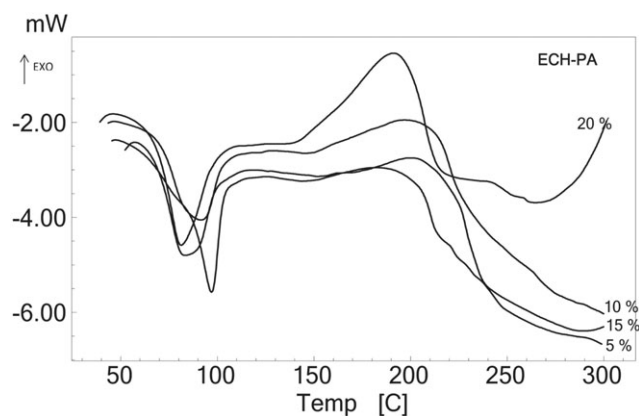


Figure 3. DSC thermograms of ECH resin with varying % of phthalic anhydride as a hardener at the heating rate of $20^{\circ}\text{C min}^{-1}$ in N_2 atmosphere.

concentration. Exothermic peak temperature increased up to 15 wt % hardener concentrations and it is decreased for 20 wt % hardener concentrations. Heat generated increased with hardener concentration except 20% DDE due to two stages curing reactions of ECH-DDE (two exothermic peaks). The values of ΔH decreased due to observed tailing towards higher temperature range. First reaction is due to ring opening polymerization in presence of diamine hardener, whereas second stage reaction is due to ultimate crosslinking and some side reactions.

DSC thermograms of ECH-DDE, ECH-DDS, and ECH-PA of 20 wt % concentrations at multiple heating rates in an N_2 atmosphere are shown in Figures 4–6, respectively. Derived curing reaction information such as T_o , T_p , curing range and heat generated are reported in Table II from which it is observed that peak exotherm shifted towards higher temperature

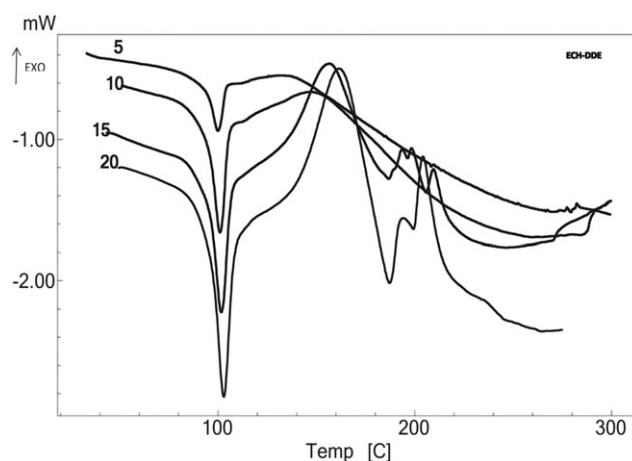


Figure 4. DSC thermograms of ECH resin with 20% 4,4'-diaminodiphenyl ether as a hardener at 5, 10, 15, $20^{\circ}\text{C min}^{-1}$ heating rates in N_2 atmosphere.

range with increasing heating rate. Heat generated increased with heating rate in case of PA and DDS (except $20^{\circ}\text{C min}^{-1}$) hardeners and it decreased at $20^{\circ}\text{C min}^{-1}$. In case of DDE it increased up to $10^{\circ}\text{C min}^{-1}$ and then it decreased at 15° and $20^{\circ}\text{C min}^{-1}$ due to two stages of curing reactions. Peak shapes is found to depend both on hardener concentration and heating rate. Endothermic DSC transition of ECH at 102°C confirmed its melting transition and from thermogravimetric study it is confirmed that ECH is thermally stable up to about 225°C and followed two-step degradation kinetics.²⁷ No crosslinking is observed in nitrogen atmosphere up to 225°C . DSC curing kinetics of DGEBA with diamines have shown only one sharp exothermic peak regardless of heating rate and shifted towards

Table I. Effect of Hardener Concentration on Curing Behavior of ECH

Hardener concen., wt %	Melting transition, ($^{\circ}\text{C}$)	Curing temp. range, ($^{\circ}\text{C}$)	Peak exotherm temp. ($^{\circ}\text{C}$)	Exothermic heat ΔH , (J g^{-1})
ECH-DDE				
5	103.0	125–241	158.21	53.15
10	102.7	131–249	162.63	87.59
15	102.5	122–248	165.32	270.58
20	103.0	128–187	161.56	110.82
		196–220	204.27	43.92
ECH-DDS				
5	102.5	199–260	198.15	7.64
10	102.2	209–282	231.81	15.27
15	101.4	193–284	232.65	38.74
20	100.7	173–289	228.90	104.32
ECH-PA				
5	96.9	144–255	181.88	238.23
10	91.5	144–272	196.85	261.60
15	83.3	146–253	198.80	287.99
20	81.3	133–228	191.30	297.84

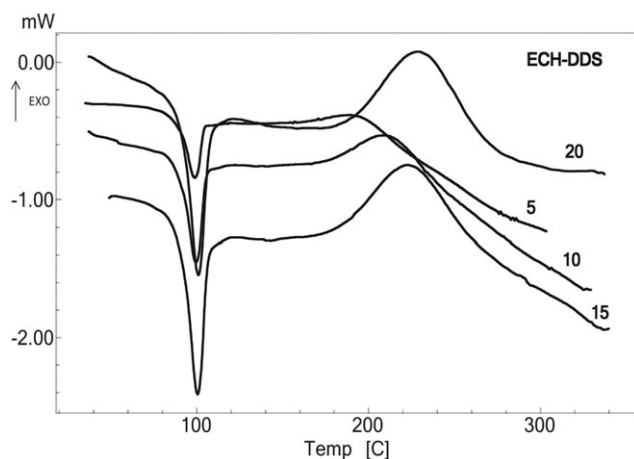


Figure 5. DSC thermograms of ECH resin with 20% 4, 4' diaminodiphenyl sulfone as a hardener at 5°, 10°, 15°, 20°min⁻¹ heating rates in N₂ atmosphere.

higher temperature range but shifted towards lower temperature range with increasing amount of diamine.¹⁴

The curing reaction of epoxy resins depends on the structure and reactivity of specific hardener. The onset of the curing exotherm depends on the nucleophilicity of the amino group. The steric restrictions to the epoxy-amine addition reaction, physical interactions among different functional groups of the constituent components, and curing extension can also influence the curing kinetics.^{14–19} The curing reaction is a complex process because many reactions sometime take place simultaneously. The final properties of the cross-linked resins depend significantly on the kinetics of the curing reaction concerned with the extent of curing, the curing conditions, etc.^{28–30} The curing

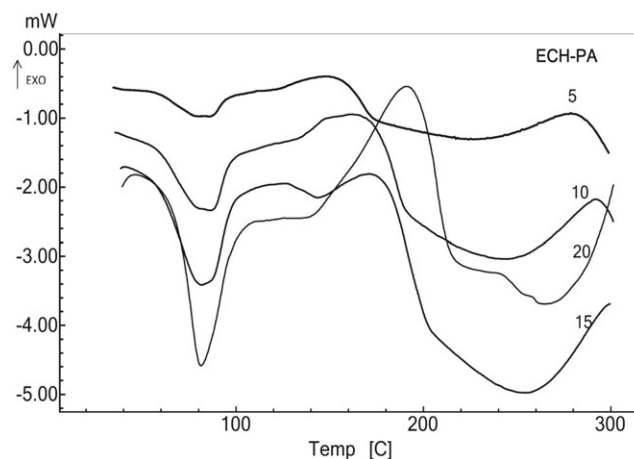


Figure 6. DSC thermograms of ECH resin with 20% phthalic anhydride as a hardener at 5°, 10°, 15°, 20°min⁻¹ heating rates in N₂ atmosphere.

kinetics provides both better knowledge of process development and an improvement of the quality of final products related to the structures of the polymer network.^{31,32}

Many kinetic models including the *n*th order reaction, the autocatalytic reaction and the diffusion control models have developed for the study of curing kinetics of epoxy resins.^{19,32–34} Various degrees of fractional curing (α) were determined by determining total areas under DSC curves (ΔH_{Total}) and areas at definite temperature (ΔH). DSC data were analyzed according to Flynn-Wall-Ozawa isoconversional method.³⁵

$$\ln \beta = \ln \frac{AE_a}{R} = -\ln g(\alpha) - 5.331 - 1.052 \frac{E_a}{RT} g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (1)$$

Table II. Effect of Heating Rate on Curing Behavior of ECH

Heating rate, β , (°C)	Melting transition, (°C)	Curing temp. range, (°C)	Peak exotherm temp., (°C)	Exothermic heat ΔH , (J g ⁻¹)
ECH-DDE				
5	99.9	114–186	132.48	87.10
10	101.0	119–210	147.2	133.86
15	101.7	134–187	156.63	86.83
		193–230	198.48	20.05
20	103.0	137–188	161.56	119.79
		196–220	204.27	43.92
ECH-DDS				
5	98.8	155–255	189.34	145.16
10	99.5	168–278	209.27	184.54
15	100.4	161–295	222.93	190.90
20	100.7	175–289	228.90	108.23
ECH-PA				
5	85.6	117–176	147.6	184.56
10	86.2	125–212	161.35	261.84
15	81.6	142–207	171.14	247.27
20	81.3	131–226	191.3	300.09

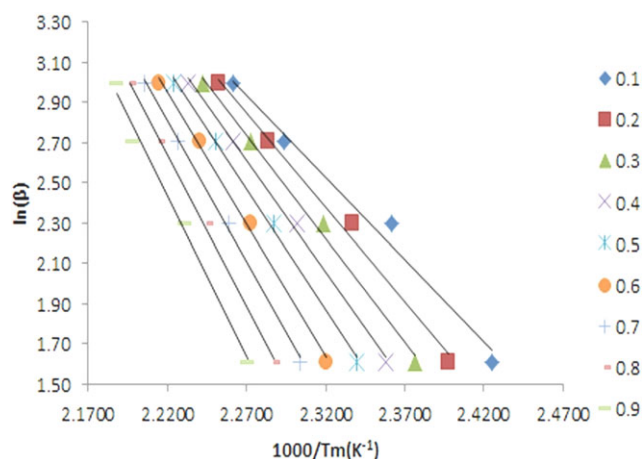


Figure 7. Flynn-Wall-Ozawa plots for ECH-DDE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where β is the heating rate, E_a is the energy of activation, A is the pre-exponential factor, $g(\alpha)$ is the integral form of the reaction model, $f(\alpha)$ is the function of degree of cure, R is the gas constant, T is the temperature, and α is the degree of cure. This method assumes that both of the activation energy (E_a) and pre-exponential factor (A) are the functions of the degree of curing. Isoconversional plots for ECH-DDE, ECH-DDS, and ECH-PA are presented, respectively in Figures 7–9. Derived values of E_a and A for different values of α are reported in Table III. In case of ECH-DDE and ECH-DDS both E_a and A increased considerably over entire range of α values but they increased to a small extent in case of ECH-PA and this is due to different nature and structures of the hardeners. The increase in E_a and A may be due to increase in the crosslinking as the curing reaction proceeds. The observed trend in E_a and A is ECH-DDS > ECH-DDE > ECH-PA. Thus, the structure of hardeners has affected the curing behavior of ECH.

The knowledge of E_a provides mechanistic clues and also useful in guessing model fitting.³⁶ Observed shoulders or peaks in DSC curves are indicative of multistep curing reactions.

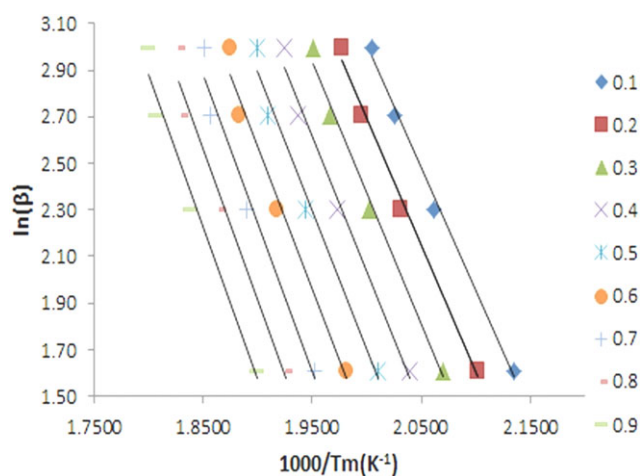


Figure 8. Flynn-Wall-Ozawa plots for ECH-DDS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

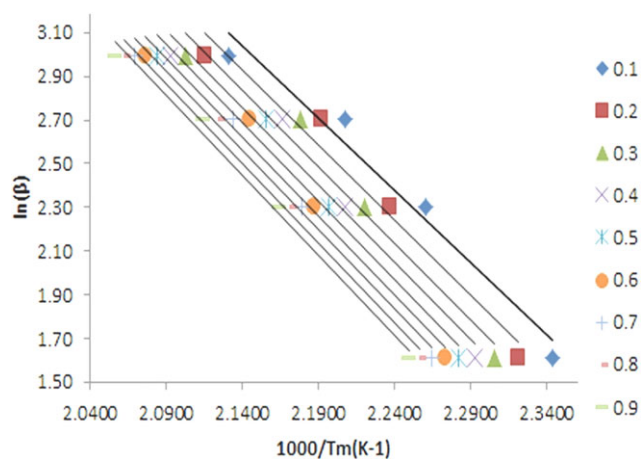


Figure 9. Flynn-Wall-Ozawa plots for ECH-PA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermally initiated processes show characteristic E_a with α dependence. Crosslinking reactions can demonstrate a change in E_a associated with vitrification that triggers a switch from chemical to diffusion control. Significant variation of E_a with α indicated that curing reaction is kinetically complex process. Observed dependence of E_a on α is also known as kinetic compensation effect.³⁴ The mechanisms of the curing reaction of thermosets usually follow two kinetic reactions namely n th order and autocatalytic reaction.

Oxirane ring strain led to the ring opening polymerization to occur under certain conditions.³⁷ The second exothermic peak is probably due to side reaction forming arylamine Manich bridge. The curing reaction is a very complex process because many reactive processes sometimes occur simultaneously. The final properties of the cross linked resins depend significantly on the kinetics of the curing reaction concerned with the extent of curing, curing conditions, etc.^{28,29,36} Recently ICTAC committee³⁸ has recommended that Kissinger and Ozawa methods are over simplified methods for studying the kinetics of thermally activated processes. ICTAC committee has recommended isoconversional method of Flynn-Wall-Ozawa as more reliable method because of its integrating character, exhibits less sensitivity to noise and provides a better visual separation of more reaction steps as well as information concerning the existence of an autocatalytically activated process.^{36,38,39}

The derived activation energies with α according to Flynn-Wall-Ozawa method are utilized to calculate $\ln[A f(\alpha)]$ according to Friedman³⁹ equation:

$$\ln[Af(\alpha)] = \ln \left[\frac{d\alpha}{dt} \right] + \frac{E_a}{RT} = \ln A + \ln(1 - \alpha) \quad (2)$$

where $d\alpha/dt$ is the change in degree of cure with time t and other symbols have same meaning as mentioned previously. The plots of $\ln[A f(\alpha)]$ against $\ln(1 - \alpha)$ are presented in Figures 10–12. Nonlinear behavior of Friedman plots implied that the curing reactions are autocatalytic in nature. In case of ECH-DDE system practically no effect of heating rate is observed on

Table III. Activation Energy (E_a) and Frequency Factor (A) for Various Curing System as Obtained from Flynn-Wall-Ozawa Method at Various Degree of Curing

Degree of curing(α)	Activation energy E_a (kJ mol ⁻¹)			Frequency factor A (s ⁻¹)		
	ECH-DDE	ECH-DDS	ECH-PA	ECH-DDE	ECH-DDS	ECH-PA
0.1	64.57	82.90	52.04	1.19×10^6	1.03×10^8	5.39×10^4
0.2	73.62	85.75	54.10	1.08×10^7	2.06×10^8	9.00×10^4
0.3	81.32	88.51	55.26	7.07×10^7	4.02×10^8	1.19×10^5
0.4	87.25	91.44	56.04	2.96×10^8	8.13×10^8	1.45×10^5
0.5	94.36	94.20	56.63	1.64×10^9	1.58×10^9	1.68×10^5
0.6	103.61	97.05	57.06	1.51×10^{10}	3.13×10^9	1.87×10^5
0.7	110.88	99.89	57.39	8.62×10^{10}	6.21×10^9	2.03×10^5
0.8	119.02	102.58	57.61	6.01×10^{11}	1.18×10^{10}	2.14×10^5
0.9	126.69	103.13	57.70	3.73×10^{12}	1.35×10^{10}	2.19×10^5

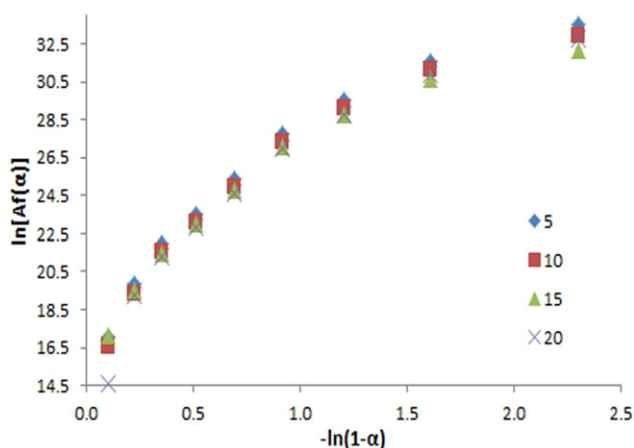


Figure 10. Friedman plots of $\ln[Af(\alpha)]$ vs. $\ln(1 - \alpha)$ of ECH-DDE at various heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

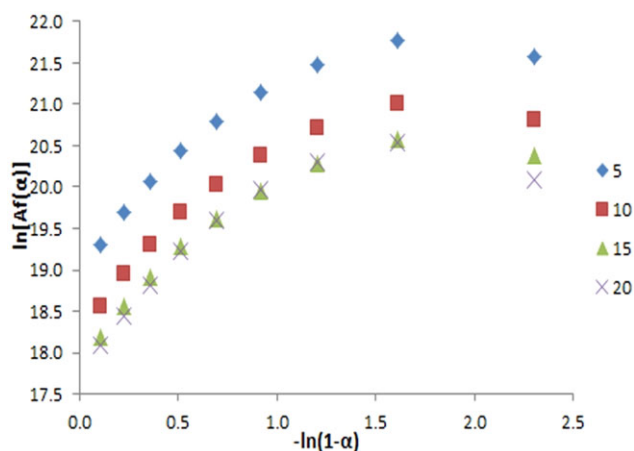


Figure 11. Friedman plots of $\ln[Af(\alpha)]$ vs. $\ln(1 - \alpha)$ for ECH-DDS at various heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

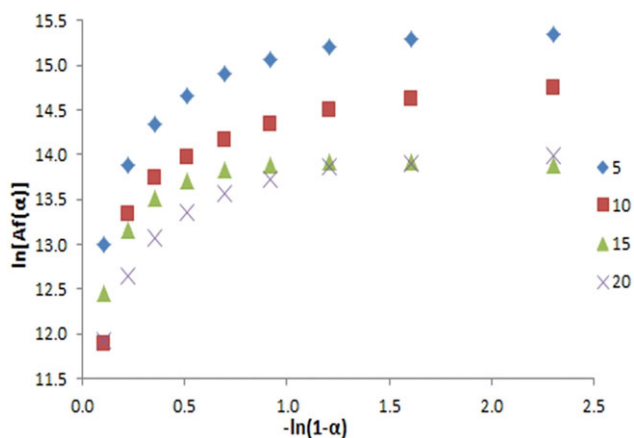


Figure 12. Friedman plots of $\ln[Af(\alpha)]$ vs. $\ln(1 - \alpha)$ for ECH-PA at various heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$\ln [A f(\alpha)]$ against $\ln(1 - \alpha)$ plots, while in case of ECH-DDS and ECH-PA prominent effect of heating rate is observed on $\ln [A f(\alpha)]$ against $\ln(1 - \alpha)$ plots confirming different structural effect of hardeners on cure kinetics of ECH.

CONCLUSIONS

The melting transition of ECH was found to remain practically constant with increasing hardener concentration and heating rate. The peak exotherms, heat of curing, and peak shapes are found to depend upon on hardener concentration, heating rate and hardener structures. ECH-DDE system followed two-stage curing reactions namely ring opening polymerization and ultimate crosslinking and also some side reactions. Both E_a and A are found to depend upon degree of cure, nature, and structures of the hardeners. The increasing trends of E_a and A indicated increase in the crosslinking density as the curing reaction proceeds. Nonlinear behavior of Friedman plots revealed autocatalytic nature of the curing reactions.

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