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KINETIC MODELING OF ESTERIFICATION OF EPOXY RESIN IN THE PRESENCE OF TRIPHENYLPHOSPHINE FOR PRODUCING VINYL ESTER RESIN: MECHANISTIC RATE EQUATION

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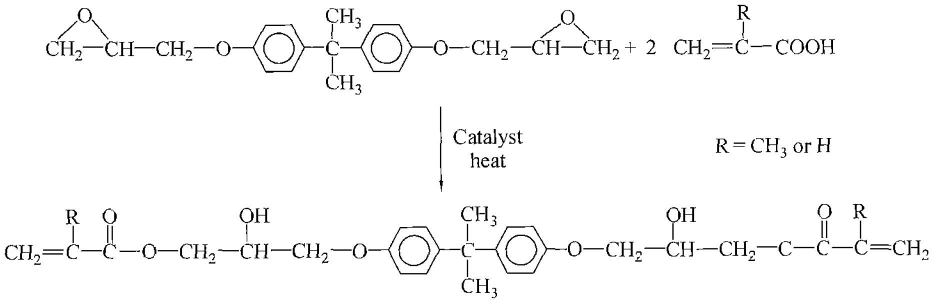
Abstract Due to its mechanical properties and ease of use, vinyl ester resin is enjoying increasing consideration. This resin normally is produced by reaction between epoxy resin and unsaturated carboxylic acid. In the present study, bis-phenol A based epoxy resin and methacrylic acid was used to produce vinyl ester resin. The reaction was conducted under both stoichiometric and non-stoichiometric conditions in the presence of triphenylphosphine as catalyst. The stoichiometric and non-stoichiometric experiments were conducted at 95, 100, 105 and 110°C and at 90 and 95°C, respectively. The first order rate equation and mechanism based rate equation were examined. Parameters are evaluated by least square method. A comparison of mechanism based rate equation and experimental data show an excellent agreement. Finally, Arrhenius equation and activation energy were presented.

Keywords: Esterification; Epoxy resin; Vinyl ester resin; Kinetic; Rate equation.

INTRODUCTION

Vinyl ester resins are crosslinkable resins, produced normally by a reaction between epoxy resin and unsaturated carboxylic acid in the presence of a suitable catalyst[1–3]. The reaction between acid group and epoxide ring is exothermic and generates a hydroxyl group without the formation of any other by-products, as follows:



(1)

The side hydroxyl groups in the vinyl ester molecule can provide adhesion and reactive sites for further modifications. Moreover, there are terminal reactive double bonds that can participate in crosslinking reaction leading to a three-dimensional structure. Most of the published literature has focused on the final production processes for articles (such as curing) and their mechanical properties[4–19].

In the literature, reaction between epoxy resins (bis-phenol A or novolac), and unsaturated carboxylic acid (acrylic or methacrylic), at different molar ratios and temperatures were studied. The molar ratio of 1 epoxy to 2 acids at 90–120°C[20, 21], the molar ratio of 1 to 1 at 100°C[22], and the molar ratio of 1 to 0.9 at 70–90°C[23–29]

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were used by some researchers. However, kinetic study results were reported in molar ratio of 1 epoxy to 0.9 acids. Pal *et al.*[23] studied the kinetics of synthesis of vinyl ester resin. They presented a first order rate reaction.

In this study, kinetics of reaction between bis-phenol A epoxy resin and methacrylic acid was studied. This reaction was conducted under stoichiometric and non-stoichiometric conditions at different temperatures. Based on the reaction mechanism, a rate equation was derived and the rate constant was calculated. The agreement between the experimental and calculated data is excellent.

REACTION MECHANISM

Reaction between bis-phenol A epoxy resin and methacrylic acid can be represented as:

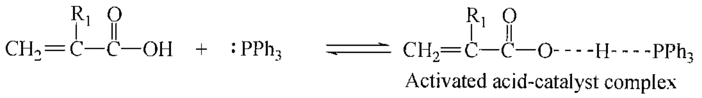
$$2A + B \rightarrow \text{product} \qquad (2)$$

where A and B are methacrylic acid and epoxy resin, respectively. Pal *et al.*[23] conducted the reaction using 1.0 mol bis-phenol A epoxy resin and 0.9 mol acrylic acid in the presence of triphenylphosphine catalyst at 70–90°C. They applied a first order rate equation, as follows:

$$-r_A = \frac{-dc_A}{dt} = kc_A \qquad (3)$$

where c_A is the acid concentration and $-r_A$ is the rate of acid consumption during the course of reaction. Their experimental data have good agreement up to 86% conversion. However, examination of $\ln(c_{A0}/c_A)$ versus time curves, reported by Pal *et al.*[23], revealed that all experimental data were above the first order rate equation. Furthermore, there was increasing deviation between the experimental data and the model, by time. It is attributed to the selection of the first order rate equation and K[acid] >>1 assumption. Hence, the reaction mechanism should be to study present more realistic rate equation.

Vinyl ester was produced under a two-step mechanism, as follows:
Step one: formation of active acid-catalyst complex:

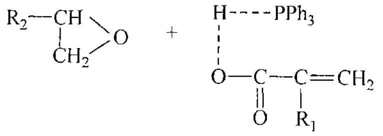


$$CH_2{=}\overset{R_1}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH + :PPh_3 \rightleftharpoons CH_2{=}\overset{R_1}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O\cdots H\cdots PPh_3$$

Activated acid-catalyst complex

(4)

Step two: opening of epoxy under the attack of complex to epoxy group oxygen and the formation of ester group and regeneration of catalyst:



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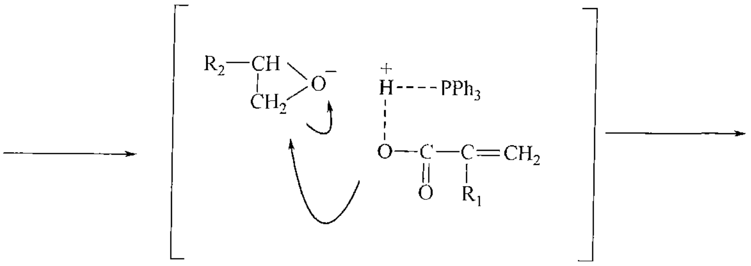

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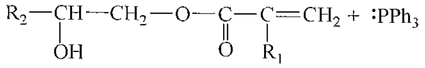
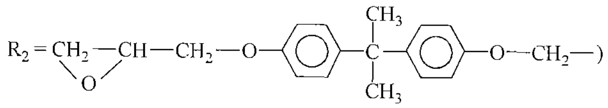


$$\mathrm{R_2{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}O{-}\underset{O}{\underset{\|}{C}}{-}\underset{R_1}{\underset{|}{C}}{=}CH_2 + :PPh_3}$$

(7)

($R_1 = CH_3$ or H



(8)

Epoxy ring is under severe strain and its bond angle deviates from hybrid bond angles. Therefore, ring opening reaction of epoxy ring and COOH acid group is dominant. Hence, there is slight chance for reaction between the produced OH group and COOH acid group. Furthermore, in this study, the acid concentration was chosen to be stoichiometric value or less than stoichiometric. Consequently, there is no extra acid to compete in the reaction by OH group. On the other hand, the regression coefficient of mechanistic rate equation curve fitting is too close to 1.0, as it will be shown. Hence, it is believed that there are no further side reactions.

The mechanism could be written as[23]:

$$\text{acid} + \text{cat} \xleftrightarrow{K} \text{X} \quad \text{acid} - \text{catalyst} \quad \text{complex} \tag{9}$$

$$\text{X} + \text{epoxy} \xrightarrow{k} [\text{Y}] \rightarrow \text{VER} \tag{10}$$

Following is the final form of rate equation:

$$\frac{-\mathrm{d}[\text{acid}]}{\mathrm{d}t} = \frac{2kK\,[\text{cat}]_T[\text{acid}][\text{epoxy}]}{1 + K\,[\text{acid}]} \tag{11}$$

or

$$\frac{-\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = \frac{2K'c_{\mathrm{A}}c_{\mathrm{B}}}{1 + Kc_{\mathrm{A}}} \quad \text{where} \quad K' = kK\,[\text{cat}]_T \tag{12}$$

Integration of Eq. (12), under stoichiometric conditions, gives:

$$\frac{1}{c} - \frac{1}{c_0} + K \ln \frac{c_0}{c} = K't \tag{12a}$$

Under non-stoichiometric condition, it will be:

$$\frac{1}{2(M-a)c_0} \ln \frac{M-ax}{M(1-x)} + \frac{K}{2a} \ln \frac{M}{M-ax} = K't \quad \text{where} \quad M = 1/0.9 \quad \text{and} \quad a = 1/2 \tag{13}$$

where c is the acid concentration.

EXPERIMENTAL

Epoxy resin from Dow Chemicals Co. with *EEW* = 186–192 (epoxide equivalent weight) and methacrylic acid supplied by Merck were used as received. Triphenylphosphine and hydroquinone, supplied by Merck, were used as catalyst and inhibitor, respectively. Table 1 gives the properties of these materials, based on the producer data sheet.

All reactions are conducted in a Buchi batch one-liter reactor. This reactor was equipped with a homemade computer data acquisition and temperature control systems. Figure 1 shows the schematic of reactor set up. Heating oil in the reactor jacket was circulated by means of a pump (15 L/min) to control the temperature of the reactants inside. The reactor was equipped with an impeller type mixer (0–2300 r/min). The circulating oil temperature was adjusted in an oil bath using an electrical heater and a water coil. There was 10 L thermal oil in the bath. The temperature could rise up to 150°C. In the stainless water coil, water flows at 15°C and was controlled by a solenoid valve. All data acquisitions and control tasks were performed *via* computer using Advantech PCL-818L. Each sampling time was chosen to be 3 s. Reacting mixture temperature is controlled based on a new fuzzy logic control algorithm. Figure 2 shows a sample of temperature control result and associated error.

Table 1. Properties of materials

Epoxy resin (DER331 Dow Chemical Co.)	Epoxy equivalent weight (g/eq)	182–192
	Viscosity at 25°C (mPa·s)	11000–14000
	Density at 25°C (g/mL)	1.16
	Shelf life (months)	24
Methacrylic acid (Merck)	Chemical formula	$CH_2C(CH_3)COOH$
	Molar mass (g/mol)	86.09
	Density at 20°C (g/cm^3)	1.015
Triphenylphosphine (Merck)	Chemical formula	$(C_6H_5)_3P$
	Molar mass (g/mol)	262.28
	Density at 20°C (g/cm^3)	1.194
Hydroquinone (Merck)	Chemical formula	$C_6H_4(OH)_2$
	Molar mass (g/mol)	110.11
	Density at 20°C (g/cm^3)	1.358

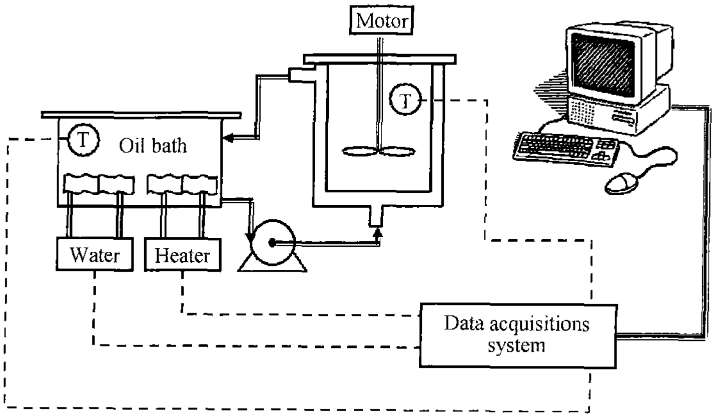


Fig. 1 Schematic diagram of reactor set up

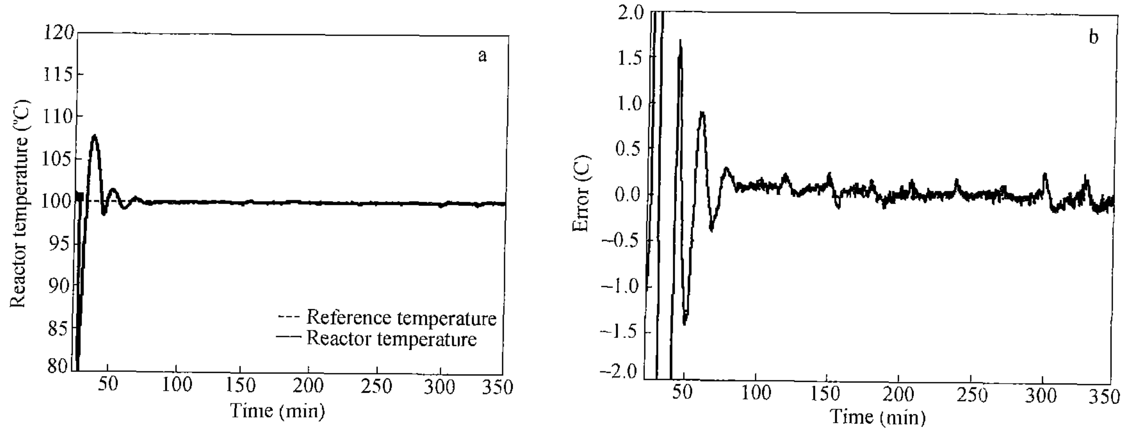


Fig. 2 Result of reactor temperature control based on the fuzzy logic method: (a) temperature; (b) error

Stoichiometric reactions, including 1 mol epoxy resin to 2 mol acid, were conducted at 95, 100, 105 and 110°C. Non-stoichiometric reactions, 1 mol epoxy resin to 0.9 mol acid, were conducted at 90 and 95°C. In all experimental runs, 1 phr catalyst (relative to epoxy resin) 0.2 g hydroquinone inhibitor were added in order to initiate the catalytic reaction and to prevent free radical reaction of vinyl group of acid. Table 2 shows the conditions of performed experiments.

Table 2. Conditions of experiments

	Stoichiometric ratio (1 to 2)	Non-stoichiometric ratio (1 to 0.9)
Mixer speed	300 r/min	300 r/min
Temperature (°C)	95–100–105–110	90–95
Epoxy weight (g)	186	186
Acid weight (g)	86	38.7
Catalyst weight (g)	1.86	1.86
Inhibitor weight (g)	0.2	0.2

Epoxy resin was preheated to the required temperature, then catalyst, inhibitor, and acid were added to the reactor, respectively. Acid value of methacrylic acid, based on the ASTM D1639, was measured. Upon the completion of the reaction, the mixture was cooled down to 50°C and *ca.* 30 wt% styrene was added and kept in the refrigerator for further studies.

FTIR spectra were recorded using a Bruker FT-IR EQUINOX55 spectrometer in the Iran Polymer and Petrochemical Institute. In Fig. 3(a) the band at 916 cm^{-1} is associated with epoxy ring[5, 30]. The band at 3514 cm^{-1} is due to OH group in the epoxy molecules, and the bands at 1718 cm^{-1} and 3460 cm^{-1} belong to carbonyl and OH groups, respectively. This result confirms the formation of vinyl ester.

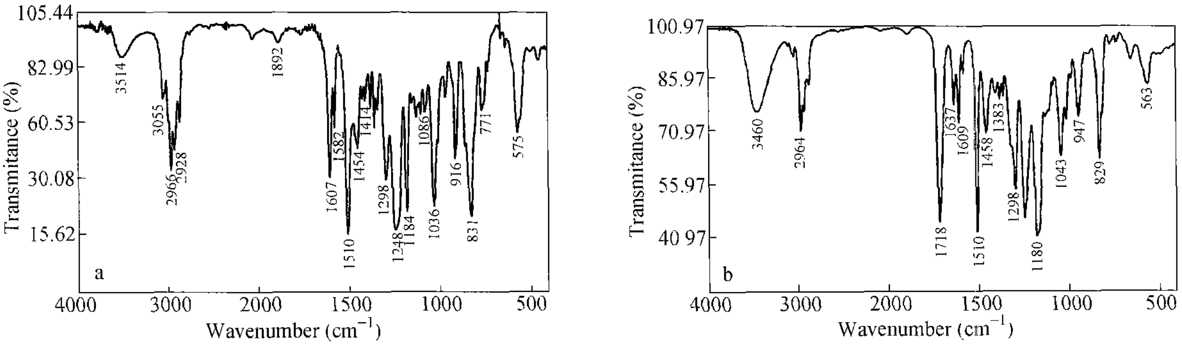


Fig. 3 FTIR of spectra epoxy and vinyl ester resins
(a) IR spectrum of epoxy; (b) spectrum of vinyl ester FTIR

Styrene content of the resin was determined by a Bruker 400 MHz NMR. In Fig. 4, the resonance peaks of protons of the methacrylate vinyl group in vinyl ester, of the vinyl group in styrene, of the methacrylate methyl endgroup in vinyl-ester, and of the pendant methyl group of bis-phenol-A are labeled a, b, c, and d, respectively. By calculating the ratio of the areas of the vinyl group of monomer, this resin was determined to contain 28% styrene by weight.

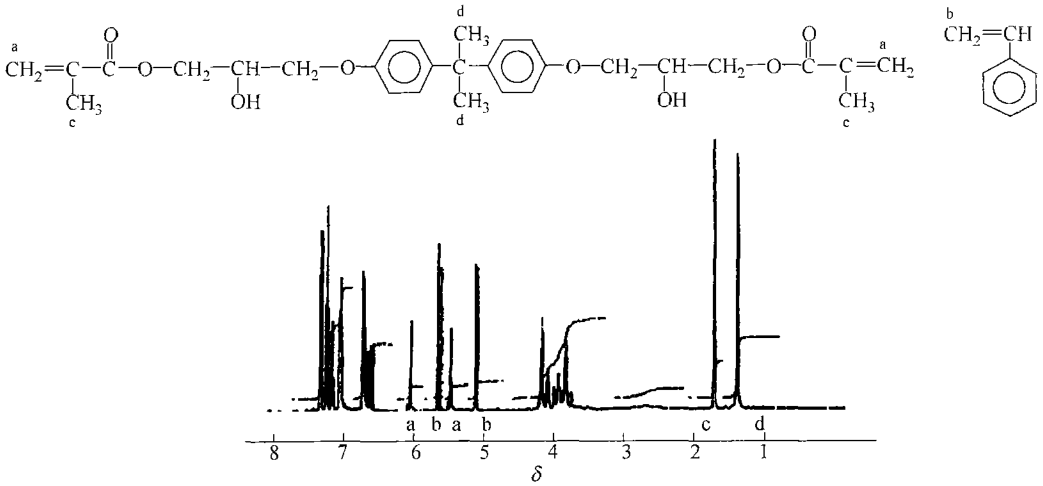


Fig. 4 NMR spectra of vinyl ester resins and corresponding protons

RESULTS AND DISCUSSION

So far, a suitable rate equation has not been reported for the reaction between bis-phenol A based epoxy resin and methacrylic acid. Figures 5 and 6 show the measured acid concentrations and conversions under stoichiometric and non-stoichiometric conditions at different temperatures. The reaction was conducted under strict control of the reaction temperature. As expected, reaction rate increases and completion occurs sooner by rise of temperature. This is due to the increase in the probability of collision among the functional groups.

In the first step, the first order rate equation (which was previously suggested by Pal *et al.*[23]) was fitted on the experimental data. Rate constants were calculated using the well-established least square method[31]. Relationship for the first order rate equation is:

$$\ln\frac{c_A}{c_{A0}}=-kt \quad\Rightarrow\quad k=-\frac{\sum_{i=1}^{n}t_i\ln\left(\frac{c_A}{c_{A0}}\right)}{\sum_{i=1}^{n}t_i^2} \tag{14}$$

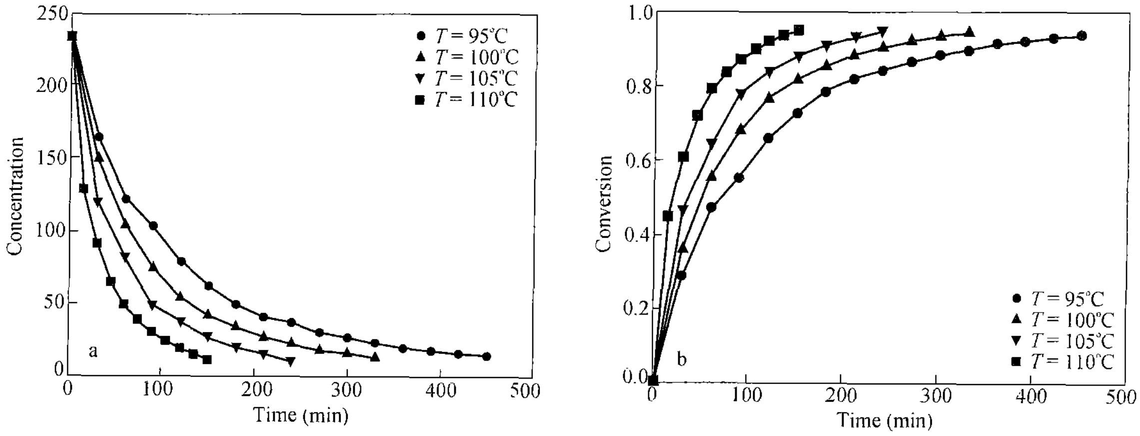


Fig. 5 Results for stoichiometric reactions: (a) concentration and (b) conversion

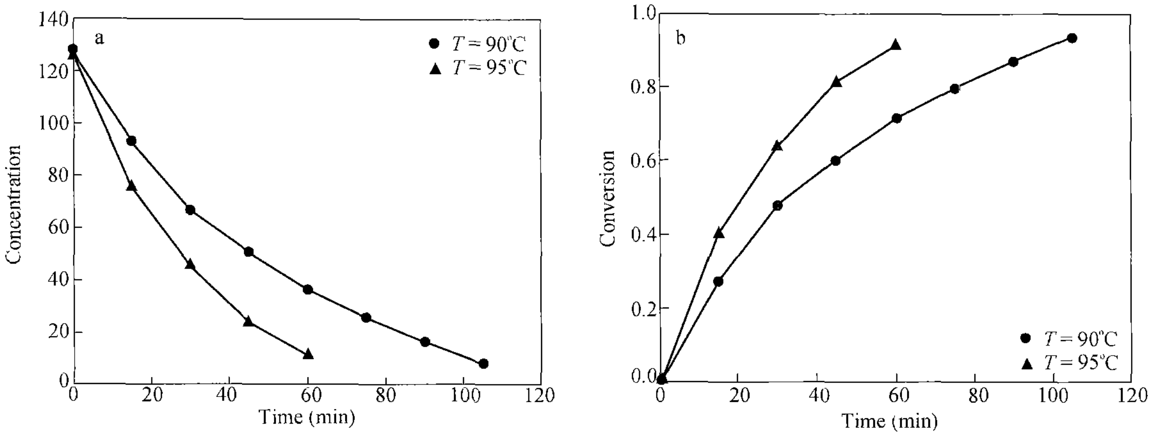


Fig. 6 Results for non-stoichiometric reactions: (a) concentration and (b) conversion

Figure 7 shows the result of the first order rate equation curve fitting on the data. In general, this result is acceptable. However, the trend of the experimental data shows that there is some systematic deviation from the first order rate equation. This sort of trend could be observed from the work of Pal *et al.*[23], although they used acrylic acid instead of methacrylic acid. Therefore, it is obvious that the first order rate equation is not necessarily adequate. Consequently, in the next step, the mechanistic rate equation was tried. Relationship of least square method application for the mechanistic based rate equation is:

$$\frac{1}{c}-\frac{1}{c_0}=K't-KA \quad \text{where} \quad A=\ln\frac{c_0}{c} \quad \Rightarrow \quad \begin{bmatrix}K'\\ K\end{bmatrix}=\text{inv}\left(\begin{bmatrix}\sum\limits_{i=1}^{n} t_i^2 & -\sum\limits_{i=1}^{n} A_i t_i\\ \sum\limits_{i=1}^{n} A_i t_i & -\sum\limits_{i=1}^{n} A_i^2\end{bmatrix}\right)\times\begin{bmatrix}\sum\limits_{i=1}^{n}\left(\frac{1}{c_i}-\frac{1}{c_0}\right)t_i\\ \sum\limits_{i=1}^{n}\left(\frac{1}{c_i}-\frac{1}{c_0}\right)A_i\end{bmatrix} \tag{15}$$

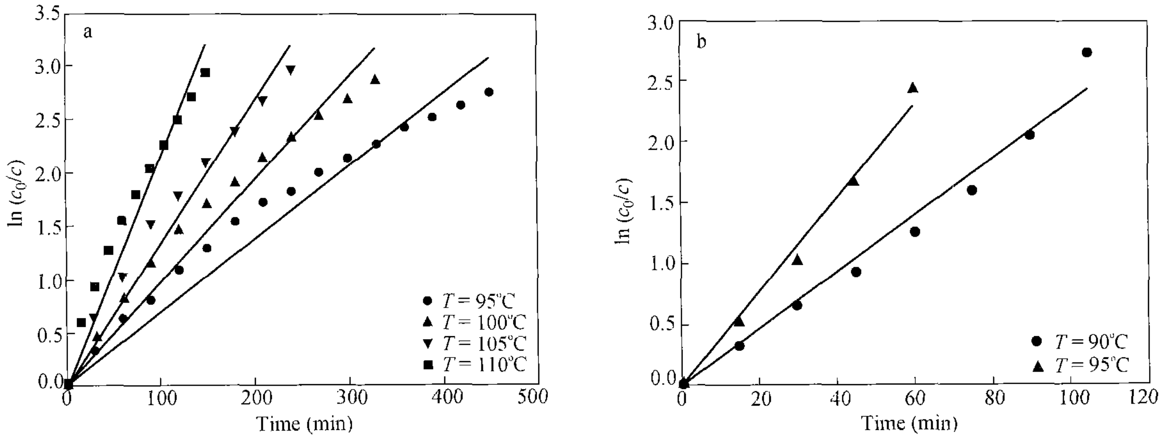


Fig. 7 Results of the first order kinetic curve fitting:
(a) stoichiometric reaction; (b) non-stoichiometric reaction

Figure 8 shows the result of the mechanism based rate equation curve fitting. The experimental data is randomly distributed around the theoretical concentrations. This distribution could be attributed to the random errors in measurements. Table 3 presents the numerical values of rate constants for both stoichiometric and non-stoichiometric conditions at different temperatures along with their regression coefficients. The regression coefficient R shows the superiority of the mechanism based rate equation. Furthermore, the order of magnitude of the first order rate constants in stoichiometric and non-stoichiometric conditions, *i.e.* k = 0.0068 and k = 0.038, respectively, at 95°C, are different. However, the rate constant should be independent of stoichiometric condition. The mechanism based rate equation gives $k = 0.43$ and $k = 0.54$ for stoichiometric and non-stoichiometric conditions, respectively, at 95°C, which is more realistic. Consequently, the K[acid] >>1 assumption is not valid and the first order rate equation could not be applied correctly. The K values are the equilibrium constant at different temperatures. The estimation of standard deviation of the K values is 6.2×10^{-3}. Therefore, there is no meaningful difference among the K values in 90–110°C range. This means that the equilibrium constant is approximately independent of temperature or the activation energy in one direction is close to the activation energy in the reverse direction.

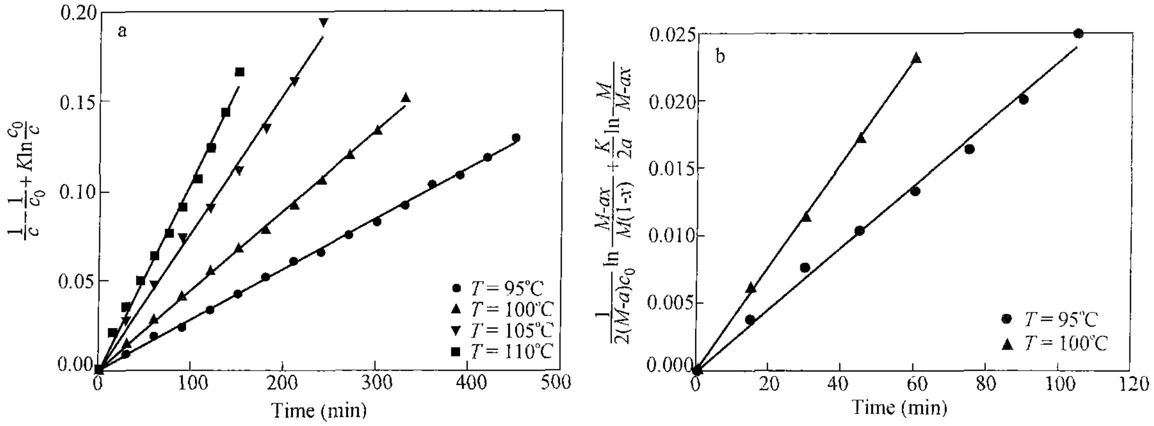


Fig. 8 Results of mechanism based rate equation:
(a) stoichiometric reaction; (b) non-stoichiometric reaction

Table 3. Rate constants and regression coefficients

Results based on the 1st order rate equation, Eq. (3)					
Stoichiometric ratio			Non-stoichiometric ratio		
T(°C)	k	R	T(°C)	k	R
95	0.0068	0.9870	90	0.0231	0.9897
100	0.0096	0.9874	95	0.0382	0.9956
105	0.0133	0.9900			
110	0.0213	0.9690			

Results based on the mechanism based rate equation, Eqs. (12 and 13)							
Stoichiometric ratio				Non-stoichiometric ratio			
T(°C)	k	K	R	T(°C)	k	K	R
95	0.429	0.023	0.999	90	0.325	0.020	0.997
100	0.572	0.028	0.999	95	0.546	0.020	0.999
105	0.732	0.037	0.997				
110	1.239	0.030	0.997				

ln$k$ versus $\frac{1}{T}$ shows a linear behavior, see Fig. 9. Hence, the well-known Arrhenius type rate constant could be fitted on the rate constant data, such as:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{16}$$

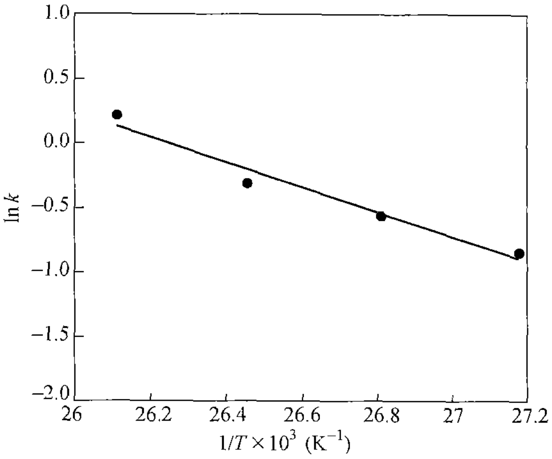


Fig. 9 Arrhenius rate constant plot

The activation energy and k_0 parameters are 80 kJ/mol and 9.63×10^{10} L/(mol• min), respectively. The Arrhenius type rate constant is the most adopted form in the chemical reaction engineering area and has shown its ability in the prediction of experimental data. From the authors knowledge, this is the first published mechanistic based rate equation.

CONCLUSIONS

The reaction of bis-phenol A based epoxy resin and methacrylic acid for the production of vinyl ester resin were studied. The reaction was conducted under stoichiometric and non-stoichiometric conditions with triphenylphosphine as catalyst at different temperatures. Reaction was performed at 95, 100, 105 and 110°C and at 90 and 95°C under the stoichiometric and non-stoichiometric conditions, respectively. The first order rate equation and mechanism based rate equation were fitted on the experimental data by the least square method. A comparison of mechanism based rate equation and experimental data shows an excellent agreement. Finally, Arrhenius equation and activation energy are presented.

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