

## Epoxy-siloxane IPN의 열적 안정성에 미치는 후기경화의 영향

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### Effects of Post-curing on Thermal Stability of Epoxy-siloxane IPN Structure

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**Abstract** - The thermal stability of the post cured epoxy-polysiloxane IPN structure was observed by using DSC and TGA. As the post curing time increased the glass transition temperature increased and the secondary exothermic peak disappeared. The thermally decomposing activation energy calculated by using Kissinger expression was 225.6 kJ/mol. The thermal stability of the grafted IPN of epoxy and silicon compound depends on the composing ratio and post curing conditions of time and temperature.

#### 1. Introduction

Plastics are inherently nonconductive and are useful for the application of electrical insulation [1]. Epoxy resin is one of the superior material being used under the harsh conditions of high thermal and mechanical stresses. The epoxy resin which has the well combined properties has been considered as the best candidate of electrical insulation under several kinds of environmental stresses [2-4]. The epoxy resins, however, should be incorporated with several kinds of additives and fillers depending on the using conditions. The conventional epoxy resin was too vulnerable to the impact stresses for the uses of base material because of its high density of cross-link. We have modified the epoxy resin by adding reactive additives of nitriles and rubber compounds. But the thermal stability of the modified epoxy resin system, as it was prophesied, decreased and the results restricted the application of the modified epoxy resin system. In this study we focused on the interpenetration network of epoxy resin and silicon compounds. We grafted the epoxy resin matrix and silicone component of poly dimethyl silicon as a reactive reagent [5]. The

polysiloxane has superior flexibility and thermal stability so that the IPN can be used for the HV electrical insulating component. But the thermodynamic incompatibility was one of the serious problems for the application [6-8]. The graft resin and the functional group terminated dimethyl polysiloxane (PDMS) was crosslinked with MDA. The sample was examined by using DSC and TGA. The effects of post curing time and temperature on the glass transition temperature and the thermally decomposing reaction kinetics parameters of decomposition activation energy are discussed.

#### 2. Experiment

##### 2-1. Materials

DGEBA(diglycidyl ether of bisphenol A, Epon 828 grade) with an EEW(epoxy equivalent weight) of 188 g/mol was dried under vacuum oven at 70°C for 12 hrs. PDMS (poly dimethyl siloxane- $\alpha,\omega$ -diol) was obtained from Dow Chemical Company and its Mn(number average molecular weight) was 2130 g/mol. TDI (Tolylene-2,4-diisocyanate) was received from Sigma-Aldrich and used as a chain extender. MDA(4,4'-methylene dianiline) was used as curing agent. Tin with powder type was used as a reaction catalyst.

##### 2-2. Specimen preparation

TDI and Tin were mixed with DGEBA and the mixture was stirred at 35°C for 5 hrs under N<sub>2</sub> gas. When the urethane reaction between TDI and secondary OH- group of DGEBA occurred, PDMS was mixed with the mixture at 65°C and stirred for 12 hrs. The mixture was reacted with dry ethanol for the unreacted NCO groups to be disappeared. MDA was mixed with the copolymer precursor. The mixture was

poured into the mould and 1st cured at 120°C for 12 hrs and then post-cured at 160°C for 12 hrs.

### 2-3. Tests

DSC and TG curves of the specimen were obtained by using Solomat DSC calorimeter and ATI Cahn 121 TGA at various heating rates, respectively. 5~6 mg of the specimen was heated at 10 °C/min under the nitrogen atmosphere of 100 ml/min.

### 3. Results and Discussion

Fig. 1 shows the DSC curves of the graft-copolymer. When the reacting mixture was heated, it was cured from 80°C and the most rapidly curing temperature or peak temperature was 150°C. When the system was 1st cured, the glass temperature was 120°C and there was a secondary exothermic peak higher than 200°C. The non-reacted functional groups which was diffusion controlled was cured under the elevated temperature. The peak temperature was 223°C. When the system was post cured at 160°C for 12 hrs the glass transition temperature reached 146°C and there was no secondary exothermic peak.

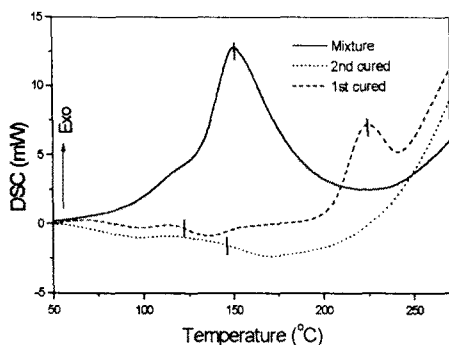


Fig. 1. DSC curves of IPN post cured at 160°C.

Fig. 2 shows the dynamic TG curves of the DGEBA/PDMS IPN structure at the different heating rates of 2, 7 and 20 °C/min. As the heating rate increased, the TG curves shift to right. By using the differential TG(DTG) curves, the thermal decomposing reaction kinetics parameters can be obtained. From the DTG peak temperature, the cure reaction

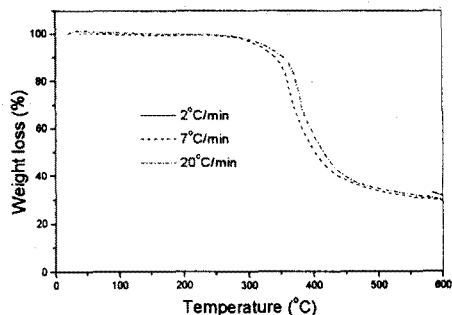


Fig. 2. TG curves of post cured DGEBA/PDMS IPN structure at different 3 heating rates (2, 7 and 20 °C/min).

activation energy and pre-exponential factor are obtained by using the following Kissinger expression, which is

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{R} \cdot \frac{1}{T_p} - \ln \frac{AR}{E_a}$$

where,  $\beta$  : heating rate,  $T_p$  : temperature at the peak value of the DTG curve,  $E_a$  : thermally decomposing activation energy,  $A$  : pre-exponential factor,  $R$  : gas constant. A plot of  $-\ln(\beta/T_p^2)$  as a function of  $1/T_p$  gives activation energy from the slope of the straight

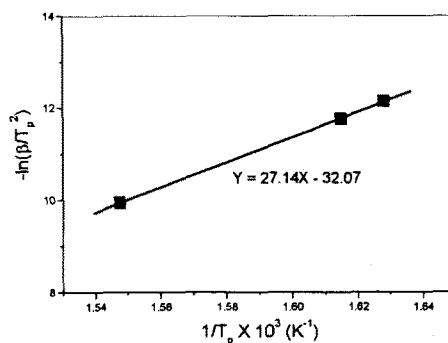


Fig. 3. Plot of  $-\ln(\beta/T_p^2)$  vs.  $1/T_p \times 10^3$  by Kissinger equation for DGEBA/MDA/TDI/PDMS system.

line as shown in Fig. 3.

The Plot of  $-\ln(\beta/T_p^2)$  vs.  $1/T_p \times 10^3$  according to the Kissinger expression showed good linear relationships. The activation energy and pre-exponential factors can be obtained

from the slope and the y-interception, respectively. The thermally decomposing activation energy was 225.6 kJ/mol from the slope of 27,140. The detail things will be shown in the presentation.

#### 4. Conclusions

The thermal stability of  $T_g$  and thermal decomposing reaction activation energy of the post cured DGEBA/PDMS IPN structure was observed by using DSC and TGA. As the post curing time increased, the  $T_g$  increased and the secondary exothermic peak was not observed. The thermally decomposing activation energy was calculated by using Kissinger equation and it was 225.6 kJ/mol. The thermal stability of the grafted IPN between epoxy resin and silicon compound depends on the composing ratio and post curing conditions of time and temperature.

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