

Thermal Properties of Interpenetrating Polymer Network Epoxy-silicone Compound

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Abstract

The thermal properties of epoxy resin/siloxane for the electrical insulation were investigated by using dynamic DSC run method. As the heating rate increased, the peak temperature on dynamic DSC curve increased. From the linear relation on the Kissinger plot, the curing reaction activation energy and pre-exponential factor could be obtained. The curing activation energy from the straight line of the Kissinger plot was 46.72 kJ/mol.

Key Words : Electrical insulation, Epoxy resin, Siloxane, Interpenetrating network

1. Introduction

Epoxy insulation which has a good combination of electrical, mechanical and thermal properties has been applied to the various electrical insulating compounds. But the fracture toughness, flexibility and impact strength of epoxy resin system should be modified for the application of HV insulation because of its high density of cross link. We have studied on the modified epoxy resin by adding new reactive nitrile additives of MN, SN, GN. But the thermal stability of the modified epoxy resin decreased and the application of the system for the HV application was restricted. So that we focused on the interpenetration network of epoxy resin and another compounds.^{1,3)} In this study, we attempted to graft the epoxy resin matrix and silicone compound as a reactive reagent.⁴⁾ 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. The graft

resin and the functional group terminated dimethyl polysiloxane (PDMS) was crosslinked with MDA. The sample was examined by using DSC. The curing kinetics and the thermal properties were discussed by using kinetic expression.

2. Experiment

2-1. Materials

The epoxy resin used in this study was 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. The bifunctional modifier PDMS (poly dimethyl siloxane- α, ω -diol) designated as SF-8427 was provided from Dow Chemical Company and its Mn(number average molecular weight) was 2130 g/mol. The chain extender TDI(Tolylene-2,4-diisocyanate) was received from Sigma-Aldrich. MDA(4,4'-methylene dianiline) used as curing agent was from Fluka Chemie AG. Sn(Tin, powder) was used as a catalyst. The chemical structures of experimental reagents are shown in Fig. 1.

2-2. Specimen preparation

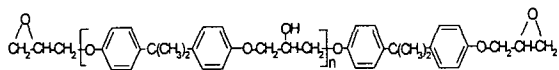
TDI and Sn were mixed with DGEBA and the mixture was stirred at 35°C for 12 hr under N₂

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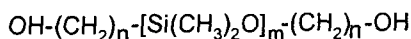
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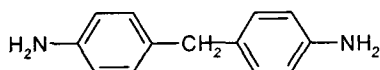
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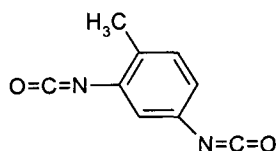
DGEBA



PDMS



MDA



TDI

Fig. 1. Chemical structures of experimental materials.

gas ambient to allow the urethane reaction between TDI and secondary OH- group of DGEBA to occur. PDMS was then mixed with the mixture at 65°C for 12 hr to ensure complete reaction. The mixture was reacted with dry ethanol for the unreacted NCO groups to be removed and then degassed under vacuum oven before casting. MDA melt at 120°C was mixed with the copolymer. The mixture was poured into the mould at 120°C and 1st cured for 12 hr and then subsequently cured at 160°C for 12 hr.

2-3. Tests

DSC curves of the mixture were obtained by using Solomat DSC calorimeter at various heating rates. To study the cure kinetics by dynamic DSC analysis, 5~6 mg of the mixture was placed on DSC Al pan and DSC analysis was performed at the heating rates of 3, 5, 10 and 20 °C/min. It was carried out under the nitrogen

atmosphere of 100 ml/min flowing rate to prevent the thermal oxidation process during the cure reaction at high temperature.

3. Results and Discussion

Fig. 2 shows the interpenetrating network structure of 2 polymers which are chemically blended. The two networks share the same region of space. The biggest problems in the IPN structure is the phase separation by the thermodynamic incompatibility.⁵⁻⁷⁾ When the two polymers are incorporated in the networks the morphology is controlled by the density of cross link. So that the combination of the superior properties between two polymer is possible. The resulting IPN polymer blend shows the improved mechanical properties, flammability resistance, weatherability, flexibility and chemical resistance. All the modified properties are required for the application of the electrical insulation.

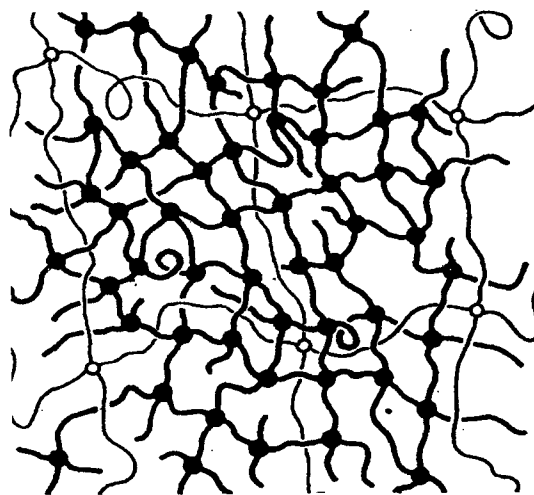


Fig. 2. IPN(interpenetration network) structure of the 2 polymers.

Fig. 3 shows the dynamic DSC curves of the DGEBA/PDMS IPN structure at the different heating rates of 3, 5, 10 and 20 °C/min. As the

heating rate increased. The cure reaction of epoxy resin composite system took place rapidly in a short time, so the peak heat flow and exothermic peak temperature increased. Each curve shows only one exothermic peak below 250 °C due to primary amine-epoxide reaction, secondary amine-epoxide reaction, catalytic reaction and epoxy-hydroxyl reaction.

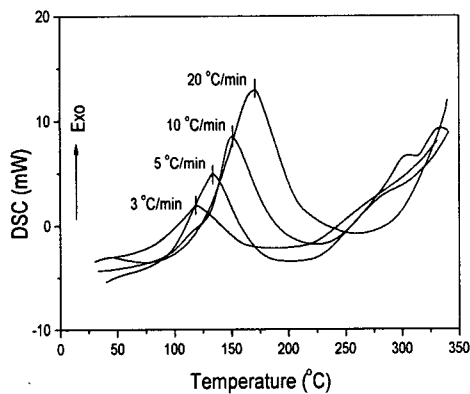


Fig. 3. DSC curves of DGEBA/PDMS IPN structure at various heating rates by dynamic DSC run method under N₂ inert gas condition.

From the DSC peak data on Fig. 3, the cure reaction activation energy and pre-exponential factor are obtained by using Kissinger expression, which is

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

where, β : heating rate, T_m : temperature at the peak value of the DSC curve, E_a : cure reaction activation energy, A : pre-exponential factor, R : gas constant. A plot of $-\ln(\beta/T_m^2)$ as a function of $1/T_m$ gives activation energy from the slope of the straight line as shown in Fig. 4.

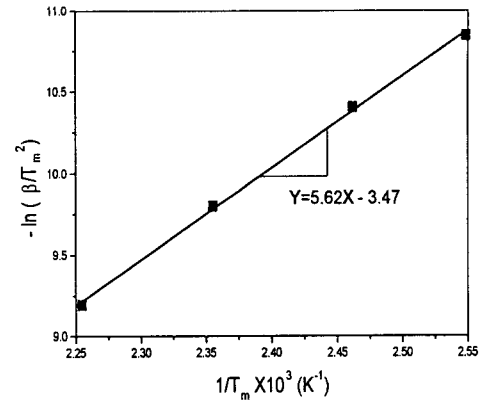


Fig. 4. Plot of $-\ln(\beta/T_m^2)$ vs. $1/T_m \times 10^3$ by Kissinger equation for DGEBA/MDA/TDI/PDMS system.

The activation energy and pre-exponential factors can be obtained from the slope and the y-interception, respectively. The thermally curing activation energy was 46.72 kJ/mol.

The thermal properties of epoxy resin composite system depend on the mixing ratio of the components and curing conditions. So the effects of curing conditions and mixing ratio on the thermal properties of epoxy-silicon IPN compounds are proceeding and the results will be presented in the next paper.

4. Conclusions

The cure characteristics of DGEBA/MDA/TDI/PDMS IPN polymer system for HV insulation were investigated by dynamic DSC run method and the following conclusions were obtained. As the heating rate increased, the DSC peak temperature increased because of the rapid cure reaction. The curing reaction activation energy from the straight line of the Kissinger plot was 46.72 kJ/mol.

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