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Kinetic research on low-temperature cure of epoxy adhesive

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ABSTRACT

Low-temperature cure of epoxy adhesives was investigated by means of differential scanning calorimetry analysis (DSC) on both isothermal and dynamic curing process and isothermal and dynamic curing phenomenological autocatalytic models were established. For dynamic curing section, an advanced isoconversional method was taken into account for computing the minimum apparent activation energy E_a value for each value of α lying between 0.05 and 0.95 with a step of 0.01. The correlation of invariant apparent activation energy and pre-exponential factor was expressed by "compensation parameters" equation. The isothermal experimental results showed that curing at low-temperatures of 10–15 °C did take place but it was difficult to reach complete reaction over a reasonable experiment time period because the curing process was significantly decelerated owing to the effects of material vitrification and diffusion control in the late curing stages. In order to match the calculated and measured data better and describe the cure in the later stages of reaction, a heating rate-dependent pre-exponential factor and diffusion control were taking into account. The modified modeling with the heating rate-dependent pre-exponential factor and diffusion control agreed well with experimental data. Moreover, analysis of nonlinear regression was carried out on the isothermal modeling, results showed that the nonlinear least squares fitting had a satisfactory effect.

1. Introduction

Epoxy resins are important thermosetting resins, as the matrix resin of adhesives which has been widely used in the field of mechanical engineering, transportation, chemical engineering, architecture, etc., owing to its better technology, mechanical and physical properties [1–4]. Additionally the composites have also been used for cryogenic applications [5]. Study on curing of matrix resin is one of the important issues. Kinetic model is commonly used, which established mathematical relationships between curing rate with temperature and curing degree from the computational standpoint [6]. The most straightforward way is to determine a kinetic triplet, that is A, E_a and $f(\alpha)$. E_a is associated with the energy barrier, A with the frequency of vibrations of the activated complex [7], and $f(\alpha)$ with the reaction mechanism [8].

Two main approaches used for cure kinetics can be divided into phenomenological and mechanistic modeling [9]. And the application of the phenomenological method mainly using semi-empirical model equation is more common, obtaining various parameters of model equation through mathematical simulation [10–12]. The kinetics of curing epoxy resins has been widely studied by using isothermal or dynamic experiments with differential scanning calorimetry (DSC) [13]. A few reports have been reported on kinetic studies of high temperature curing of epoxy resins [14,15] but not much with low temperature curing [16]. Experience has told us that the mechanical properties are strongly dependent on the curing conditions [17], particularly long periods of low temperature are frequent in winter, the curing reaction may not be fully complete and the mechanical properties may change during use if the temperature is too low. Therefore, an understanding of the low-temperature curing mechanism is essential to control and optimize mechanical properties [18,19].

All experimental data have noise. The amount of noise can affect the choice of the kinetic analysis method. Since the differential isoconversional methods being more reliable for the treatment of thermoanalytical data [20–28] do not make use of any approximates on the temperature integral, they are more accurate than the integral methods. For differential isoconversional DSC data, it would be natural to use a differential method. According to Nicolas Sbirrazzuoli's literature [29], using compensation effect and the isoconversional method to compute a model-free estimate of the logarithm of the pre-exponential factor (ln$A$), ABS (Achar-Brindley-Sharp's) method and Tang method obtained the lowest

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errors and are more accurate than other methods. However, Tang method is an integral method and ABS method is a differential method, thus, we chose the ABS method to compute the ln$A$. Moreover, the E_a value for each value of α lying between 0.05 and 0.95 with a step of 0.01 was computed by the NLN Vyazovkin method [30–32].

This research work is now focused on two aspects: (I) looking for model parameters of a new system through the existing model, as providing a theoretical basis for the development of processing routes [33,34]. (II) Correcting the existing model or processing the new model to adapt to a new system. In this experiment, for the study on low-temperature curing of epoxy resin by DSC, a minimum curing temperature was 10 °C, used the aspect of (I). Assessing the validity of a kinetic model fitting by comparing the measured with calculated reaction profiles (either rates or extents of conversion, or both versus temperature) is required. Only by showing satisfactory matching can the parameters have some effectivity.

2. Experimental

2.1. Materials

The epoxy resin was diglycidyl ether of bisphenol A (DGEBA) type E-44 supplied by Yueyang Petrochemical and the curing agent was TU-DETA synthesized by our experiment. The structures of these chemicals were depicted in Table 1.

2.2. Methods

A differential scanning calorimeter (Shimadzu DSC-60, equipped with a liquid nitrogen cooling system and performed by TA analysis software for data acquisition) was used for dynamic and isothermal cure experiment and data analysis. The flux of nitrogen providing an insert atmosphere was set to 50 ml min^{-1}.

The weight of each sample was measured prior to scanning by a ultramicro balance (XP6, Mettler Toledo). By the requirement of the Shimadzu instrument, the amount of sample was in the range of 5–10 mg. The samples were placed in an empty aluminum pan covered with a lid. An aluminum pan loading aluminum oxide as reference compound of the same type and size was used as a reference during every scan.

2.2.1. Dynamic heating runs

Dynamic runs at constant heating rates were made in order to determine the total heats of reaction released during dynamic curing for uncured samples. Before testing, all uncured samples were deposited in refrigerator under −18 °C.

In order to determine the dosage of curing agent, the reactants E-44 and TU-DETA were mixed under −18 °C in a equivalent ratio of 2:1, 3:1, 4:1, 5:1, 6:1 and 7:1, respectively. These uncured samples of 5–10 mg were installed in aluminum pans and placed in the instrument furnace. After cooling to −50 °C rapidly, the heat evolution was monitored from −50 °C to 250 °C using the heating rate of 10 °C min^{-1}. After determining the optimum dosage to curing agent, dynamic scans were conducted in the temperature range of −50 °C to 250 °C at constant heating rates of 5, 10, 12.5, 15 and 20 °C min^{-1}. By re-scanning the completely cured sample at 10 °C min^{-1}, the corresponding glass transition temperature (T_g) was obtained.

2.2.2. Isothermal runs

Isothermal DSC scans were performed at temperatures ranging from 10 to 80 °C, where 10 °C was low temperature, 80 °C was high temperature below T_g in this experiment. This range was chosen in accordance with the planned architecture application. The furnace was first heated up to a desired fixed temperature at the heating rate of with 10 °C min^{-1} and kept for a certain period of time. When the system reached the equilibrium state, the sample was quickly set on the calorimetric detector plate. The reaction was considered to be complete until the heat flow curve approached a plateau.

In this experiment, the sample used was fresh and uncured. The curing heat of each sample at its corresponding time period was determined by integrating the curve of heat flow from the beginning to the determined time [35–37], so the degree of cure was calculated in the form [38]:

$$\alpha = \frac{\Delta H_t}{\Delta H_{total}} \quad (1)$$

where α is the degree of cure, ΔH_t is the reaction heat at time t, and ΔH_{total} is the total reaction heat of reaction.

2.2.3. Glass transition temperature

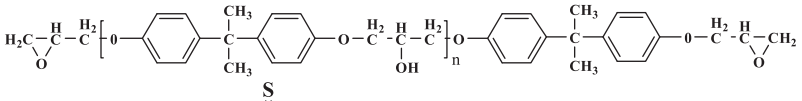
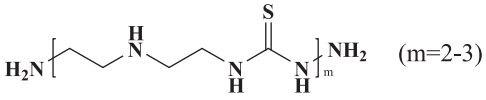
The reactants E-44 and TU-DETA were mixed under −18 °C with the mass ratio of 6:1 from −50 °C to 250 °C firstly and then re-scanning the completely cured sample at 10 °C min^{-1}, the glass transition temperature (T_g) was found to be at a temperature of 116 ± 2 °C, presented in Fig. 1. T_g was determined as the midpoint of the step (defined according to ASTM E 2602) [16] in the curve presenting curing exotherm during the dynamic re-scanning.

3. Results and discussion

3.1. Determining the dosage of curing agent

For the sake of determining the optimum dosage of curing agent, a series of different mass ratios of E-44 and TU-DETA uncured component samples for DSC measurement was weighed, wherein the upward direction of the peaks in the curve representing exothermic reaction. The change in heat flow versus temperature and time during cure at the heating rate of 10 °C min^{-1} is shown in Fig. 2. A straight baseline was used to integrate the peak of heat flow versus time to give the reaction heat. The value of heat released is listed in Table 2.

Table 1
Structures of the chemicals.

Materials	Molecular structures
E-44	
TU-DETA	 (m=2-3)