



Curing kinetics of Benzoxazine–epoxy copolymer investigated by non–isothermal differential scanning calorimetry

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ABSTRACT

The reaction of epoxy novolac resin cured with benzoxazine resin (BA-a) was investigated under non-isothermal DSC at different heating rates. The kinetic parameters and the kinetic models of the curing processes of the benzoxazine–epoxy novolac mixtures were examined utilizing isoconversional methods, Flynn–Wall–Ozawa and Friedman methods. The benzoxazine–epoxy novolac mixture exhibits two dominant curing processes. The reaction 1 at lower temperature is attributed to the reaction among the benzoxazine monomers, while the reaction 2 corresponds to the formation of an etherification between hydroxyl group of polybenzoxazine and epoxide group or homopolymerization reaction of epoxide group at high temperature. The average activation energies of the reaction 1 and reaction 2 were determined to be 81 kJ mol^{−1} and 118 kJ mol^{−1}, respectively. The autocatalytic kinetic model was found to be the best description of the investigated curing reactions. In addition, the predicted curves from our kinetic models fit well with the non-isothermal DSC thermogram.

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1. Introduction

Polybenzoxazine has been developed as a new class of thermosetting polymers based on the ring opening polymerization of benzoxazine precursors only by thermally cure without generating byproduct or volatiles. The polymer has been reported to render high glass-transition temperature (T_g) and high modulus [1–8]. Some properties of polybenzoxazine exceed many epoxy resin, as well as conventional phenolics. Recently, several US patents have been issued on the applications of the benzoxazine compound or resin that has utility especially for use within semiconductor fabrication industry [9–14]. Moreover, the use of the resin as a matrix for highly filled composites has been achieved [15,16]. Furthermore, the ability of benzoxazine resin to alloy with other polymers [2,6,17–22], provides the resin with even broader range of applications.

In the past decades, epoxy resins have been widely used in those applications required thermosetting characteristics. However, the hardeners used for the epoxy resins including amines and anhydrides, have some drawbacks such as high toxicity or low storage stability [23]. In a number of recent works, alloying between

benzoxazine resin and epoxy has been reported to be a potentially effective measure for thermal and mechanical property enhancement of the resulting copolymer because both polymers have been shown to compatibly undergo hybrid network formation as reported [9,19,24]. In addition, Rimdusit and Ishida [25] recently reported the characteristic of the curing reaction of the benzoxazine–epoxy systems. The curing reaction of the benzoxazine–epoxy resins shows two exothermic peaks, and the two peaks will be more distinguishable with an increasing amount of epoxy resin. However, the kinetic aspects of the curing of these resins were not discussed. In order to understand the nature of curing process of the benzoxazine–epoxy resins, the curing kinetic of the system is investigated in this work.

The cure kinetics of a thermosetting polymer is conveniently monitored by differential scanning calorimetry (DSC). The heat flow measured in DSC is proportional to both overall heat release and cure rate [26]:

$$\frac{dQ}{dt} = Q_{\text{cure}} \frac{d\alpha}{dt} = Q_{\text{cure}} k(T) f(\alpha) \quad (1)$$

where dQ/dt is the heat flow, t is the time, Q_{cure} is the total heat released when an uncured samples is brought to complete cure, $d\alpha/dt$ is the cure rate, α is the extent of a monomer conversion to a crosslinked network, $k(T)$ is the Arrhenius rate constant, and $f(\alpha)$ is the differential conversion function depending on the reaction

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mechanism. The rate constant, k , is dependent on temperature according to Arrhenius equation shown in Eq. (2).

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where A is the pre-exponential factor and E is the activation energy which are Arrhenius parameters and R is the gas constant (8.314 J mol⁻¹ K⁻¹).

The explicit temperature dependence of the rate constant, k , is introduced by replacing $k(T)$ with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

Kinetic analysis of non-isothermal resin-cured system in which a sample is heated at a constant rate, is eliminated through the trivial transformation.

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (4)$$

Where $\beta = dT/dt$ is a constant heating rate.

1.1. Kinetic analysis

Kinetic analysis of non-isothermal resin-cured system can be performed by the multiple heating rates [27–31]. A multiple heating rates method, which is isoconversional method, provides a good example to produce reliable kinetic parameters as well as to accomplish agreement with isothermal conditions. Two different isoconversional methods are as follows.

1.1.1. Flynn-Wall-Ozawa method

The isoconversional integral method was also proposed independently by Flynn, Wall and Ozawa [27,28] using Doyle's approximation of the temperature integral. This method is based on Eq. (5) and (6).

$$\ln\beta = \ln\left(\frac{AE_a}{R}\right) - \ln g(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \quad (5)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (6)$$

where $g(\alpha)$ is the integral conversion function.

This method has been used in present computations of the activation energy at different values of conversion. Thus, for a constant α , the plot of $(\ln \beta)$ vs. $(1/T)$ obtained from DSC thermograms using various heating rates, should render a straight line where the slope allows the determination of the apparent activation energy. The experimentally evaluated values of the activation energy were used to determine the appropriate kinetic model which best describes the conversion function of the process studied.

1.1.2. Friedman method [30]

The Friedman method is also used to determine a kinetic model of the curing process. The method is based on Eq. (7):

$$\ln \frac{d\alpha}{dt} = \ln \beta \frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E_\alpha}{RT} \quad (7)$$

$$\text{In case of the } n^{\text{th}} \text{ - order reaction : } f(\alpha) = (1 - \alpha) \quad (8)$$

$f(\alpha)$ in Eq. (7) is substituted by Eq. (8)

$$\ln[Af(\alpha)] = \ln\left[\frac{d\alpha}{dt}\right] + \frac{E_\alpha}{RT} = \ln A + n \ln(1 - \alpha) \quad (9)$$

The value of $\ln[Af(\alpha)]$ can be obtained from the known values of $\ln[d\alpha/dt]$ and E_α/RT . Therefore, the plot of $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ yields a straight line where the slope corresponds to the reaction order (n). The intercept is the natural logarithm of the frequency factor if the reaction mechanism of the n th-order kinetics. Otherwise, for autocatalytic process, the Friedman plot would reveal a maximum of $\ln(1-\alpha)$ approximately around -0.51 to -0.22 which is equivalent to degree of curing (α) of about 0.2–0.4.

As aforementioned, the advantage of two kinetics methods under non-isothermal condition is that they do not require prior knowledge of the reaction mechanism in order to quantify kinetic parameters [32]. In the past, the curing kinetic of benzoxazine resin (BA-a) with and without catalysts by using both isothermal and non-isothermal differential scanning calorimetry was determined [3,33]. The authors reported that the curing of benzoxazine precursors was an autocatalysed reaction prior to diffusion control stage. The apparent activation energy calculated by Ozawa and Kissinger method of the curing process in uncatalysed system was found to be 107 kJ mol⁻¹ and 116 kJ mol⁻¹, respectively, with an overall reaction order ($m + n$) of about 2. Recently, the kinetic analysis of other systems of benzoxazine resins such as random copolybenzoxazine of bifunctional benzoxazine (BA-a) type and monofunctional benzoxazine (P-a) type with low viscosity at room temperature has also been reported [34]. Under the dynamic DSC experiments, the curing process of the copolybenzoxazine precursor involves an autocatalytic-type curing mechanism and the activation energy was found to be 72 kJ mol⁻¹ based on the Kissinger method and 84 kJ mol⁻¹ using the Flynn-Wall-Ozawa method.

Meanwhile, numerous studies on curing kinetics of epoxy resin have been reported in the past decade [35]. The literature values of the activation energies and the kinetic equation for epoxy-anhydride cure under isothermal and non-isothermal conditions. The activation energy values were reported to be in a range of 28–158 kJ mol⁻¹ and the kinetic analysis of epoxy resins performed by several kinetic methods showed the autocatalytic cure [36,37]. Moreover, the curing kinetics of various epoxy resin systems utilizing the isoconversional method was investigated [26,28,36,38].

The present paper reports the cure kinetics of benzoxazine-epoxy novolac resin mixtures. The cure kinetics of the studied system was examined by non-isothermal differential scanning calorimetry (DSC) at different heating rates in order to understand the reaction kinetics of the benzoxazine-epoxy systems for achieving optimal processing.

2. Experimental

2.1. Materials

The BA-a type benzoxazine based on bisphenol-A, formaldehyde, and aniline was synthesized by patented solventless technology [4]. Bisphenol-A and paraformaldehyde were obtained from Thai Polycarbonate Co., Ltd. and Merck Company, respectively. An aromatic amines, i.e. aniline (99%), was purchased from Fluka Chemika. The *o*-cresol novolac epoxy (EPON164, epoxy equivalent weight 200–240 g/equiv., value for $n = 3.5$) was obtained from Shell Chemicals and was used as-received without further purification. The resin is light yellow solid at room temperature.

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