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Temperature dependence of isothermal curing reaction of epoxy resin studied by modulated differential scanning calorimetry and infrared spectroscopy

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ABSTRACT

The isothermal curing reaction of bisphenol A diglycidyl ether epoxy (BADGE) resin with dimethyl diamino methane (DDM) hardener was investigated by means of modulated differential scanning calorimetry (MDSC) and infrared (IR) spectroscopy at 90, 100 and 120 °C.

It was confirmed that the behavior of the bands assigned to the epoxy group, ether group, secondary amine and tertiary amine were different depending on temperature. At stoichiometric amounts of DDM and BADGE, the reaction at 90 and 100 °C compared with that at 120 °C, the oxirane or glycidyl group of epoxy resin and the secondary amine group were left even if reached at the end point of the reaction, and those reaction proceed as diffusion control continues longer. The reaction between 90 and 100 °C, it was different from the reactivity of the epoxy resin, various amino groups and ether group. Hence, the cured epoxy resin had a different composition. Moreover, it was also verified that the reactivity of the various amino groups and the etherification were difference, therefore, it was suggested that the cross-linkage construction of the cured resin at different temperature was different.

1. Introduction

A process of epoxy curing shows thermosetting properties during the complicated three-dimensional cross-linking reactions among epoxy monomer and hardening agent. Cured resin is widely used for various industrial materials owing to their excellent adhesiveness, heat resistance, chemical resistance, etc. There are many kinds of epoxy resins and hardening agents, and chosen combination influences not only the physical properties of the cured resins but the process of curing reaction. The physical properties of the cured resin are mainly dependent on the monomer properties as well as the final cross-linkage structure formed during the reaction [1–4].

The curing reaction of a bisphenol A epoxy resin and an amine hardening agent is widely known as shown in Scheme 1.

First, the primary amine adds to an oxirane group to generate a secondary amine and hydroxyl group. In the early stage, the chain lengthening reaction occurs preferentially and the molecular weight of a system gradually increases. Subsequently, an oxirane ring begins to add to the secondary amine and hydroxyl group to form of cross-linkage structure. The polymerization reaction continuously increases the crosslink density [4–9].

Each hardener has a characteristic cure temperature region, and as the curing reaction rate increases, the cure temperature increases. However, high-temperature curing often significantly diminishes physical properties of the cured resin. Furthermore, proper amount of hardening agent must be added to the system considering the equivalence ratio, chemical properties of the hardening agent, the target characteristic of the cured resin, etc. In the case of a polyamine hardener, a stoichiometric amount is generally used.

In this study, the effect of temperature on the curing process using stoichiometric amounts of diphenyl dimethyl methane (DDM) and a bisphenol A diglycidyl ether epoxy (BADGE) were investigated using modulated differential scanning calorimetry (MDSC) and time-scanning infrared spectroscopy.

The chemical formulas of BADGE and DDM are shown in Fig. 1. Thermal events of capacitive and kinetic variations during the

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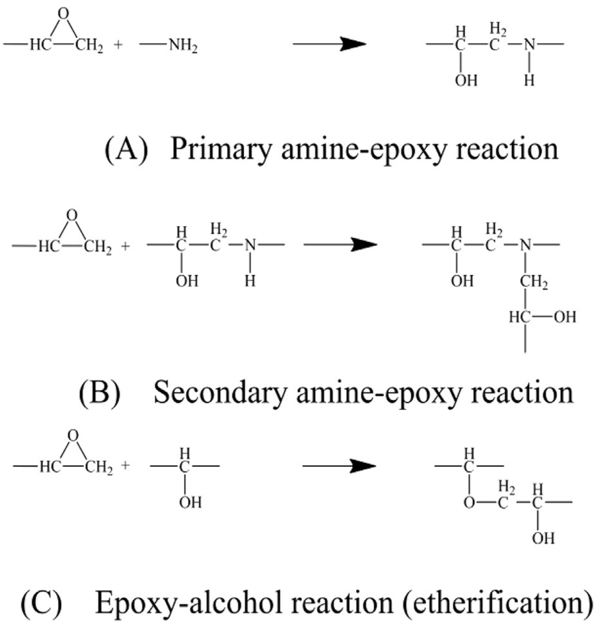
(A) Primary amine-epoxy reaction

(B) Secondary amine-epoxy reaction

(C) Epoxy-alcohol reaction (etherification)

Scheme 1. The curing reaction of a bisphenol A epoxy resin and an amine hardening agent.

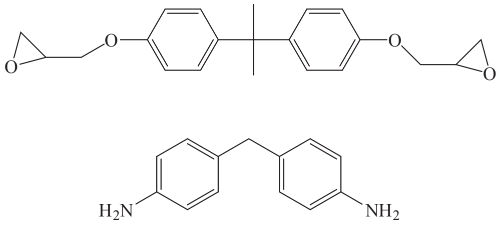
Fig. 1. The chemical constitution formulas of BADGE and DDM.

isothermal curing process were captured using MDSC by quasi-isothermal mode, which can separate the non-reversing curing process from heat capacity [10–14].

The chemical reactions at a functional group level were characterized by time-scanning mid-infrared (MIR) and near-infrared (NIR) spectroscopy. The changes of the system during the curing reaction at each inflection point are discussed. It was revealed that the macroscopic behavior of the system explored using MDSC and the microscopic chemical reactions captured using the spectroscopic measurements are consistent. The quantitative changes in concentration of each functional group, epoxy resin and the various amino groups during the curing reaction will be discussed using the NIR spectroscopy, while that of ether group using the MIR spectroscopy. The bands arising from primary and secondary amines in the NIR spectra are assigned using generalized two-dimensional (2D) correlation spectroscopy [15–21]. Perturbation-correlation moving-window 2D correlation spectroscopy (PCMW2D) was performed to evaluate the correlation among NH groups and ether group during the curing reaction [22–24].

2. Experimental

A commercial grade BADGE (jER828, epoxide equivalent of 190 ± 5) was purchased from Mitsubishi Chemical Corporation. The hardening agent of DDM having melting temperature of 88 °C was obtained from Wako Pure Chemical Industries, Ltd. All chemicals were used as received.

Samples for MDSC and IR spectroscopy were prepared by mixing BADGE with DDM just before the measurements at an equivalent ratio of the oxirane groups in BADGE and the N—H bonds, i.e., twice the primary amine group, in DDM. MDSC was performed using a TA instrument Q2000 under a quasi-isothermal mode at 90, 100 or 120 °C. The modulation amplitude and period were set to be 0.5 °C and 60 s, respectively, to achieve sufficient sensitivity for the heat capacity measurements. For MDSC analysis, 10 mg of each sample was sealed in an aluminum pan, and carried out under a nitrogen gas flow of 50 mL/min^{-1}. All the transmission MIR and NIR spectra were measured using a Fourier-transform infrared spectrometer (Varian, FTS 3000) equipped with a KBr/Ge or quartz beam splitter and a mercury–cadmium–telluride (MCT) detector coupled with a microscope unit (Varian, UMA 600). The MIR spectra were recorded in the 4000 to 700 cm^{-1} range, while the NIR spectra were obtained in the 7200 to 4400 cm^{-1} range at 8 cm^{-1} resolution with 256 scans. The MIR and NIR spectra were collected every 60 s. The isothermal curing reaction was carried out on a Linkam Heat-Stage 10036 at 90, 100 or 120 °C under N_2 atmosphere. For MIR analysis, the samples were sandwiched between two BaF_2 windows. A thickness of the sample was 2 μm. For NIR analysis, 0.5 mm thick samples were prepared between a slide glass board and a cover glass. All of the generalized 2DCOS and PCMW2D spectra were constructed using the public free software of the 2Dshige software (https://sites.google.com/site/shigemorita/).

3. Results and discussion

3.1. MDSC

Fig. 2 shows the heat flow curve, reversing C_p curve, and first derivative heat flow curve of the epoxy/polyamine curing system at various temperatures. After stabilizing the temperature modulations of ca. 5 min, exothermal peaks were observed in the heat flow curves at 41, 26 and 12 min under the curing conditions of 90, 100 and 120 °C, respectively.

It was confirmed that a higher curing temperature resulted in a faster curing reaction. The first derivative heat flow curves featured different valley formations, suggesting that the curing process was affected by the curing temperature. Curing reactions are initially chemically controlled, but become diffusion controlled, but it is presumed that these reactions start differ.

Although the reversing C_p is equivalent to the information regarding heat capacity changes, which relate to molecular mobility, the signal intensity increased as the curing reactions processed and the molecular weight increased under all conditions. Subsequently, the signal intensity decreased due to the restriction of molecular movement, i.e., vitrification [12,14,15,25,26]. The evidences of the vitrification were found after 73, 51 and 31 min for the curing conditions of 90, 100 and 120 °C, respectively. In order to read the vitrification point from reversing C_p curve, line C was drawn in Fig. 2 as a bisection of the angle between lines A and B. The vitrification points were evaluated to be 82, 57 and 35 min for 90, 100 and 120 °C, respectively. These results demonstrate that vitrification occurred over a long time period at low curing temperatures.

The MDSC were not sufficient to determine the change of the molecular structure during the curing reactions. Therefore, these details were elucidated using IR spectroscopy.

3.2. NIR spectroscopy

Fig. 3 shows time-scanning NIR spectra of the epoxy curing