

Synthesis and Kinetics Study of Vinyl Ester Resin in the Presence of Triethylamine

Golrokh Heidari Hamedani, Morteza Ebrahimi*,
and Seyed Reza Ghaffarian

Polymer Engineering Department, Amirkabir University of Technology,
P.O. Box: 15875-4413, Tehran, Iran

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ABSTRACT

The synthesis of an epoxy vinyl ester resin was carried out using a bisphenol-A based epoxy resin and methacrylic acid in the presence of triethylamine as a catalyst. The reaction was performed in the temperature range of 90-120°C and epoxy to carboxyl group ratio of 1. In all conditions a conversion of more than 95% was achieved. The reaction time (for conversions more than 95%) was different from 1.5 h at 120°C to more than 8 h at 90°C. The results indicated that reaction followed a first-order kinetics. The order of reaction with respect to methacrylic acid was also investigated by using excess method. It was found that in the reaction conditions, the reaction rate was independent of carboxyl group concentration. The specific rate constant, calculated by the regression analysis, was found to obey Arrhenius expression. The activation energy and frequency factor were found to be 82.61 kJ/mol and $5.43 \times 10^9 \text{ min}^{-1}$, respectively. FTIR Analysis of vinyl ester resin revealed that addition esterification reaction between carboxyl and epoxy groups took place and no side reactions (i.e., etherification reaction between epoxy and hydroxyl groups) occurred during the synthesis.

Key Words:

vinyl ester resin;
triethylamine;
esterification;
kinetics;
methacrylic acid.

INTRODUCTION

Vinyl ester resins are thermosetting resins that usually consist of an epoxy resin backbone and they are prepared by addition of ethylenically unsaturated acids to epoxy resins in the presence of basic catalysts [1-3]. These materials were developed in an attempt to combine the chemical, mechanical and thermal properties of epoxy resins with

the rapid cure of unsaturated polyester resins which make them a suitable product for various industrial applications such as surface coatings, adhesives, printed circuit board coatings, ultraviolet cured inks, composites and fibre reinforced plastics [3-7].

Three main chemical reactions that can be involved during acid-

(*) To whom correspondence to be addressed.
E-mail: ebrahimi@aut.ac.ir

epoxy reaction are as follows [8,9]:

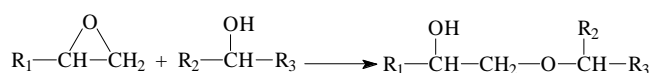
1) Addition esterification takes place between a carboxyl group and an epoxy group:



2) Condensation esterification takes place between a carboxyl group and a hydroxyl group situated along the epoxy resin chain or which is the result of the reaction of the epoxy group with a carboxylic acid:



3) Etherification results from reaction between an epoxy group and a hydroxyl group.



During the acid-epoxy reaction, the acid value and epoxy value decrease, whilst the viscosity of the epoxy vinyl ester increases. The esterification reactions (1) and (2) result in a relatively small viscosity increase for a correspondingly large decrease in acid value. This is in contrast to the etherification reaction (3). In many cases it is necessary to try to keep the viscosity as low as possible. In addition to the above reactions it is possible that unsaturated acid reacts with a free radical mechanism thereby linking the acids. In the extreme case this results in gelation. In vinyl ester resin synthesis, addition esterification (1) is normally promoted by the use of suitable catalysts (such as basic catalysts) and reaction conditions. In addition, using free radical inhibitor prevents the gelation [8-10].

Several research works including Gawdzika and Matynia [11], Agrawal et al. [12,13] and Bajpai et al. [14] have studied the kinetics of the reaction of carboxyl groups with epoxides. The kinetics of addition esterification of cycloaliphatic epoxies with methacrylic acid in the presence of triphenylphosphine [15] and monoepoxy compounds with benzoic acid [16], and caproic acid [17] in the presence of tertiary amines has been investigated. Pal et al. [18,19] have synthesized vinyl ester resins using bisphenol-A based epoxy resin, acrylic acid and triphenylphosphine as catalyst, in the presence and absence of

monoepoxies as a reactive diluent. Srivastava et al. [20], have studied kinetics of vinyl ester resin synthesis using bisphenol-A based epoxy resin and methacrylic acid in the presence of tertiary amines (i.e., triethyl, tripropyl and tributyl amines) in the temperature range of 80-100°C. Almost all previous researchers have reported an overall reaction order, however, reaction order with respect to each reactant has rarely been investigated.

In the present work, we report the results of kinetics studies of vinyl ester resin synthesis via esterification of epoxy resin with methacrylic acid in the presence of triethylamine as catalyst in the temperature range of 90-120°C. First we estimated an overall reaction order by using differential methods and then we confirmed it by integral method. We also investigated the reaction order with respect to acid by using an excess amount.

EXPERIMENTAL

Materials

A bisphenol-A based epoxy resin (Epiran 6, EEW=192) from Khuzestan Petrochemical Co. (Iran), methacrylic acid, triethylamine and hydroquinone from Merck Chemical Co., were used in this study.

Apparatus

Synthesis reaction was performed in a 500 mL five-necked flask equipped with a stirrer, nitrogen inlet tube, condenser and thermometer. The reaction mixture was heated to desired temperature using an electromantle.

Synthesized resins were characterized by using an FTIR spectrophotometer. The acid value of the reaction mixture was evaluated according to ASTM D1636.

Procedure

A reaction mixture consisting of 1:2 molar ratio (5:1 for the excess condition) Epiran 6 and methacrylic acid with hydroquinone (200 ppm) were charged into the reactor. In this situation, equimolar epoxy group to acid group (10:1 for the excess condition) was used. The mixture was stirred and heated up to a desired temperature followed by addition of triethylamine

(1 phr by weight of the resin). The esterification reaction was carried out at 90°C to 120°C (90°C for the excess condition), and the progress of reaction was monitored intermittently by measuring the acid value until the vinyl ester resin of desired acid value (<10 mg KOH/g solid) was obtained.

Concentration dependence of the reaction rate equation was investigated by determination of acid concentration changes. Since the acid value (AV) of reaction mixture relates to acid groups concentration according to eqn (1), it was used for kinetics study.

$$AV = \frac{[Acid] \times 56.1}{d} \tag{1}$$

where,

AV: acid value (mg KOH/g)

[Acid]: acid group concentration (mol/L)

d: reaction mixture density (g/mL)

The power law model was chosen for kinetics study and the total reaction order was estimated by differential method, which was then confirmed by integral method.

The activation energy (E_a) and frequency factor (k_0) were calculated using Arrhenius equation, based on the following equation:

$$k = k_0 e^{-E_a/RT} \tag{2}$$

where,

T: temperature (K)

R: gas constant (cal/mol.K)

RESULTS AND DISCUSSION

Figure 1 shows the changes of reaction mixture acid value in relation to time at different temperatures. It is apparent from this figure that acid value decreases with an increase in reaction time and its reduction is faster in the initial stages of the reaction because of a higher concentration of the reactive groups, i.e. acid and epoxide.

FTIR Spectra of epoxy resin, methacrylic acid and one of the synthesized vinyl ester resins are shown in Figures 2a-2c and main absorption bands are presented in Table 1.

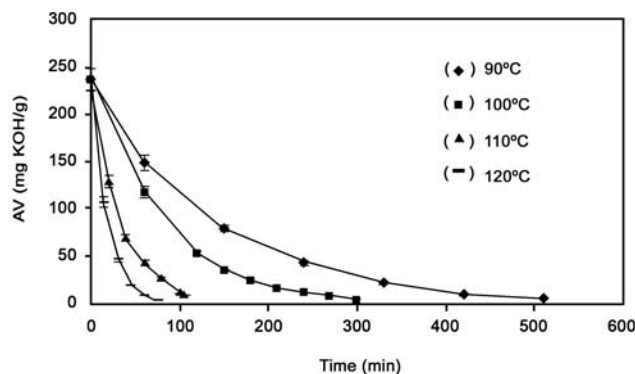


Figure 1. Acid value versus reaction time.

As it can be observed, the band at 910 cm^{-1} associated with the oxirane ring of epoxy resin (Figure 2a) is replaced by a band at 1722 cm^{-1} in vinyl ester spectrum (Figure 2c), which is due to the carbonyl group of the ester formed. Another band was observed at 1636 cm^{-1} in vinyl ester spectrum that is attributed to the acryloyl double bond which confirms formation of vinyl ester. The band at 3487 cm^{-1} in vinyl ester spectrum is associated with hydroxyl group which its absorption intensity increased compared to epoxy resin spectrum. This is due to hydroxyl group formation during addition esterification reaction (reaction (1)). The absence of oxirane ring absorption band in vinyl ester resin spectrum reveals that epoxy groups were completely consumed in the reaction. Furthermore, the lack of ether bond absorption band

Table 1. FTIR Absorption bands.

Relevant spectrum	Wavenumber (cm^{-1})	Functional group
2a	910	oxiran
2a	1223	ϕ -O-C
2a, 2c	3300-3600	-OH
2b	1700	C=O
2b	810	H ₂ C=C
2b	2400-3000	-OH
2c	1722	C=O
2c	1040-1238	ϕ -O-C
2c	943, 1636	H ₂ C=C

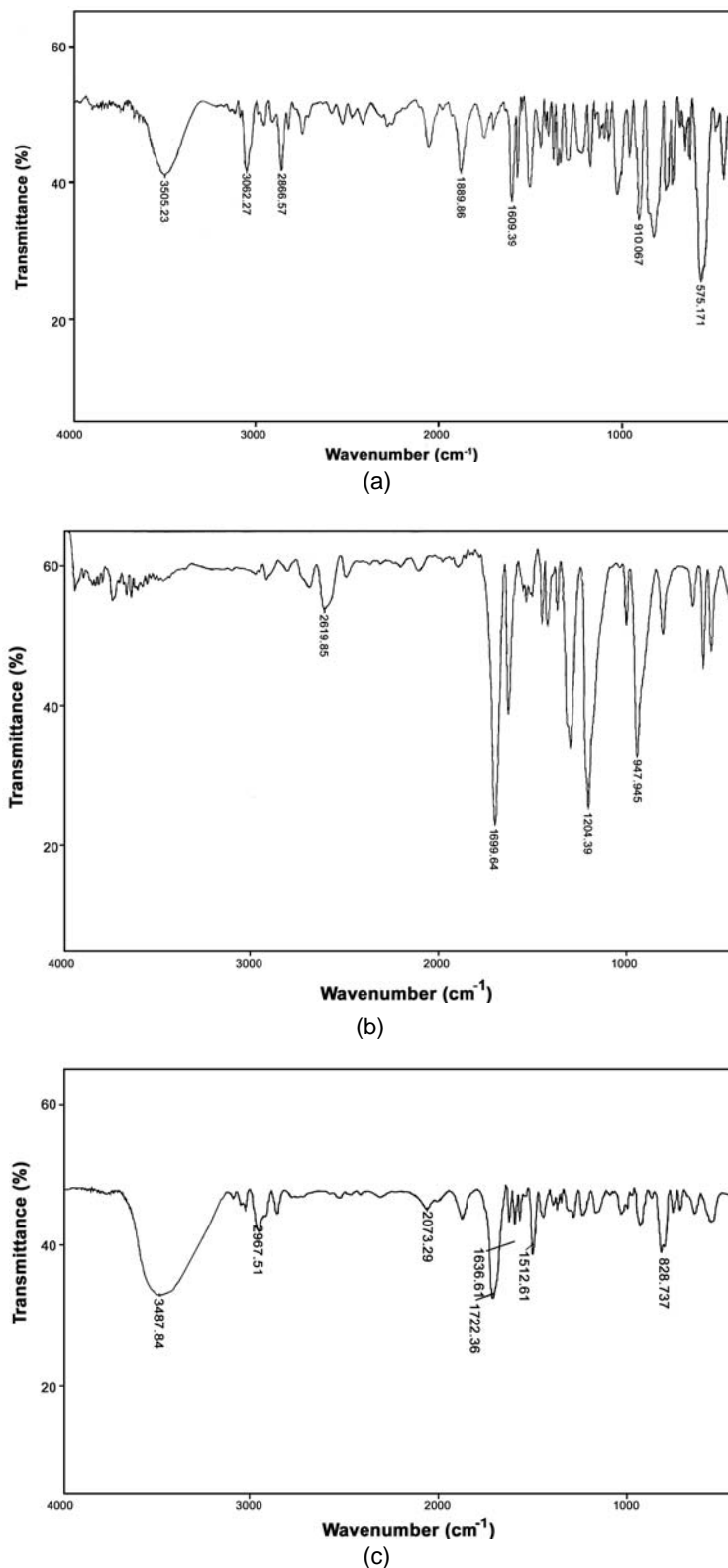


Figure 2. FTIR Spectra of (a) epoxy resin; (b) methacrylic acid; and (c) vinyl ester resin.

at 1120 cm⁻¹ shows that, in the reaction conditions, epoxy groups did not react with hydroxyl groups. Absence of absorption band at 1700 cm⁻¹ (attributed

to the carboxyl group in methacrylic acid, Figure 2b) in vinyl ester resin spectrum, also confirms the completion of acid-epoxy esterification reaction.

To determine the kinetics parameters, the power law model was applied. Therefore, the vinyl ester resin synthesis reaction rate is expressed as:

$$-r_{Acid} = k[Acid]^{\alpha} [Epoxy]^{\beta} \quad (3)$$

Since the synthesis of vinyl ester resin was carried out with an equimolar concentration of acid and epoxy groups ([Acid]=[Epoxy]), the following equation may be considered for simplifying the rate of reaction based on the acid concentration:

$$-r_{Acid} = k[Acid]^{(\alpha+\beta)} \quad (4)$$

According to eqn (1), the reaction rate in terms of acid value (AV) may be obtained as:

$$-r_{AV} = k\left(\frac{d}{56.1}\right)^{(\alpha+\beta)-1} AV^{(\alpha+\beta)} \quad (5)$$

Using differential method, total reaction order was estimated by plotting logarithmic form of reaction rate (-r_{AV}=-dAV/dt) versus logarithmic form of acid value (AV) based on the following equation:

$$\ln(-r_{AV}) = \ln k' + (\alpha + \beta) \ln AV \quad (6)$$

where,

$$k' = k\left(\frac{d}{56.1}\right)^{(\alpha+\beta)-1} \quad (7)$$

As it is shown in Figure 3, the plots were linear at all temperatures with very good correlation coefficients (r²), wherein the equations are as follows:

T = 90°C:
 $\ln(-r_{AV}) = 0.967 \ln(AV) - 4.7549 \quad (r^2 = 0.987) \quad (8)$

T = 100°C:
 $\ln(-r_{AV}) = 0.9334 \ln(AV) - 4.1071 \quad (r^2 = 0.994) \quad (9)$

T = 110°C:
 $\ln(-r_{AV}) = 1.1147 \ln(AV) - 4.0932 \quad (r^2 = 0.990) \quad (10)$

T = 120°C:
 $\ln(-r_{AV}) = 0.9526 \ln(AV) - 2.7045 \quad (r^2 = 0.999) \quad (11)$

It could be estimated from the slope of the plots, that

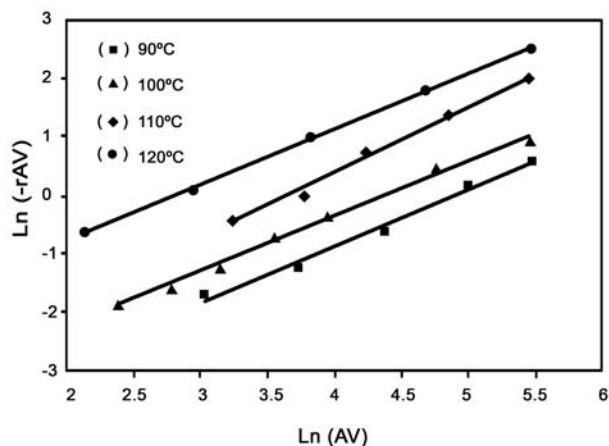


Figure 3. Ln (-r_{AV}) versus Ln (AV).

the reaction followed almost a first-order kinetics (i.e., $\alpha + \beta = 1$).

Integral method was used to confirm the above result. The integral form of a first-order reaction is as follows:

$$\ln \frac{AV_0}{AV} = kt \quad (12)$$

where,

AV₀: acid value at t=0

AV: acid value at time 't'

Figure 4 shows plots of (Ln AV₀ / AV_t) versus reaction time using the experimental data.

The plots were linear at all temperatures with very good correlation coefficients (r²), wherein the equations are as follows:

T = 90°C:
 $\ln(AV_0 / AV_t) = 7.5 \times 10^{-3} t \quad (r^2 = 0.998) \quad (13)$

T = 100°C:
 $\ln(AV_0 / AV_t) = 1.31 \times 10^{-2} t \quad (r^2 = 0.997) \quad (14)$

T = 110°C:
 $\ln(AV_0 / AV_t) = 3.01 \times 10^{-2} t \quad (r^2 = 0.992) \quad (15)$

T = 120°C:
 $\ln(AV_0 / AV_t) = 5.81 \times 10^{-2} t \quad (r^2 = 0.992) \quad (16)$

Above equations confirm that the reaction follows a first-order kinetics (i.e., $\alpha + \beta = 1$) rather than a second-order generally observed for catalyzed esterifica-

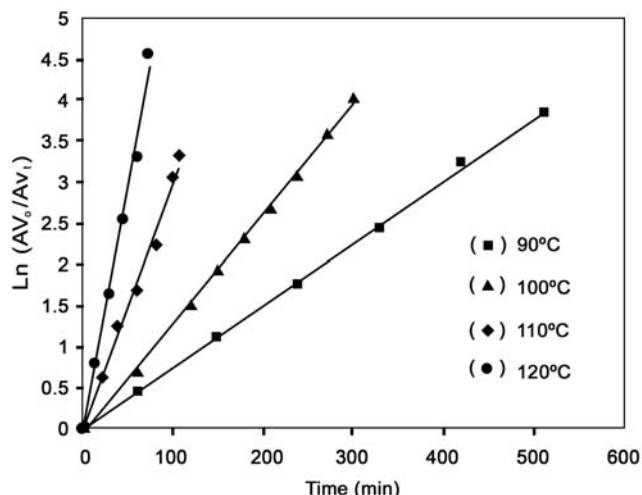


Figure 4. $\ln AV_o/AV_t$ versus reaction time.

tion reactions [21]. The values of specific rate constant at different temperatures (k) are calculated from the slope of the plots (Figure 4) and presented in Table 2.

Most researchers have reported a first-order reaction rate for the esterification of epoxy, although Srivastava and Agrawal [15] reported a second-order reaction kinetics for this type of reaction. Somewhere else, Srivastava et al. [20] reported a first-order kinetics for the reaction of epoxy with methacrylic acid in the presence of tertiary amine, however, they proposed a second-order mechanism for the reaction, i.e. $-r_A = k [\text{Acid}][\text{Epoxy}]$. They stated that according to the mechanism the reaction was first-order with respect to acid and emphasized that it was in agreement with the experimental results, i.e. overall reaction order. We think, first of all since the carboxylic and epoxide groups were not equimolar in their work, therefore using the formula of $-\ln(AV/AV_o) = kt$ for determining the overall reaction order was not completely justified. Secondly, the comparison of the overall reaction order with the order of carboxylic group needs some more experimental data.

In the present work, the excess method was applied to find the reaction order with respect to each reactant (i.e., α and β). For this purpose a reaction mixture consisting of a 5:1 molar ratio of Epiran 6 and methacrylic acid was used. The reaction temperature of 90°C was chosen in this condition.

Since epoxy group concentration is in excess (10 times of acid group concentration), it is assumed to be

Table 2. Amount of specific rate constants.

Reaction temperature (°C)	Specific rate constant (min^{-1})
90	0.0075
100	0.0131
110	0.0301
120	0.0581

constant during the reaction time and the reaction rate equation can be written as follows:

$$-r_{\text{Acid}} = k^* [\text{Acid}]^\alpha \quad (17)$$

where,

$$k^* = k [\text{Epoxy}]^\beta \quad (18)$$

Suppose that the reaction follows zero-order kinetics with respect to acid; hence the reaction rate equation in terms of acid value may be obtained as:

$$k^{**} = \left(\frac{56.1}{d} \right) k^* \quad (19)$$

where,

$$-\frac{dAV}{dt} = k^{**} = \text{cte} \quad (20)$$

Figure 5 shows the relationship of AV and reaction time in the excess condition.

The plot was found to be linear with a very good correlation coefficient, wherein the equation is as follows:

$$AV = 25.062 - 0.516 t \quad (r^2 = 0.979) \quad (21)$$

This equation confirms that the reaction follows a zero-order kinetics with respect to acid and since the overall reaction order was determined to be one (i.e., $\alpha + \beta = 1$), it follows first-order kinetics with respect to epoxy.

Figure 6 shows plots between $\ln k$ (driven from Table 2) and the reciprocal of the reaction temperature. It is apparent from Figure 6 that they obey

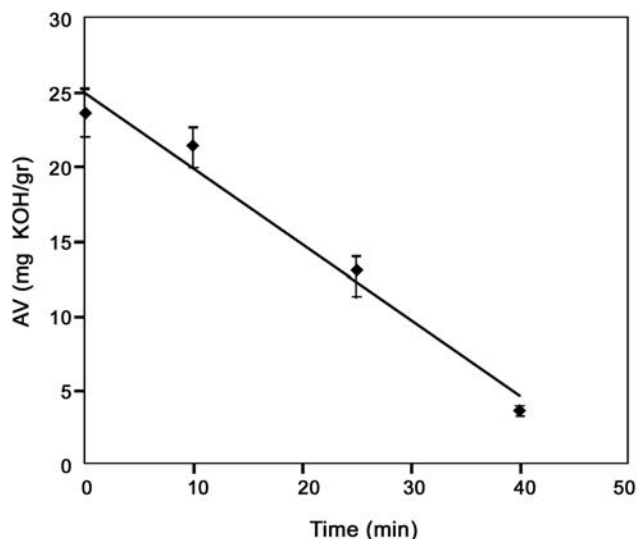


Figure 5. Acid value (AV) versus reaction time (Temperature = 90°C).

ture. It is apparent from Figure 6 that they obey Arrhenius law.

The slope and intercept of the plots obtained by regression analysis were used to calculate the energy of activation (E_a) and frequency factor (k_0). The amounts of E_a and k_0 were found to be 82.61 kJ/mol and $5.434 \times 10^9 \text{ min}^{-1}$, respectively. Srivastava et al. [20] found that using triethylamine catalyst in comparison to tripropylamine and tributylamine, a maximum reaction rate was attained. They reported E_a and k_0 for triethylamine catalytic system to be 57.02 kJ/mol and $1.077 \times 10^6 \text{ min}^{-1}$, respectively, which are less than what we have obtained in this study.

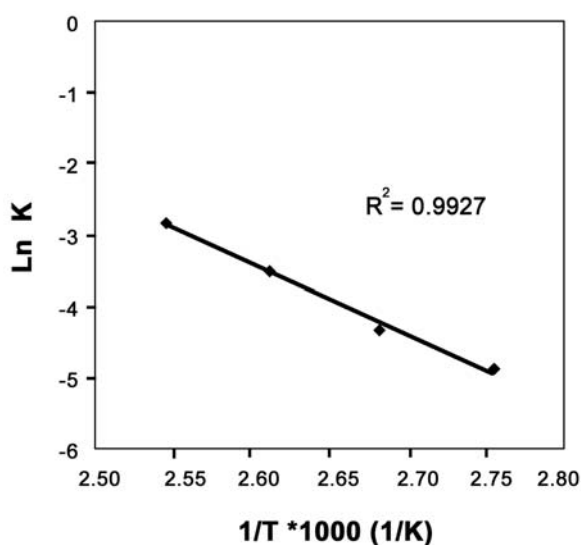


Figure 6. Plot of Ln k versus reciprocal of temperature.

CONCLUSION

It can be concluded from the obtained results that the esterification reaction of a bisphenol-A based epoxy resin with methacrylic acid in the presence of triethylamine as catalyst follows a first-order kinetics. The reaction was found to be zero-order with respect to acid by using excess method. The amounts of E_a and k_0 were calculated to be 82.61 kJ/mol and $5.434 \times 10^9 \text{ min}^{-1}$, respectively.

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