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Identification of the epoxy curing mechanism under isothermal conditions by thermal analysis and infrared spectroscopy

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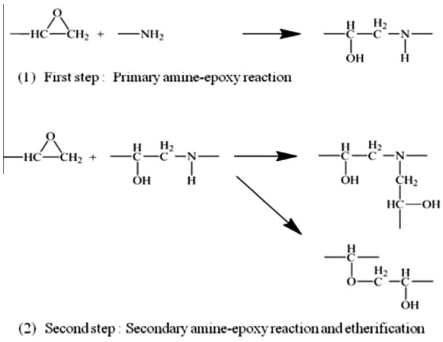
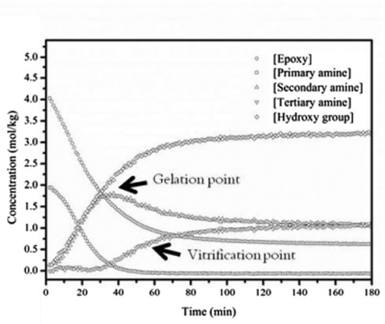
HIGHLIGHTS

- We examined the relation between change in the physical properties and molecular structures.
- The gelation point was the maximum concentration of the generated secondary amine.
- The vitrification point was the process of the change to the tertiary amine from secondary amine.
- We report the information about the relation between formation of ether groups and change of amino groups.

GRAPHICAL ABSTRACT





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ABSTRACT

A curing reaction of bisphenol A diglycidyl ether epoxy resin with 4,4′-diaminodicyclohexyl methane hardener was investigated by means of modulated differential scanning calorimetry (MDSC), thermal scanning rheometer (TSR), near-infrared (NIR) and mid-infrared (MIR) spectroscopy. The relation between change in the physical properties and molecular structures during the isothermal curing reaction were studied. MDSC and NIR results corroborated vitrification with the secondary to tertiary amine conversion; the process afforded a three-dimensional cross-linking structure. TSR estimation of the gelation point was corroborated with the NIR-determined maximum concentration of the generated secondary amine. Two-dimensional correlation spectroscopy confirmed that reaction between the primary amine and epoxy occurred more rapidly than any other functional group reaction. The ether groups were generated at the early stage of the curing reaction, and their formation occurred immediately with the generation of hydroxyl groups.

1. Introduction

Epoxy resins are widely used as an adhesive agent, coating material, electric insulation materials, etc., and their versatile applicability is due to their excellent material properties, which excel in electrical property, adhesiveness, heat resistance, and chemical resistance [1–4]. The curing reaction of the epoxy resins take place either between the epoxy group of their molecules themselves or by the reaction between the epoxy group and other reactive molecules with or without the help of the catalyst. The former is known as homopolymerization, and the latter is an addition or catalytic curing reaction. The curing process of an epoxy resin proceeds as a function of time or temperature, and it involves a series of complicated chemical reactions. The curing reaction is initiated by

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mixing it with a hardening agent, such as polyamine, and the properties of the cured resin are controlled by this hardening agent and the conditions of the curing process (temperature, pressure, etc.) [4,7–9].

Changes in the rheological properties of the mixture during the curing process, in which a viscous fluid becomes a plastic resin at its gelation point, are caused by the formation of a three-dimensional network via cross-linking polymerization reactions. Scheme 1 illustrates typical curing reactions among the oxirane group of the epoxy monomer and amine groups of the hardening agent. During the early stage of the curing process, the chain-growth polymerization reaction is dominant. Following that, the cross-linking point is generated by the reaction between the oxirane group and the secondary amine group. Finally, the three-dimensional cross-linking structure is formed via the tertiary amine and etherification of a hydroxyl group [4–6].

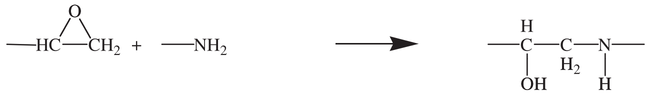
In the present study, an isothermal curing process of a bisphenol A diglycidyl ether (BADGE) epoxy resin with a 4,4′-diaminodicyclohexyl methane (DDHM) hardener was investigated by means of modulated differential scanning calorimetry (MDSC), thermal scanning rheometry (TSR) and infrared (IR) spectroscopy. Fig. 1 shows the chemical structures of BADGE and DDHM.

MDSC allows us to capture the thermal events of capacitive and kinetic variations during the isothermal curing process, whereas TSR allows the rheological changes to be measured. MDSC can separate the total heat flow (nonreversing heat flow) from the change in heat capacity (C_p) [10–14]. TSR gives information about the variations in stiffness and elasticity during the thermal treatment through the measurements of loss and storage moduli, which are sensitive to changes in internal molecular mobility [15–17]. We explored the changes in the structure by employing time-dependent mid-infrared (MIR) (for ether groups) and near-infrared (NIR) (for hydroxyl and amino groups) spectroscopy at each inflection point observed during MDSC and TSR [18–21].

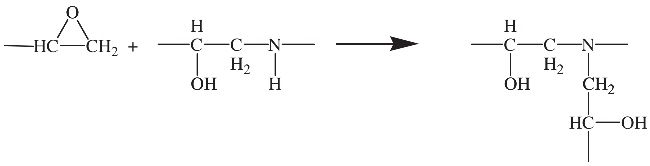
In order to unravel the complex chemical reactions during the curing process at the functional group level, two-dimensional (2D) MIR–NIR hetero-spectral correlation analysis was also conducted [22–26].

2. Experimental

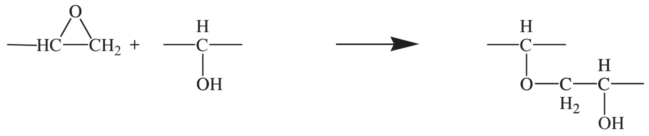
A commercial grade epoxy resin of BADGE (jER828, epoxy equivalent of 190 ± 5, number average molecular weight of 380) was purchased from Mitsubishi Chemical Corporation. DDHM, the curing agent, was obtained from Tokyo Chemical Industry Co., Ltd. All chemicals were used as received.



(A) Primary amine-epoxy reaction

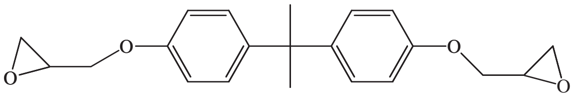


(B) Secondary amine-epoxy reaction

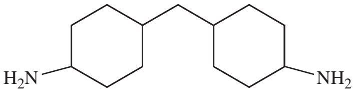


(C) Epoxy-alcohol reaction (etherification)

Scheme 1. Multiple curing reactions among oxirane group in the epoxy resin and amine group in the polyamine hardener. (A) Primary amine–epoxy reaction, (B) secondary amine–epoxy reaction, (C) epoxy–alcohol reaction (etherification).



Bisphenol A diglycidyl ether (BADGE) epoxy resin



4,4’-diaminodicyclohexyl methane (DDHM)

Fig. 1. Chemical structures of (top) BADGE and (bottom) DDHM.

The samples were prepared for MDSC, TSR, and IR spectroscopic analyses by mixing BADGE with DDHM just before the measurements, and the ratio of the oxirane group in BADGE to the N–H bonds in DDHM was 1:1, i.e., 2:1 with respect to the primary amine group.

All MDSC was performed using a TA Instruments Q2000 under a quasi-isothermal condition at 70 °C for 180 min. In quasi-isothermal conditions, information about both the total heat flow and heat capacity can be acquired by introducing modulation. The modulation amplitude and period were set to be 0.5 °C and 60 s, respectively, to achieve a sufficient sensitivity for the heat capacity measurement. A 5.7 mg sample of MDSC was sealed in an aluminum pan. The thermal analysis was carried out while purging with nitrogen gas at 50 mL min^{-1}.

All TSR was carried out using a TA Instruments ARES-G2 under isothermal conditions at 70 °C for 90 min; the strain value could not be followed after that. The TSR can monitor the viscoelastic state and particularly the changes in the rheological properties with temperature or time. A sample having a thickness of ca. 5 mm was sandwiched between an aluminum cup of 42 mm in diameter and an aluminum plate 40 mm in diameter. The prepared sample is connected via a spring of known force constant amplitude and frequency. The position of the sample is continuously monitored using accurate transducer. When the viscosity of the sample increases, the motion is gradually damped by viscous drag. The measurement was carried out using a frequency of 1 Hz and an initial strain of 50% under nitrogen gas purge.

All the microscopic, transmission MIR and NIR spectra were measured using a Fourier-transform infrared spectrometer (Varian, FTS 3000) equipped with either 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 range of 4000–700 cm^{-1}, whereas the NIR spectra were obtained in the range of 7200–4400 cm^{-1} at a resolution of 8 cm^{-1} with 256 scans. MIR and NIR spectra were collected every 60 s for 180 min. The isothermal curing reaction was carried out on a Linkam Heat-Stage 10036 at 70 °C under a N_2 atmosphere. A 3-μm-thick sample was sandwiched between two BaF_2 windows and used for the IR measurement. A 1.0-mm-thick sample was prepared between a slide glass and a cover glass for the NIR measurement. All of the 2D hetero-correlation spectra were constructed using the 2D-Shige software (https://sites.google.com/site/shigemorita/home/2dshige/).

3. Results and discussion

3.1. MDSC

Fig. 2 shows the MDSC curves of the mixture of BADGE and DDHM plotted as a function of time measured under a