

# DGEBA/DDS 에폭시수지계의 개별적 반응기구 및 물성

민 병 각\*

## Individual Reaction Mechanisms and Properties of a DGEBA/DDS Epoxy Resin System

Byung-Gak Min\*

KEY WORDS: epoxy resin, curing agent, cure temperature, reaction mechanism, near infrared spectroscopy.

### ABSTRACT

Near infrared spectroscopy techniques were used to study the cure reactions of epoxy resin system based on diglycidyl ether of bisphenol A(DGEBA) resins cured with 4,4' diaminodiphenyl sulfone (DDS) hardner. Stoichiometric DGEBA/DDS resin formulation was involved in this study. The infrared absorption spectra of the prepared formulation were obtained on an FTIR spectrometer operating in the region of 11000 to 4000cm<sup>-1</sup>. The chemical group peaks of interest in a DFEBA/DDS spectrum were identified by a comparative study with individual spectra of DGEBA and DDS monomers. Where necessary, special model compounds were used to identify unknown bands, such as the primary amine band at 4535cm<sup>-1</sup>. The absorption bands of interest were integrated to quantify the areas and then converted to molar concentrations. This series of quantitative analyses of the major chemical groups led us to understand not only the reaction mechanism but also the cure kinetics. In this paper, the reaction mechanisms observed in stoichiometric DGEBA/DDS resin formulation and the various properties of the resin system as a function of cure temperature are described.

### 1. INTRODUCTION

Although epoxy resins have been used as matrix materials for many advanced composites, the intrinsic brittleness associated with their highly crosslinked structures still remains a major drawback. In the last few decades, extensive research work has contributed to methods of improving the relatively poor fracture properties of epoxy resins through (more or less successful) approaches based on reducing the crosslink density of the epoxy network or modifying commercially available epoxy resins with secondary components such as low molecular weight liquid rubbers<sup>1,2</sup>, inorganic fillers<sup>3</sup>, or ductile engineering thermoplastics<sup>4</sup>

The developing network structure of the epoxy resins, arrested at different times during the cure will be influenced various parameters according to the reaction mechanism, and the exact nature of this molecular network will determine the system properties. A clear

understanding of this network structure, which would allow further improvements in fracture properties of epoxy network to microscopic analysis methods. Various indirect approaches, such as the measurement of glass transition temperature, liquid absorption characteristics, or crosslink density of cured resins, have been followed as a means of characterizing network structure. These approaches have generally not been able to provide adequate information about the true network structure. Recently, the analysis of reaction mechanisms and cure kinetics, which determine the parameters of network formation during cure, have attracted much interest. A Differential Scanning Calorimetry (DSC) technique has been used frequently to investigate the cure kinetics of tetraglycidyl diaminodiphenylmethane (TGDDM) or diglycidyl ether of bisphenol A (DGEBA) epoxy resins cured with DDS<sup>5</sup>. However, DSC gives overall cure kinetics only. In addition, solid state <sup>13</sup>C NMR<sup>6</sup>, and Fourier Transform Infrared Spectroscopy (FTIR)<sup>7</sup> have also been used within their applicable ranges for

\* Dept of Polymer Engineering, Chungju National Univ., Chungju, Chung-Buk, 380-702 Korea

analyzing cure reactions of epoxy resins. The epoxy group consumption has been used mainly as a parameter indicating the overall conversion of the curing system in these infrared studies.

In this study, the near infrared technique is used to quantify the progress of individual chemical reactions occurring during the cure of stoichiometric DGEBA/DDS epoxy resin formulation and the various properties of the system as a function of cure temperature are investigated.

## 2. EXPERIMENTAL PROCEDURES

### Materials and Apparatus

The epoxy resin used in this study was the diglycidyl ether of bisphenol A (DGEBA; Epikote 8283, Shell chemicals,  $M_n=380$ , liquid) and the amine curing agent was 4,4'-diaminodiphenyl sulfone (DDS; Anchor chemicals,  $M_n=248$ , powder). The infrared apparatus employed in this study was an Alpha Centauri FTIR Spectrophotometer (Mattson Instruments Inc, USA) for recording near infrared absorption spectra in the region from 11000 to 4000 $\text{cm}^{-1}$ . The operating conditions for obtaining the spectra involved 32 scans at a resolution of 8 $\text{cm}^{-1}$ . Samples of 18-25mg were used to measure the glass transition temperatures ( $T_g$ 's) on a Mettler differential scanning calorimeter (DSC) at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . Water uptake was measured gravimetrically after immersing the samples in liquid at 80  $^{\circ}\text{C}$  for 14 days. The mechanical tests for obtaining fracture toughness values were carried out on a testing machine (Instron 4505) with a crosshead speed of 1.0mm/min at room temperature. Small compact tension specimens (15.8 x 15.2 x 10mm) were precracked by inserting a thin razor blade into the machined notch and impacting with a small hammer.

### Sample preparation

The intimate mixtures of DGEBA and DDS in stoichiometric ratio, based on the functionality of the two monomers, were prepared in a rotary evaporator under vacuum condition starting from a temperature of 80  $^{\circ}\text{C}$  and finishing at 120  $^{\circ}\text{C}$ . In order to minimize chemical reaction between the monomers during the mixing process, the heating time was limited to less than 30 minutes. The flask was rotated at a constant speed during the process. When the temperature reached 120  $^{\circ}\text{C}$ , the mixture became a clear transparent solution. At that point set volumes of the mixtures were cast into aluminum foil cups to form disks of about 15mm diameter and 2mm thickness. The samples were placed in an air oven at two different temperatures, 130  $^{\circ}\text{C}$  and

205  $^{\circ}\text{C}$  for various intervals so that different degrees of cure were achieved. Samples prepared in this way were used for the near infrared studies without further machining or preparation.

For the preparation of the samples for measuring properties the mixtures were poured into a Teflon mold and cured at different isothermal temperatures ranging from 160 to 240  $^{\circ}\text{C}$ . The cure time was standardized at 6hrs. This length of time has been reported as sufficient to vitrify the resin even at the lowest cure temperature of 160  $^{\circ}\text{C}$ .

## 3. RESULTS AND DISCUSSION

### Reaction mechanisms in a stoichiometric DGEBA/DDS formulation

The epoxy group conversions increased almost linearly up to gelation (166min at 130  $^{\circ}\text{C}$  and 141min at 205  $^{\circ}\text{C}$ ) and slowed down afterwards due to an increase of the system viscosity and depletion of reacting species. The maximum conversions, 89% at 130  $^{\circ}\text{C}$  and 100% at 205  $^{\circ}\text{C}$  were achieved at and ahead of vitrification (325min at 130  $^{\circ}\text{C}$  and 141min at 205  $^{\circ}\text{C}$ ) respectively. The consumption of the primary amine group against epoxy group conversion showed that most of the primary amine groups were consumed by reaction with epoxy groups well before gelation (65% conversion of epoxy group). It is noteworthy that the consumption of the primary amine during cure for two different temperatures, 130  $^{\circ}\text{C}$  and 205  $^{\circ}\text{C}$ , follows exactly in the same path (against epoxy group conversion). This observation indicates that at least the reaction between epoxy and primary amine groups is not affected by cure temperature. We believe this is due to the fact that the system viscosity, determining the mobility of the reactant species in the curing system, is low enough even at low temperature for autocatalytic reaction up to the gel point, at which point the epoxy-primary amine reactions are already exhausted. Meanwhile the secondary amine group is produced by the reaction between epoxy and the primary amine groups, and consumed by the reaction with another epoxy group to produce tertiary amine group. The concentration of the secondary amine group in the system increases to reach its maximum value at about 50% conversion due to the high reaction rate of the primary amine group compared to that of the secondary amine group in the early stage of the cure. At the transition point (at 50% conversion) the rates of production and consumption of the secondary amine groups are equivalent, or in other words, the rates of reaction of the primary and the secondary amine groups are similar. Above the transition point the rate of reaction of the secondary amine becomes higher than that of primary amine.

The conversion of the secondary amine group was calculated from the production of the tertiary amine group. It is noteworthy that 88% of the primary amine groups are converted to the secondary amine groups at the 50% transition point, whereas only 13% of the secondary amine groups have reacted with epoxy groups and converted to tertiary amine groups, showing that the reaction between epoxy and secondary amine starts only when most of the primary amine groups are consumed. The reaction is considered to be diffusion controlled due to the rapid increase of the system viscosity after gelation. The secondary amine conversion at the 130 °C and 205 °C cure temperatures are not noticeably different from each other, a similar match of the conversion curves as is seen in the primary amine group conversion. But with the 130 °C cure, a considerable amount of the secondary amine species remained unreacted, similar to what was observed in the conversion of epoxy group.

In the study of reaction mechanisms the occurrence of the side reactions has been an interesting subject in that these affect the formation of the network structure and final properties of the network. In recent publications, it was reported that side reactions occur only in the presence of the catalyst in DGEBA/DDS resin system<sup>8</sup> while it was observed even in noncatalytic environment in TGDDM/DDS resin system<sup>9</sup>. But the reasons for the occurrence of side reactions are not clearly understood. In our stoichiometric DGEBA/DDS system, the side reactions, which we expect to be mainly the etherification reaction and the epoxy group homopolymerization, could be detected by monitoring the relationship between the conversions of epoxy and amine groups during cure. Based on the assumption that the amine group is consumed only by the reaction with an epoxy group, the following relationship can be established when the ideal reactions occur only:

$$\alpha_{EPt} = \alpha_{At} = (\alpha_{PA_t} + \alpha_{SA_t}) / 2$$

where  $\alpha_{EPt}$  is the conversion of epoxy group at time  $t$ ,  $\alpha_{At}$  is the conversion of the amine group at time  $t$ ,  $\alpha_{PA_t}$  is the conversion of the primary amine group at time  $t$  and  $\alpha_{SA_t}$  is the conversion of the secondary amine group at time  $t$ . Any deviation from this relationship would suggest the occurrence of side reactions in the system. Up to the transition point (the onset of gelation) we see greater conversion of amine groups than that dictated by the ideal reactions as defined by above equation. This trend is reversed for conversions above the transition point. Meanwhile for the 130 °C cure 89 % of epoxy group and 80% of amine group were consumed whereas 100% of epoxy and amine groups were consumed at the 205 °C cure. The excess 9% conversion of epoxy group at 130 °C can be treated as the amounts converted by the side reaction. The side reaction observed at low temperature cure may attribute to the higher system viscosity especially after gelation which will reduce the

mobility of reactant chains and finally allow the low possibility of side reactions which will occur between nearby unreacted species. It was not possible to distinguish between the two likely side reactions in this study due to insufficient information about the hydroxyl group concentrations. The appearance of a broad hydrogen bonded hydroxyl group banded hydroxyl group band in the infrared spectrum prevents accurate hydroxyl measurement.

### Thermal and Mechanical Properties

The data of thermal and mechanical properties obtained as a function of cure temperature are presented in Table 1. The glass transition temperature ( $T_g$ ) increases linearly with increasing cure temperature, and then tend to level off from the cure temperature of 200 °C, approaching their maximum glass transition temperature (209 °C). Since the cure time is fixed at 6hr for all samples, the variation in  $T_g$  observed here can be taken as a consequence of (i) the extent of cure resulting from varying the cure temperature, or (ii) network topology and the associated free volume, or (iii) both of the effects combined.

Table 1. The data of  $T_g$ , water uptake and fracture toughness of DGEBA/DDS resin systems, cured at different temperatures.

Cure temp. (°C)	$T_g$ (°C)	Water uptake (%)	$G_{Ic}$ (J/m <sup>2</sup> )
160	169	2.48	96
170	170	2.38	106
180	188	2.45	129
190	194	2.54	147
200	202	2.63	186
220	208	2.80	221
240	209	3.01	213

The water uptake data obtained in this study, shown in Table 1 increases with increasing cure temperature. This result implies that the highly crosslinked systems, cured at higher temperatures, contain greater free volume.

The fracture toughness is also strongly dependent on cure temperature. At cure temperatures over 200 °C the toughness values tend to level off. This tendency was also observed in  $T_g$  although its dependence on cure temperature was not as strong. Here we can derive an important proportional relationship between the fracture toughness and the crosslink density. This proportional relationship of fracture toughness with crosslink density is quite unusual and contrary to most reported results obtained under conditions of varying reactant ratio or varying molecular weight of epoxy prepolymers<sup>10</sup>. The workers reported

that the crack initiation fracture toughness values decreased with increasing crosslink density. This different result obtained by us using slightly different parameters implies that the crosslink density is not always a strong determining factor for fracture toughness but that the other structural parameters such as free volume, chain flexibility, and the degree of intermolecular packing are more likely to be responsible.

#### 4. CONCLUSIONS

Near infrared spectroscopy was used for quantitative analysis of cure reactions in a stoichiometric DGEBA/DDS resin system. The work has shown that the quantitative analysis of chemical groups during the cure, using near infrared spectroscopy can let us understand reaction mechanisms and further estimate network structure of the system. The experimental data for stoichiometric DGEBA/DDS formulation has confirmed a straightforward reaction mechanism in the formulation. Side reactions were not observed at high temperature cure while at low temperature cure 9 % of epoxy groups were consumed by the side reactions. The high system viscosity found in such a low temperature cure, especially after gelation, was considered as a major factor for the occurrence of the side reaction. As we consider that 130 °C is a rather low temperature to be employed in practical (uncatalyzed) cures of DGEBA/DDS, we can conclude that this side reaction is not significant in a stoichiometric DGEBA/DDS system.

The  $T_g$ , water uptake and fracture toughness increased with increasing cure temperature and the tendency observed in fracture toughness values were interpreted in terms of structural parameters.

#### REFERENCES

- (1) L. T. Manzione and J. K. Gillham, *J. Appl. Polym. Sci.*, **26**, 907 (1981).
- (2) A. F. Yee and R. A. Pearson, *J. Mater. Sci.*, **21**, 2462 (1986).
- (3) A. C. Moloney, H. H. Kausch and H. R. Stieger, *J. Mater. Sci.*, **18**, 208 (1983).
- (4) Z. Fu and Y. Sun, *Polym. Prepr.*, **29**(2), 177 (1988)
- (5) G. Wisanrakkit and J. K. Gillham, *J. Appl. Polym. Sci.*, **41**, 2885 (1990).
- (6) A. J. Attias and B. Bloch, *J. Polym. Sci. part A.*, **28**, 3445 (1990).
- (7) X. Wang and J. K. Gillham, *ACS, PMSE Proc.*, **63**, 305 (1990).
- (8) A. Sabra, T. M. Lam, J. P. Pascault, M. F. Grenier-Loustalot and P. Grenier, *Polymer.*, **28**, 1030 (1987).
- (9) N. A. St. John and G. A. George, *Polymer.*, **33**, 2679 (1992).
- (10) G. Levita, S. D. Petris, A. Marchetti and A. Lazzeri, *J. Mater. Sci.*, **26**, 2348 (1991).