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Curing reaction of epoxy resin composed of mixed base resin and curing agent: Experiments and molecular simulation

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ABSTRACT

In this study, we investigated the influence of base resin and curing agent and their mixture on the curing characteristics by performing experiments and molecular simulations. In the curing experiment of epoxy resin, we used differential scanning calorimetry (DSC) to obtain the conversion by mixing curing agents and base resins. We used the molecular orbital method (MO) and the molecular dynamics method (MD) to simulate the curing reaction in molecular scale and investigate the effect of differences in resin composition on the curing characteristics. This simulation took into consideration activation energy, heat of formation, and polarization in the curing reaction. The simulation captures the trend of curing reaction obtained by the experiment. We found that the selection and mixture of curing agents are very important when controlling the curing characteristics of epoxy resin.

1. Introduction

Among thermosetting resins, epoxy resins have superior heat resistance, adhesion, and mechanical properties. They are widely used for adhesives, electric insulating materials, and matrix resins for fiber-reinforced plastic (FRP) [1,2]. Epoxy resins are widely used as matrix resins, especially for carbon-fiber-reinforced plastic (CFRP). Since CFRP has high-specific strength and stiffness, its application is increasing in transportation system (e.g., airplanes) requiring weight reduction. Because the characteristics of CFRP depend on the characteristics of matrix resin, numerous studies have investigated the mechanical and physical properties of matrix resin. However, analysis of curing characteristics is necessary in order to aid in research and technological development which aimed to increase the productivity of CFRP.

Differential scanning calorimetry (DSC) is generally used for experimental study of epoxy cure reaction [3–5]. In addition, the overall model known as Kamal's model has been used in order to characterize the cure kinetics. For example, Rosu et al. [4] and Silvia et al. [6] investigated the cure kinetics of epoxy resin using the addition of reactive diluent and the modifier of epoxy thermoset. However, this model does not consider the chemical reactions based on the molecular structure in the curing reaction process. Komarov et al. [7] evaluated the mechanical characteristics of a cured product using the coarse-grained molecular dynamics method (MD) at the functional group level. They assumed that chemical reactions occur when the reactive sites approach a fixed distance. Their reaction model is widely used [8–10]. But, this technique is problematic in that it does not consider chemical reactivity. Since it is desirable for cure time to be controllable with the selection of base resin and curing agent, the simulation should consider chemical reactivity.

In this study, we investigated the influence of base resin and curing agent and their mixture on the curing characteristics. We conducted curing experiments focusing on epoxy resin with mixed base resin and curing agent, and compared the curing characteristics. We also simulated the curing reaction process on a molecular scale using molecular simulation, and investigated the effect of differences in resin composition on the curing characteristics. In the molecular simulation, the curing of an epoxy resin was simulated by considering the effect of activation energy, heat of formation, and polarization of a molecule.

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2. Epoxy curing experiment

In this study, Diglycidyl Ether of Bisphenol A (DGEBA), Diglycidyl Ether of Bisphenol F (DGEBF), and Tetraglycidyl Diamino Diphenylmethane (TGDDM) were used as base resins (Fig. 1). The curing agents were Diethylenetriamine (DETA), 1,3-Phenylenediamine (MPDA), and 4,4′-Diaminodiphenil Sulfone (DDS).

The experiment involved the following six systems: (DGEBA/DETA/MPDA), (DGEBA/DETA/DDS), (DGEBA/MPDA/DDS), (DGEBA/DGEBF/DDS), (DGEBA/TGDDM/DDS), and (DGEBF/TGDDM/DDS). In the first three systems, we changed only the combination of curing agents. In contrast, we changed only the combination of base resins in the latter three systems (Table 1). In each resin composition, a sample number was assigned to every mixture ratio. In addition, the mixture ratio was described by mole ratio.

2.1. Experiment method

DSC was used to measure the difference between the heat of a measurement sample and that of a standard substance. DSC is often used to investigate the curing behavior of various thermosetting resins [11,12].

In this study, we used DGEBA (jER825), DGEBF (jER806) and TGDDM (ELM434) for base resins. We used DETA, MPDA, and DDS for curing agents. An empty aluminum pan was used for the standard substance in DSC. The experiment procedure was as follows.

1. The mass of base resin and the curing agent were measured with an electronic balance (Ek300i, A&D Company, Ltd.).
2. The base resin was mixed with the curing agent at required ratio. In this process, the three base resins and two curing agents (MPDA and DDS) are solid at room temperature, so they were mixed after being dissolved.
3. The mass of mixed epoxy was measured with a highly precise electronic balance (AB135-S/FACT, METTLER TOLEDO), and measurement test pieces were created. The sample mass was 7 g.
4. Heat flow when a sample cured was measured using DSC (DSC 200 F3 Maia, NETZSCH).

This experiment was conducted under two different temperature conditions. The three systems with a change in only the combinations of curing agents were measured with a temperature increase of 10 °C/min from 30 °C to 220 °C. The three systems with a change in only the combination of base resins were measured with a temperature increase of 10 °C/min from 30 °C to 250 °C.

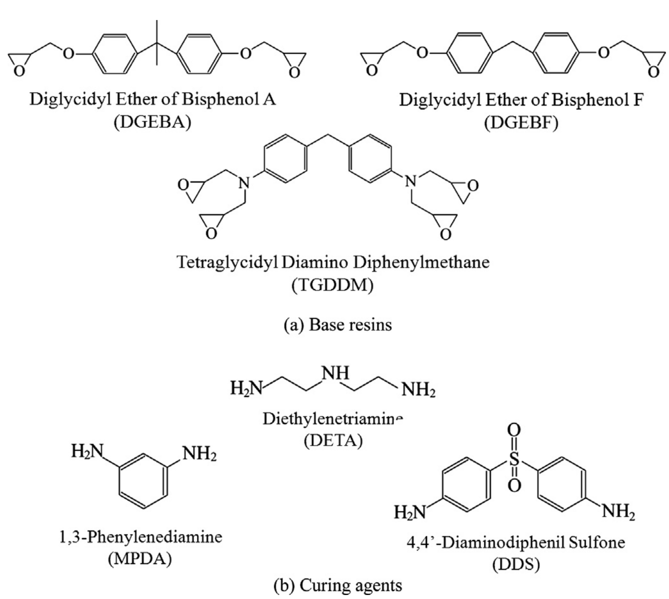

Fig. 1. Structures of base resins and curing agents.

Table 1
Sample ratios.

Sample	Mole ratio of the components		
	DGEBA/DETA/MPDA	DGEBA/DETA/DDS	DGEBA/MPDA/DDS
(a) Mixture of DGEBA and curing agents			
1	1/1/0	1/0.5/0.5	1/1/0
2	1/0.5/0.5	1/0.3/0.7	1/0.8/0.2
3	1/0.3/0.7	1/0.2/0.8	1/0.6/0.4
4	1/0.2/0.8	1/0.1/0.9	1/0.4/0.6
5	1/0.1/0.9	1/0/1	1/0.2/0.8
6	1/0/1	–	1/0/1

Sample	Mole ratio of the components		
	DGEBA/DGEBF/DDS	DGEBA/TGDDM/DDS	DGEBF/TGDDM/DDS
(b) Mixture of DDS and base resins			
1	1/0/1	–	–
2	0/1/1	–	–
3	–	–	0/0.5/1
4	1/1/2	–	–
5	–	1/0.5/2	–
6	–	–	1/0.5/2

The heat flow of the epoxy curing process was measured using DSC; then the degree of conversion α was calculated from the result. The relationship between degree of conversion α and heat flow φ is given by the following equation [5,13].

$$\alpha = \frac{1}{\Delta H}\int \phi \mathrm{d}t \tag{1}$$

Here, ΔH is the enthalpy of the chemical reaction. The graph that depicts the relationship between α and elapsed time is called the curing curve. Curing start time or temperature was measured from this curve, and the curing characteristics were compared by investigating each curing temperature and the shape of the curing curve.

2.2. Experiment results

The reactivity of each curing agent with base resin DGEBA was first investigated as a preliminary experiment. DGEBA/DETA/MPDA Sample 1, which used only DETA for a curing agent, cured in the mixing process at room temperature. For DGEBA/DETA/MPDA Sample 2, the mixed curing agent (DETA/MPDA = 1/1) was used. The other curing agents were used alone, and the heat flow was measured using DSC. Fig. 2 depicts the curing curve. Curing started in the order of DETA/MPDA, MPDA, and DDS. Results confirmed that DETA has the highest reactivity with DGEBA among the three curing agents.

Next, we changed the mixture ratio in each combination used in the experiment. The conversion α for DGEBA/DETA/MPDA was calculated from the DSC results (Fig. 3). Results indicated that the curing temperature decreased as the mixing ratio of DETA increased when DETA and MPDA were mixed with DGEBA. The chemical reactivity of DETA with DGEBA is higher than that of MPDA, so curing started at a lower temperature. Due to the heat that occurs in the curing reaction of DETA, the cure of MPDA started earlier than DGEBA/DETA/MPDA Sample 6 which used only MPDA as the curing agent. Therefore, it is thought that the curing temperature decreased.