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Mechanism Studies on Water Sorption and Permeation in Epoxy Resin by Impedance Spectroscopy. II. Cure Kinetics of O-Cresol Novolac Resin with Esterfied Phenol Novolac Resin

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MECHANISM STUDIES ON WATER SORPTION AND PERMEATION IN EPOXY RESIN BY IMPEDANCE SPECTROSCOPY. II. CURE KINETICS OF O-CRESOL NOVOLAC RESIN WITH ESTERFIED PHENOL NOVOLAC RESIN

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ABSTRACT

To study the effect of water affinity of the cured epoxy resin on water sorption and permeation in the cured epoxy resin, a novel hardener (esterfied phenol novolac was synthesized and used for obtaining the cured product without free hydroxyl group. Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FT-IR) were used to study the cure kinetics of o-cresol novolac epoxy resin using esterfied phenol novolac resin as curing agent in the presence of 2-methylimidazole as accelerator. Some kinetic parameters of the curing reaction such as the reaction order, activation energy, and frequency factor were obtained in the temperature range studied. The results show that this curing process is a first-order kinetic mechanism, which was different with that cured with phenol novolac resin.

INTRODUCTION

Epoxy resins are one of the oldest and most vigorously developed high-temperature polymers in many industrial fields. With the development of very large scale integrated circuit (VLSI), a high quality (high moisture resistance, etc.) of epoxy encapsulation material for semiconductor electronic device is requested.

Although o-cresol novolac epoxy resin has excellent mechanical, electrical and chemical properties, it produces some polar groups (hydroxyl) if one uses phenol novolac, amines, and carboxylic acids as hardener. The cured epoxy resin obtained in this way may absorb moisture from humid environments due to moisture affinity of polar functional groups in the cured epoxy resin [1-4]. The moisture sorption and permeation in this cured material and the consequent corrosion of aluminum wire in the IC chips degrade IC quality and make IC low reliability. Investigation for a novel hardener has a great interest to improve performance of cured epoxy resin and to avoid polar functional groups produced in curing process. Nakamura and Nishikubo found that no free hydroxyl groups were formed in the cured epoxy resin if polyfunctional active esters were used as curing agents [5]. In our laboratory, it was found that a esterfied phenol novolac used as hardener can efficiently reduce moisture sorption in cured epoxy resin.

Besides residual polar group in epoxy resin, the moisture sorption and permeation in the cured epoxy resin relates to the structure (such as crosslink density, etc.) and morphology of cured product. It is, therefore, important to study the mechanism and kinetics of cure reaction to evaluate curing process, network structure and property relationships of cured epoxy resins.

The curing mechanism of epoxy resins is generally classified into two types. One is an autocatalytic mechanism and the other is a nth order kinetic mechanism. The mechanism and kinetics of the curing reaction of epoxy resins with diamines has been analyzed and reviewed by several investigators [6-9]. However there is only limited information concerning the cure characteristics and kinetics of epoxy and phenol reaction in presence of imidazole as accelerator in spite of its importance in the encapsulation of integrated circuits [10-12]. It is therefore essential to know how the esterfied phenol novolac cures o-cresol epoxy resin in the presence of imidazole as accelerator in order to establish the relationships between structure and water sorption and permeation in the epoxy resin, and improve its moisture resistance.

DSC and IR are two general methods used to study the kinetics of epoxy curing reaction [6-16], according to the rate of heat production (isothermal DSC) or peak exothermic temperature (dynamic DSC), and to the intensity changes in absorption band (910cm^{-1}), respectively. Both are more sensitive to the early stage of the process, where the rate of chemical reaction is the highest.

This work is a part of our research on sorption and permeation of water in epoxy resins by electrochemical impedance spectroscopy, in which, the curing kinetic of o-cresol novolac epoxy resin cured with esterfied phenol novolac was studied by DSC and FT-IR in comparison with that cured with phenol novolac resin.

EXPERIMENTAL

Materials

O-cresol novolac epoxy resin (YDCN-702, Tohto Kasei, Japan) (ECN, epoxy equivalent (200~230g/eq), phenol novolac resin (H-1, Sumitomo, Japan) (NOV, hydroxyl equivalent (107g/eq) and four kinds of accelerators, i.e., 2-methylimidazole (Wuhan Pharmaceutical, China) (2MI), triphenylphosphine (Aldrich, America) (TTP), tetraethylammonium (Shanghai Reagent, China) ($(C_2H_5)_4NBr$), or 1,8-diazabicyclo[5,4,0]-7-undecene (Tokyo Kasei, Japan) (DBU) were used without further purification.

Synthesis of Phenol Novolac Acetate Resin (NOVA)

Phenol novolac resin (20g) was dissolved in 75 ml of acetic anhydride and 2.5 ml of pyridine. The mixture was thoroughly stirred with a mechanical stirrer under nitrogen for 24 hours at 100°C. After evaporating the excess of the acetic anhydride, the residue was dissolved in $CHCl_3$ (100 ml), the solution was washed three times with 3 wt% of $NaHCO_3$ aqueous, three times with distilled water, then dried with anhydrous $MgSO_4$ for 2 days and filtrate. After distilling chloroform, the residue was dried in a vacuum oven and 24.8g product (yield 86%) was obtained. The conversion of the esterfication reaction is nearly complete, this is confirmed by NMR and FTIR, which showed no free phenol hydroxyls with a detectable extent.

Samples

The samples used in this study were composed of the constant stoichiometry of epoxy resin and hardener (1:1) and 0.5 wt% of accelerator.

Differential Scanning Calorimetry (DSC)

(a) Glass Transition Temperature (T_g)

Freshly mixed resin samples were dissolved in acetone solution (12 wt%), Specimens smeared over carry glass sheets were successively cured at 45 °C/15 min., 80°C/15min, 120°C/3h, 150 °C/3h and 180°C/4h followed by cooling slowly to room temperature. Before DSC measurement, about 10 mg cured epoxy resin sample was contained in an aluminum pan, treated at 220°C for 5 minutes to

TABLE 1. Glass Transition Temperature (T_g) of Cured Epoxy Resins with Different Accelerators

Accelerator (0.5 wt%)	2MI	$(C_2H_5)_4NBr$	TTP	DBU
T_g(°C)	145	107	105	96

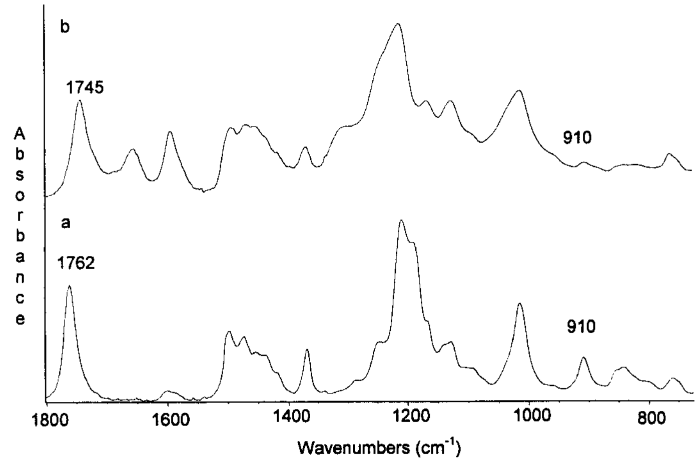


Figure 1. IR spectra of ECN/ANOV in (a) freshly mixture and (b) complete reaction product.

eliminate its thermal history and then quenched in liquid nitrogen. T_g was measured using a Seteram Differential Scanning Calorimetry (DSC 92) with a heating rate of 10°C/min and defined as the inflection temperature in DSC scan.

(b) Dynamic DSC Scan

Freshly mixed resin samples, about 10mg, were used. Dynamic DSC scans were run in nitrogen atmosphere at heating rates of 2.5, 4, 5, 7.5 and 10°C/min, respectively. The dependence of peak exothermic temperature on the heating rate was measured.

Fourier Transform Infrared Spectroscopy (FT-IR)

The fresh resin in acetone was spread as a thin film on a KBr crystal plate. After evaporation of solvent, the spectra were recorded with a Fourier Transform Spectrometer (Nicolet Magna-550). All operations were run under a nitrogen purge.

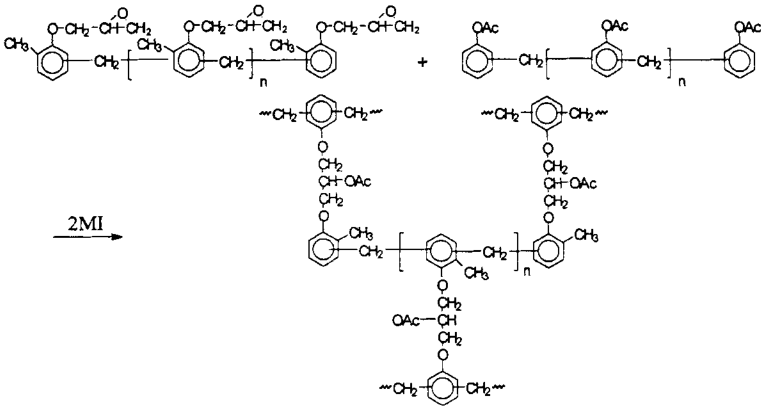
To eliminate the effect of variation of specimen thickness and transparency on peak intensity during measurement, the epoxide peak area at 910 cm^{-1} was normalized referring to an internal reference peak at 1600 cm^{-1} assigned to benzene rings stretching. The extent of reaction was calculated by A_{910}/A_{1600}, A_{910} and A_{1600} correspond to the absorption area at 910cm^{-1} and 1600 cm^{-1}, respectively.

RESULTS AND DISCUSSION

Curing Reaction of ECN and NOVA

Curing reaction was performed in the presence of an appropriate accelerator. Four kinds of accelerators were used to compare their effect on curing extent. The earlier experimental and theoretical works found that T_g is uniquely related to the fractional conversion, (that is, T_g for a given conversion is independent of the cure path), despite competing reaction, T_g increases nonlinearly with conversion [17-19], so the curing extent in the same resin system can be qualitatively represented by T_g. The higher T_g, the higher curing extent. Table 1 shows that the epoxy resin with 0.5 wt% 2MI has the highest T_g, so 2MI was used as an accelerator in following experiments.

As shown in FT-IR spectra (Figure 1), it is noticed that the absorption band at 910 cm^{-1} attributed to stretching vibration of epoxy rings, nearly vanishes after curing reaction. It implies that ECN and NOVA are completely consumed. Further analysis of IR spectra shows that the band at 1762 cm^{-1} shifts to 1745 cm^{-1}, attributed to C=O stretching vibration of aromatic acetate and aliphatic acetate respectively. It indicates that a transformation of aromatic acetate to aliphatic acetate occurs during the reaction. Therefore, the mechanism of the reaction is proposed as followed (Scheme 1).



SCHEME 1

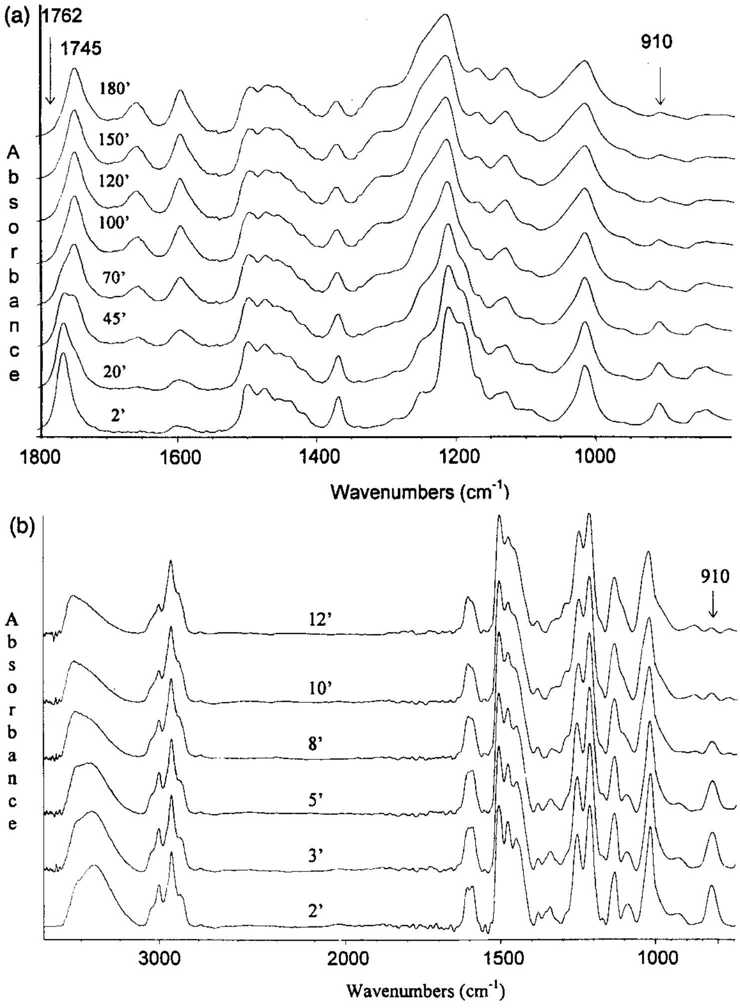


Figure 2. IR absorption as a function of time
(a) NOVA as hardener at 150°C
(b) NOV as hardener at 110°C

Kinetic Study by FT-IR

IR spectra were successively obtained every 5 minutes *in situ* (Figure 2). It is found that the absorption intensity at 910 cm^{-1}(epoxy group) and 1762 cm^{-1} gradually reduces as a function of time at 150°C and almost vanishes until 200 minutes, while the absorption intensity at 1745 cm^{-1} increases in the presence of NOVA as hardener (Figure 2a). However, in the case of NOV as a hardener, it is found that the absorption intensity at 910 cm^{-1} (epoxy group) gradually reduces

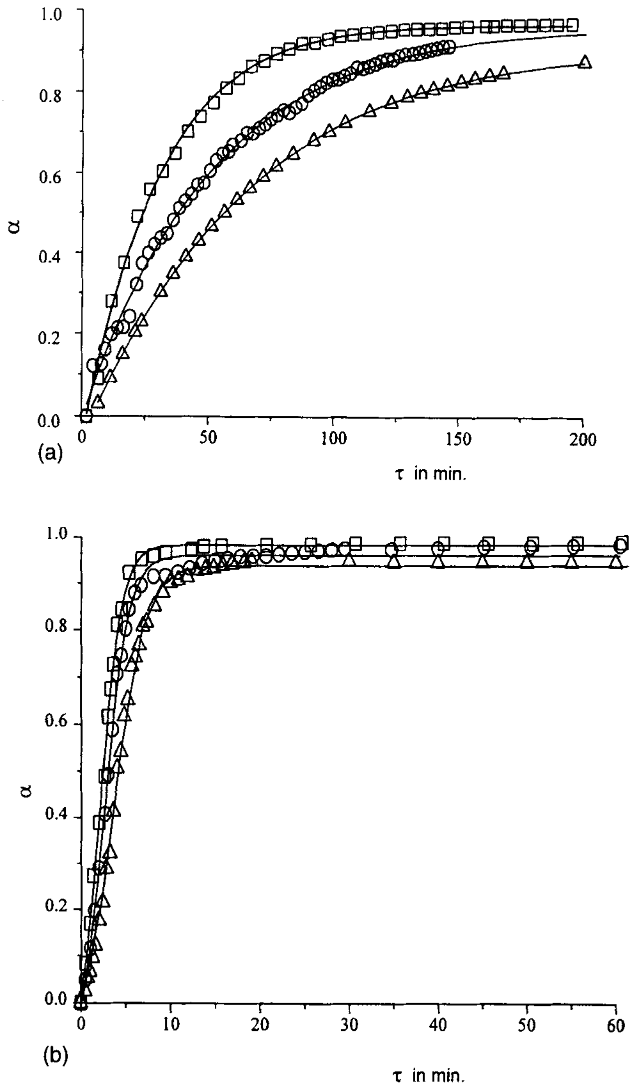


Figure 3. Isothermal reaction conversion as a function of time
(a) NOVA as hardener □:170°C; o:160°C; Δ:150°C
(b) NOV as hardener □:170°C; o:160°C; Δ:110°C

during the reaction, while the intensity at 3400cm^{-1} attributed to hydroxyl group hardly varies, but its frequency shifts higher (Figure 2b), it is inferred a conversion of aromatic hydroxyl to aliphatic hydroxyl (sec-hydroxyl).

A series of isothermal cure curves of conversion (α) vs. time (τ) have been drawn (Figure 3). Figure 3 shows that the curves are all similar to that of most

TABLE 2. The Apparent Activation Energy (*Ea*) of Different Extent of Reaction Using NOVA and NOV as Hardeners, Calculated from Isothermal Experiments

Hardeners	Conversion (α)	Activation energy *Ea*(kJ/mol)	Average activation energy *Ea*(kJ/mol)
NOVA	0.3	64.6	66.0
	0.4	65.0	
	0.5	65.7	
	0.6	66.6	
	0.7	68.3	
NOV	0.2	13.6	13.6
	0.25	13.7	
	0.3	13.5	
	0.6	7.40	7.40
	0.7	7.40	
	0.8	7.40	

epoxy resins system [6, 15, 16]. While in the case of NOV, the curves of α via τ have a turning point. To confirm this phenomenon clearly, the time (τ) to reach a given extent of conversion at different temperature is calculated from Figure 3, according to the Arrhenius kinetics Equation 1.

$$\tau = \tau_0 \exp(\frac{Ea}{RT}) \tag{1}$$

where τ_0 is a constant, *Ea* is the apparent activation energy of curing reaction, *R* is the gas constant and *T* is isothermal curing temperature. The activation energy (*Ea*) of curing reaction can be obtained by the slope of plot ($\ln\tau$ vs. $\frac{1}{T}$). The results are listed in Table 2, and show that the activation energy calculated at different reaction extent is almost the same in the case of NOVA. However, in the case of NOV, it varies with reaction extent, the activation energy of initial stage is larger than that of later stage.

In order to visualize this phenomenon, the conversion rate ($\frac{d\alpha}{d\tau}$) was plotted as a function of conversion (α). It is worth noting here that the conversion rate using NOVA as hardener trends to decrease with reaction extent (Figure 4a), while the

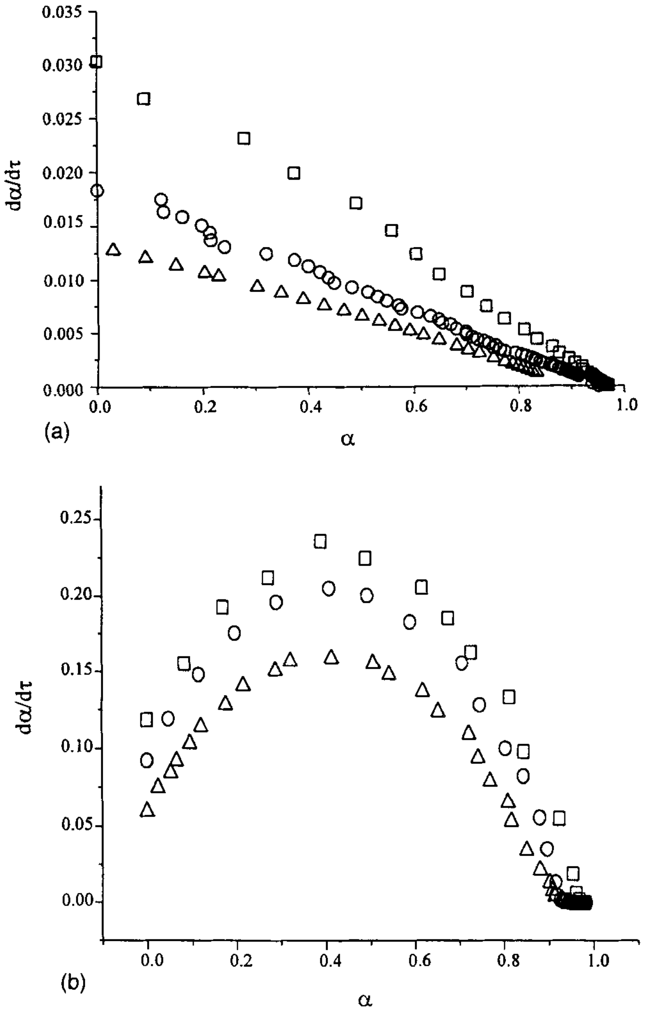


Figure 4. Isothermal conversion rate versus conversion curve
(a) NOVA as hardener □:170°C; o:160°C; Δ:150°C
(b) NOV as hardener □:170°C; o:160°C; Δ:110°C

conversion rate exists a maximum in the case of NOV (Figure 4b). It means that in the case of NOVA the entire reaction is hold over by identical kinetics followed with nth order mechanism, but in the NOV case, the curing reaction proceeds via two stages and it goes through the autocatalytic curing kinetic mechanism [10, 15].

According to Figure 4a, the reaction order n and the rate constant *k* of the curing reaction with NOVA can be calculated from Equation 2:

TABLE 3. Kinetic Parameters of Different Isothermal Curing Temperature using NOVA as Hardener

Temperature t(°C)	Rate constant k (min^{-1})	Activation energy E (kJ/mol)	Frequency factor A (min^{-1})	Reaction order m, n
150	0.0142			1.15
160	0.0203	65.6	1.79x10^{6}	1.19
170	0.0330			1.12

TABLE 4. Kinetic Parameters of Different Isothermal Curing Temperature using NOV as Hardener

Temperature t(°C)	Rate constant k_1, k_2 (min^{-1})	Activation energy E_a, E_b (kJ/mol)	Reaction order m, n
110	0.0676, 0.721		1.14, 1.34
160	0.110, 0.944	13.8, 7.0	1.26, 1.29
170	0.123, 0.964		1.23, 1.20

$$\frac{d\alpha}{d\tau}=k(1-\alpha)^n \tag{2}$$

The results show that the kinetic mechanism is a first order with the rate constant of about 10^{-2} min^{-1}. A linear relationship is gotten when ln$k$ is plotted against $\frac{1}{T}$. The apparent activation energy and frequency factor, Ea and A, are obtained from slope and intercept of line (Table 3). As shown in Table 3, Ea values obtained from the phenomenological Equation 2 agree very well with that calculated from α- τ isothermal plots (Figure 3, Table 2).

In the case of NOV, the kinetic parameters k_1, k_2, m and n can be calculated by nonlinear fitting according to Equation 3:

$$\frac{d\alpha}{d\tau}=(k_1+k_2(\alpha^m)(1-\alpha)^n \tag{3}$$

TABLE 5. Kinetic Paramters Obtained Using Equal Heating Rate Dynamic DSC Scans in NOVA as Hardener

Heating rate (^{o}C/min)	Peak temperature *Tm* (K)	1/*Tm* (×10^3)	lnφ	ln(φ/Tm^2)	Activation energy *E*(kJ/mol)	Frequency factor A(min^{-1})	Reaction order n
2.5	432	2.31	0.916	-11.2	62.2	2.51×10^6	0.89
4	439	2.28	1.39	-10.8			
5	445	2.25	1.61	-10.6			
7.5	454	2.20	2.02	-10.2			
10	465	2.15	2.30	-9.98			

where k_1, k_2 is the kinetic rate constants and m + n is the overall reaction order. It is found that activation energy of two stages is 13.8kJ/mol and 7.03kJ/mol, respectively, and the kinetic reaction order is about 2.5 (Table 4), which basically agrees with published values [10]. The little difference between both cases may be attributed to different accelerator. The kinetic analysis indicates that the curing process in phenol novolac cured o-cresol novolac epoxy resin is similar to that of diamine cured epoxy resins [6, 16], therefore, it might be a typical autocatalytic reaction due to the generation of catalytic hydroxyl group by phenol-epoxy addition. The results illustrate that the cured reaction takes place following the different mechanism due to the structure difference of the curing agent.

Kinetic Study by Dynamic DSC Scan

Dynamic DSC scan was also used to study kinetic mechanism of cured reaction of NOVA and ECN. The data obtained by DSC are usually apparent kinetic parameters of the overall process. The kinetics of the curing reaction under the scanning mode is obtained from the DSC information according to Kissinger (Equation 4) [20] and Crane equations (Equation 5) [21] for a non-isothermal process.

$$\ln(Q/Tm^2) = \ln(AR/E) - E/RTm \tag{4}$$

$$d(\ln Q)/d(1/Tm) = -E/nR \tag{5}$$

where Q is the heating rate in °C/min, Tm is the absolute peak exothermic temperature of the DSC curves, R is the gas constant, E is the activation energy of curing, A is an Arrhenius frequency factor. The results are listed in Table 5.

Though the E_a obtained by different DSC scans (Kissinger method) does not necessarily agree with the E_a values obtained from isothermal experiment [22, 23], in our case, a good agreement between two methods was observed. It is further confirmed that the proposed kinetic model is reasonable. Further work concerning the mechanism of curing reaction of ECN and NOVA is currently under investigation using model monofunctional compounds.

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