Curing Kinetics of Epoxy Resin of (2E, 6E) 2,6-Bis (4-hydroxy benzylidene) Cyclohexanone

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ABSTRACT

The curing of epoxy resin of (2E, 6E)-2,6-bis(4-hydroxy benzylidene) cyclohexanone (EBHBC) was carried out at four different heating rates in the nitrogen atmosphere by using 4,4'-diamino diphenylmethane (DDM), 4,4'-diamino diphenyl sulfone (DDS), and 1,2,3,6-tetrahydrophthalic anhydride (THPA) as hardeners. From DSC curves onset, peak exotherm and end set temperatures, as well as heat release, were derived. The energy of activation was derived following Kissinger and Ozawa methods. Observed trend in Ea is EBHBC-THPA > EBHBC-DDS > EBHBC-DDM > EBHBC. Nature and chemical structure of the hardeners affected the curing of EBHBC.

KEYWORDS: *DSC curing kinetics, Epoxy resin, Hardeners, Kinetic parameters.*

INTRODUCTION

Epoxy resins are very important thermoset materials for industries[1] and find their various uses in the field of high-performance composites[2], coating[3], aerospace engineering[4], and encapsulants for electronic composites[5]. Generally, epoxy resins can be easily cured by using different amines and anhydrides. When epoxy resin reacts with a curing agent, it becomes an insoluble thermosetting polymer material because of its cross-linked network. Good thermal stability, low coefficient of thermal expansion, high mechanical strength and low modulus, low dielectric constant, and dissipation factor with low water absorption and low internal stress of epoxy resins can be achieved by using different curing agents of

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different structures[6-11]. Superior thermal, mechanical, and electrical properties, chemical and moisture resistance, low shrinkage, and adhesive properties of epoxy resins make them high-performance materials for several applications.

Several investigators have studied curing kinetics of epoxy resins of different structures using aliphatic and aromatic anhydrides and aromatic diamines of different chemical structures. Patel et al.[12] studied comparative curing kinetics of biobased epoxies of n-alkyl diphenolate esters and diglycidyl ether of bisphenol A (DGEBA). The reaction rate constants were derived by isothermal conversion analysis and Kamal–Sourour model fitting. They found comparable reaction orders. The autocatalytic rate constant of DGEBA was found larger than those of the biobased epoxies. They observed decreased autocatalytic rate constant with increasing alkyl chain length. The non-catalytic rate constant of DGEBA was found smaller than the biobased epoxies.

Gamal et al.[13] have investigated the effect of the Cloisite 25A (C25A) nano-organoclay particles on the kinetic parameters of the curing reaction of the epoxy resin by dynamic differential scanning calorimetry (DSC). They loaded different amounts of the Cloisite 25A and found a little effect on the curing kinetics. They found the non-isothermal Šesták–Berggren autocatalytic model suitable for the curing kinetics. Epoxy nanocomposites were found more thermally stable than pure epoxy resin. 10 wt % loaded Cloisite 25A exhibited high energy of activation, indicated stabilizing effect on the degradation of the matrix.

Saba et al.[14] studied the effect of cellulose nanofibers (CNFs) on the thermal and dynamic mechanical properties of the epoxy composites. They loaded 0.5-1% CNFs into epoxy resin and observed increased thermal stability, char content, storage modulus (E'), loss modulus (E"), and glass transition temperature (Tg) of the nanocomposites than the pure epoxy. 0.75% CNFs loaded nanocomposite revealed superior thermal stability than its counterparts.

Chiu et al.[15] studied curing kinetics of sulfone epoxy (SEP) resin using aromatic and aliphatic amine hardeners and found a two-step curing process. The first step curing showed the SEP/electron donation process, while the second step involved the curing of SEP by the semi-electron-withdrawing curing agents. They adopted iso conversion Ozawa's and Kissinger's methods to determine the kinetic parameters. High melting and bulky aromatic amine hardeners resulted in higher energy of activation and higher Tg of the cured materials than aliphatic amine hardeners cured resins.

Fanica et al.[16] have studied the non-isothermal curing kinetics of diglycidal ether of bisphenol A by differential scanning calorimetry using aromatic anhydrides/acids and simultaneous TG/FTIR/MS. Kissinger, Flynn–Wall–Ozawa methods were used to calculate the kinetic parameters. They used thermokinetic software to determine kinetic parameters and thermal degradation mechanisms. They observed three-step pyrolysis depending upon the chemical structures of the samples and also calculated the lifespan of the cured resins. Recently we have also investigated[9-11] curing kinetics of epoxy resins of 2,4,6-tris(4-hydroxyphenyl)-1,3,5-triazine, 1,3-bis(4-hydroxyphenyl)prop-2-

en-1-one and 9,9'-bis(4-hydroxyphenyl) anthrone-10 using different concentrations of aromatic diamines and anhydrides. Kinetic parameters were determined by Ozawa, Kissinger, Flynn–Wall–Ozawa, and Friedman's isothermal conversion methods. Depending upon the nature and the structure of the hardeners and the epoxies, kinetic parameters of different magnitudes were obtained. The curing of the resins had shown autocatalytic effect due to dehydration of secondary alcohol groups with simultaneous formation of allylic double bonds.

The main objective of the present work was to investigate curing kinetics of epoxy resin of (2E, 6E)-2,6-bis(4-hydroxy benzylidene) cyclohexanone (EBHBC) using 4,4'-diamino diphenylmethane, 4,4'-diamino diphenyl sulfone, and tetrahydrophthalic anhydride hardeners. Kissinger and Ozawa's methods are employed to determine the energy of activation of the curing reactions to understand the curing mechanisms.

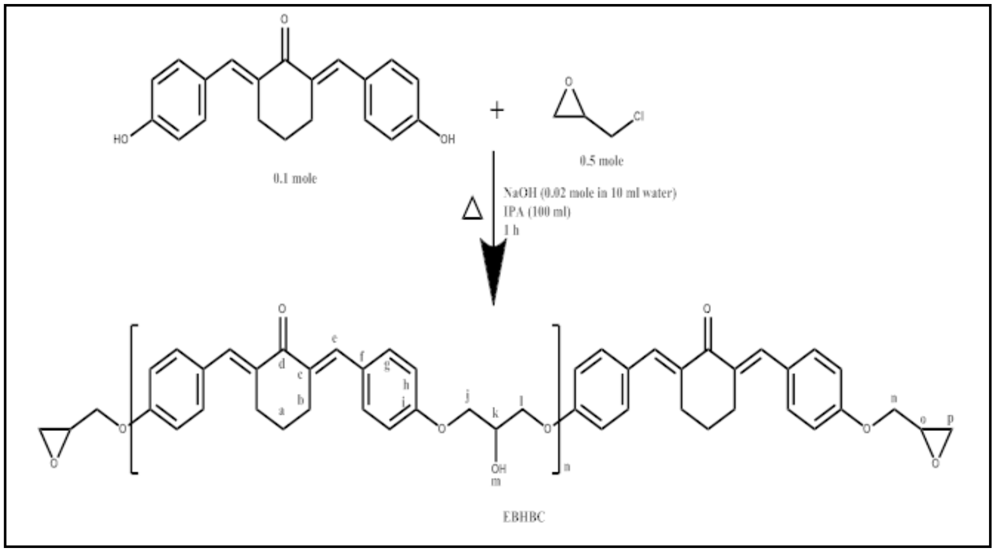
EXPERIMENTAL

Materials

Epoxy resin of (2E, 6E)-2,6-bis(4-hydroxy benzylidene) cyclohexanone (EBHBC) (Scheme I) was synthesized and purified according to our recent work[17]. The epoxy equivalent weight of EBHBC used in the present study was 341.4. 4,4'-Diamino diphenylmethane (DDM) (Spectrochem, Mumbai), 4,4'-diamino diphenyl sulfone (DDS) (National Chemicals, Vadodara), and 1,2,3,6-tetrahydro phthalic anhydride (THPA) (Merck, Germany) were used as received.

Measurements

DSC measurements on EBHBC were carried out on a Shimadzu DSC 60 at four different heating rates in a nitrogen atmosphere (100 mL min^{-1} flow rate). DSC was calibrated by pure indium metal before the curing study of EBHBC. Samples were prepared by mixing and grinding EBHBC and a stoichiometric amount of DDM/DDS/THPA. Samples were weighed accurately in aluminum pans, covered with aluminum lids, and



Scheme I.

sealed by a crimper. DSC curves were scanned over the temperature range from room temperature to 400°C.

RESULTS AND DISCUSSION

For understanding the curing kinetics of epoxy resins, many kinetic models such as nth order reaction, diffusion control, and auto-catalytic models[18,19] have been developed. The kinetics of curing relies on the rate of conversion at a constant temperature as a function of the concentration of the reactants[20]. Isothermal and non-isothermal methods are used to study curing kinetic parameters[21-24]. Non-isothermal methods are very simple, rapid, and more accurate.

DSC thermograms at four different heating rates for EBHBC, EBHBC-DDM, EBHBC-DDS, and EBHBC-THPA in nitrogen atmosphere are presented in Figures. 1-4, from which it is observed that peak exotherms are shifted towards the higher temperature side with the increasing heating rate (β). Moreover, peak exotherms are smaller and broader with comparatively lower heat flow. The onset of curing (T_i), peak exotherm (T_p), and end set of curing (T_f), as well as heat release, i.e. heat of curing reaction (ΔH) for EBHBC, EBHBC-DDM, EBHBC-DDS, and EBHBC-THPA at four different heating rates, are reported in Table 1 from which it is observed that no systematic trend for ΔH is found with heating rate due to shifting in baseline and a small amount of heat release.

In the present investigation, we have followed Kissinger[25] and Ozawa[26] methods for the determination of the energy of activation (Ea) from peak temperature as a function of heating rate (β): At the peak temperature, the rate of curing is maximum[27].

Kissinger method

The values of Ea can be determined from the slopes of ln β / T_p^2 against $1/T_p$ plots:

$$\ln \frac{\beta}{T_p^2} = ln \frac{Q_p A R}{E_a} - \frac{\mathrm{E_a}}{\mathrm{RT}} \tag{1}$$

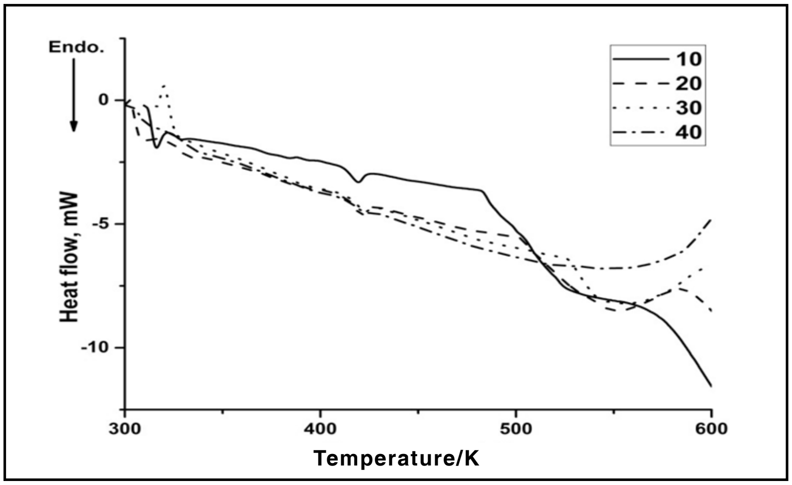


Figure 1. DSC curves for EBHBC at 5, 10, 15, and 20°C min^{-1} heating rates in a nitrogen atmosphere.

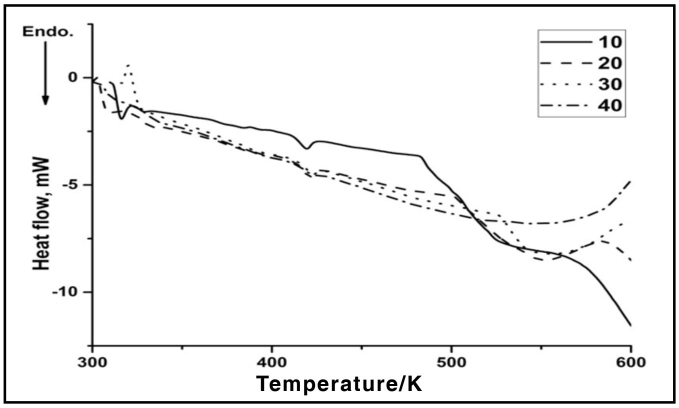


Figure 2. DSC curves for EBHBC-DDM at 5, 10, 15, and 20°C min^{-1} heating rates in a nitrogen atmosphere.

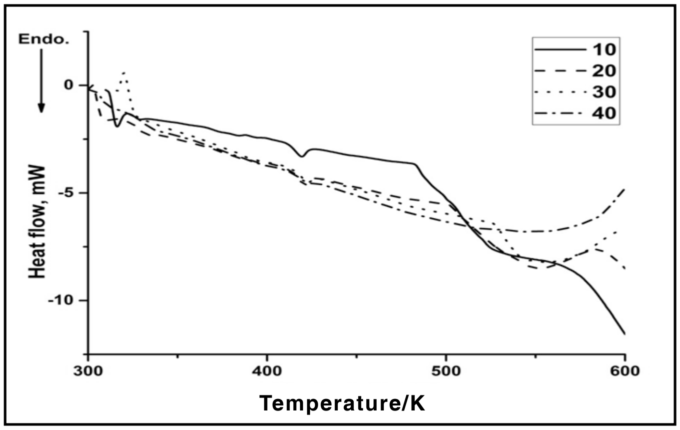


Figure 3. DSC curves for EBHBC-DDS at 5, 10, 15, and 20°C min^{-1} heating rates in a nitrogen atmosphere.

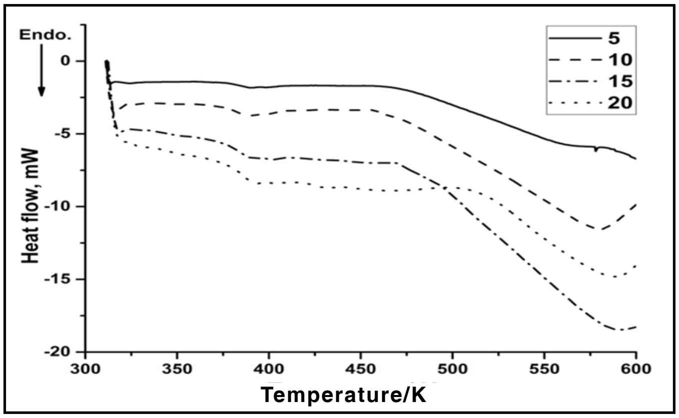


Figure 4. DSC curves for EBHBC-THPA at 5, 10, 15, and 20°C min^{-1} heating rates in a nitrogen atmosphere.

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TABLE 1. Dynamic DSC curing data of EBHBC, EBHBC-DDM, EBHBC-DDS and EBHBC-THPA at multiple heating rates.

System	Heating rate / °C min^{-1}	T_i/°C	T_p/°C	T_f/°C	ΔH/J g^{-1}
EBHBC	10	263.2	263.0	332.6	87.0
	30	282.7	327.2	358.6	73.6
	40	282.6	339.3	396.1	170.2
EBHBC-DDM	5	95.2	131.4	158.3	97.9
	10	93.9	147.0	214.3	-187.6
	30	116.08	161.1	250.1	281.3
EBHBC-DDS	5	293.9	293.8	357.3	72.6
	10	306.7	311.4	339.2	35.0
	15	317.5	329.3	383.3	139.9
	20	317.0	351.6	383.8	89.6
EBHBC-THPA	5	147.1	163.3	203.8	121.0
	10	149.5	174.0	223.7	152.7
	15	157.3	177.4	213.2	104.4
	20	163.3	184.9	233.5	108.7

The plots of ln β / T_p^2 against $1/T_p$ for EBHBC, EBHBC-DDM, EBHBC-DDS, and EBHBC-THPA are presented in Figure 5 and the values of E_a are presented in Table 2.

Ozawa method

The values of Ea can be determined from the slopes of ln β against $1/T_p$ plots:

$$\ln\beta = \ln\left(\frac{\mathrm{AE_a}}{\mathrm{R}}\right) - \ln f(\alpha) - 5.331 - 1.052\,\frac{E_a}{RT} \qquad (2)$$

The plots of ln β against $1/T_p$ for EBHBC, EBHBC-DDM, EBHBC-DDS, and EBHBC-THPA are presented in Figure 6 and the values of Ea are presented in Table 2.

From Table 2, it is observed that Ea values derived from the Ozawa method are higher than that of the Kissinger method due to approximation made in the derivation of the Ozawa method. Observed trend in Ea is EBHBC-THPA > EBHBC-DDS > EBHBC-DDM > EBHBC. THPA hardener required considerably more energy of activation than those of DDM and DDS. Thermal curing of EBHBC required a much lower energy of activation. Thermal and DDS curing of EBHBC took above 250°C, while DDM and THPA curing took above 150°C. From Table 2 it is clear that nature and chemical structure of hardeners affected the curing of EBHBC.

CONCLUSION

The curing of EBHC revealed broader and smaller peak exotherms with lower heat release. Thermal and DDS curing of EBHBC

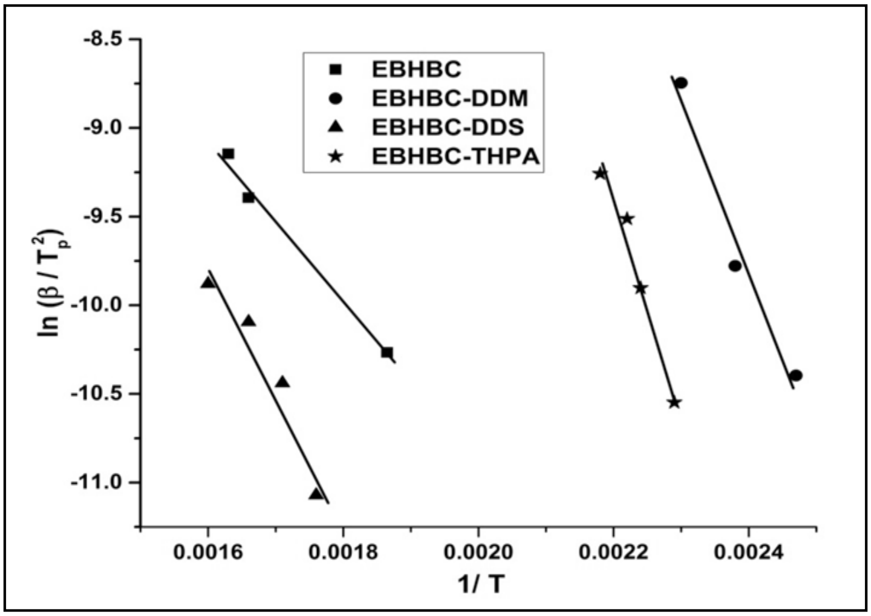

Figure 5. Kissinger plots for EBHBC, EBHBC-DDM, EBHBC-DDS, and EBHBC-THPA.

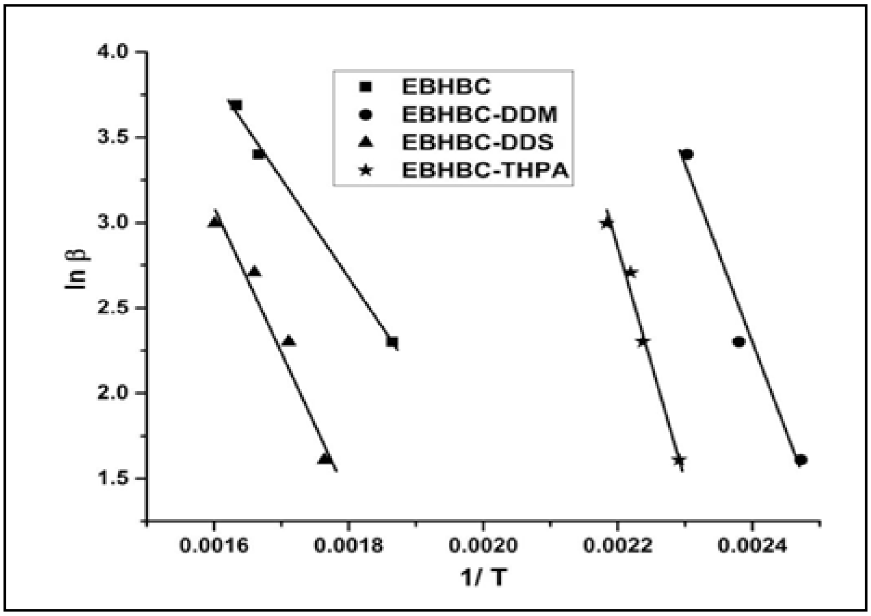

Figure 6. Ozawa plots for EBHBC, EBHBC-DDM, EBHBC-DDS, and EBHBC-THPA.

TABLE 2. Kinetic parameter E_a for EBHBC, EBHBC-DDM, EBHBC-DDS, and EBHBC-THPA derived according to Kissinger and Ozawa methods.

Resin code	**Kissinger method**	**Ozawa method**
	E_a, kJ mol^{-1}	**E_a, kJ mol^{-1}**
EBHBC	38.8	45.9
EBHBC-DDM	80.5	83.1
EBHBC-DDS	83.1	88.4
EBHBC-THPA	102.4	104.4

was observed above 250°C, while DDM and THPA curing reaction was observed above 150°C. The energy of activation was derived by the Kissinger and the Ozawa methods and the following trend was observed: EBHBC-THPA > EBHBC-DDS > EBHBC-DDM > EBHBC due to different chemical structures and reactivity of THPA, DDM, and DDS.

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