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Thermal Properties of DGEBA/MDA/SN/zeolite System Degraded by Moisture Absorption

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Abstract

Cured epoxy resins are extensively used for the electrical insulation in high-voltage equipments. The bisphenol A-based epoxy resins cured with amine show, especially, good thermal properties and mechanical resistances. For the technical and economic reasons, varing amount of inorganic fillers are added to endow the required special properties. In the large generators and motors of power plants, epoxy insulation is disclosed to the harsh conditions like the superheated steam and abrupt temperature variation. Hygrothermal aging at elevated temperatures tends to induce degradation in epoxy resins. To predict the effect of this degradation in DGEBA/MDA/SN/zeolite system, we proceeded the forced moisture absorption experiment using the autoclave. The thermal properties of the untreated and treated specimens were analyzed by DSC and TGA under the nitrogen flowing condition. The moisture absorption results showed a weight increase during hygrothermal aging at 120℃. At the initial aging period, the system leaded to more or less postcuring but more prolonged environmental aging leaded the discoloration of specimen and lowering the T_g.

Key Words : Epoxy resin, Zeolite, Composite, Electrical insulation, Moisture absorption, Thermal properties.

1. Introduction

The epoxy resins which have the good combined characteristics of thermal and mechanical properties are used as various types of impregnation, molding, casting, etc. Epoxies can be found in applications ranging from high performance aerospace composites to encapsulants for the microelectronics industry. All insulating materials and systems absorb moisture from the surrounding environments. The rate of absorption of moisture is governed by the nature of material and the difference in water vapour pressure inside and outside the insulation. The absorption of moisture plasticizes the matrix, induces differential swelling stresses, and generally degrades the physical properties. Considerable quantities of research have focused on this problem of moisture in epoxy, yet the exact molecular details of the transport process still remain vague.[1,2]

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The mechanism of moisture absorption is explained by diffusion process.[3] Over the years, a few aspects of the moisture transport process in epoxy have become clear. The most significant development is realizing the role of polarity in determining the ultimate moisture uptake.[4-6] Typically, primary or secondary amines are used as the reactive species in the curing agent to open the glycidal rings of an epoxide, thus creating a hydroxyl group. This incorporates both the hydroxyl and the amine into the covalent network. Water is a polar molecule and capable of hydrogen bonding with other polar species such as hydroxyls and amines.[5,6] In this study, to predict the effect of this degradation in DGEBA/MDA/SN/zeolite system, we proceeded the forced moisture absorption experiment using the autoclave. The thermal properties of the untreated and treated specimens were analysed by DSC and TGA under the nitrogen flowing condition. The moisture absorption results showed a weight increase during hygrothermal aging at 120℃. At the initial aging period, the system

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2. Experiment

2-1. Materials

The epoxy resin used in this study was DGEBA(Epon 828 grade) of Shell Co. and its EEW, MW and viscosity were 188 g/mol, 385 g/mol and 11,000-14,000 cps, respectively. 30 phr (parts per one hundred resin by weight) of MDA was used for curing the resin. SN(10 phr) as a new reactive additive was supplied from Fluka Chemie AG. Natural zeolite(clinoptilolite type) from Kampo area in Korea[7] was used in 60 phr content after sieving with #270 mesh and drying in 120℃ vacuum oven for 5 hrs. The average diameter of zeolite particle was 64.86 ㎛. Fig. 1 shows the particle size distribution of natural zeolite used in this study.

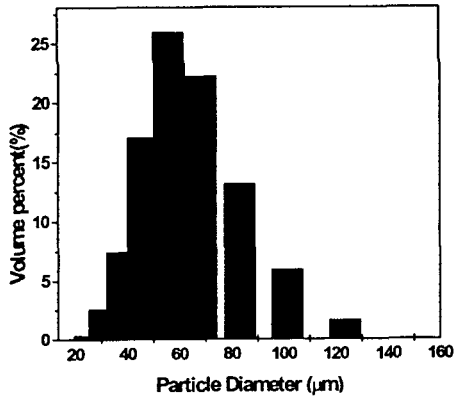

Fig. 1 The particle size distribution of natural zeolite.

2-2. Specimen preparation

DGEBA and SN(10 phr) were well mixed with dried natural zeolite(60 phr) at 80℃, then MDA(30 phr) was added to the mixture. The mixture was cured on the plate mold at 150℃ for 1 hr after curing at 80℃ for 1.5 hr. After curing it was sliced to the test specimen with dimension of 10(W) × 20(L) × 2(T) mm. Before moisture absorption, samples were dried in a vacuum oven at 80℃ for 2 hrs and weighed to ㎍ scale. The weight of dry resin was then recorded as the initial weight of the resin(W_0).

2-3. Forced moisture absorption experiment

The samples were then placed in the autoclave filled with saturated steam at 120℃. After 1 hr, samples were taken out, dried superficially, and then weighed. After 1 hr drying in room condition, the samples were placed again in an autoclave. This procedure was set as a cycle. It was proceeded to 7th cycle. Drying was continued at the room temperature and samples periodically weighed.

2-4. DSC analysis

The cured sample(5~7 mg) was tested by DSC. The temperature rising rate was 10 ℃/min and nitrogen gas was flowed into the furnace at 80 ml/min. T_g was detected from the base-line shift on DSC curve. T_g of moisture absorbed sample was compared with untreated sample.

2-5 TG analysis

Treated and untreated specimens were analysed by TGA. The rate of temperature rising was 10 ℃/min, and N_2 gas flow rate was 50 ml/min.

3. Results and Discussion

3-1. Moisture absorption properties

The absorption rate of epoxy resin was obtained by using the following equation

$$absorption\ rate = \frac{W - W_0}{W_0}$$

where, W: the weight of specimen after treat. W_0: the initial weight of the cured resin. Fig. 2 shows the absorption rate of epoxy composite filled with zeolite and without zeolite at various cycle.

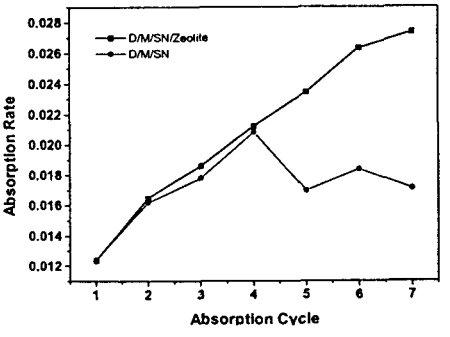

Fig. 2 Moisture absorption rate of epoxy composite filled with and without zeolite.

Zeolite particle has a hygroscopic property and absorbing serious amount moisture when it is opened to the atmosphere. As shown in Fig. 2, weight of epoxy composite with zeolite particle increased with increasing the cycle. In other words, the zeolite absorbed the water molecules which penetrate through the epoxy resin and take part a role of decreasing the electrical properties. Otherwise, in the case of composite without zeolite, the absorption rate increased initially and saturated abruptly afterwards. However, the absorption was not accompanied by any visible damage to the material except discoloration of the specimen. The molecules of a polymer crystal pack together very compactly, and leave very little room for the moisture to be penetrated into the molecule. Consequently, crystalline polymers absorb very little water. In polymer glasses, such as epoxy, the packing is far less efficient, and there is ample room for a small penetrant molecule, such as water and gases, to occupy[2].

3-2. DSC analysis

To compare T_g of hygroscopic and thermally degraded specimen with that of undegraded specimen, we performed the DSC analysis. Fig. 3 shows the thermograms of the hygrothermally degraded and undegraded specimen. Degraded specimen was treated for 7 cycles in an autoclave.

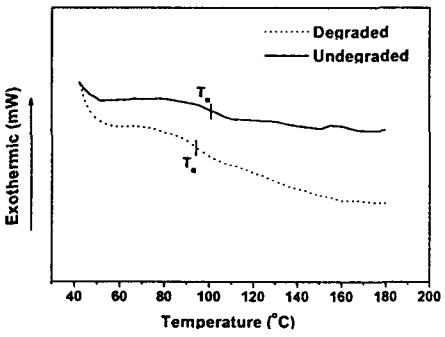

Fig. 3 The comparison of T_g between the degraded and the undegraded specimen.

The hygrothermal aging caused the decrease of glass transition temperature. In the thermogram of degraded specimen, the continuous endothermic behavior above T_g was shown. It is thought that the water molecules absorbed by epoxy resin and zeolite particles need the heat to evaporate by the temperature rising. The T_g of the degraded epoxy composite filled with natural zeolite depends on the deterioration cycle under the high thermal stresses and the high moisture containing environment. The effects of moisture absorbing cycle on the glass transition temperature of the system is shown in Fig. 4. As the absorption cycle increased, the T_g decreased step by step. The gap between 7 time deteriorated sample and pure specimen was about 10℃. So that it is clear the absorbed moisture under high thermal stress decreases the thermal properties of the zeolite filled epoxy composite.

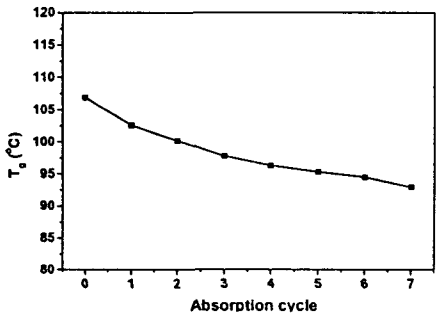

Fig. 4 T_g with absorption cycle

3-3. TG Analysis

The above discussion is very clear in the TG analysis. Fig. 5 is the thermogravimetric weight loss of the hygrothermally degraded and undegraded epoxy composite filled with zeolite particles. Degraded epoxy composite was the sample deteriorated by 7 cycles. Degraded epoxy composite shows the more decrease of weight above 100℃ to 350℃ than the undegraded

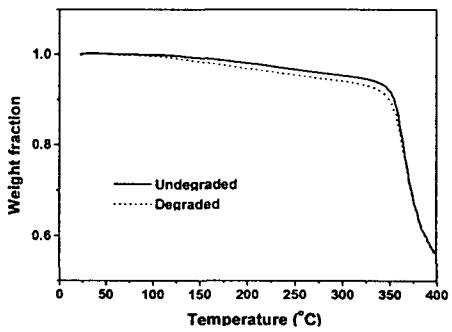

Fig. 5 TG analysis of the degraded and undegraded specimen

composite. This initial weight loss indicates the desorption of moisture exisisted in the resin matrix and zeolite particles. The moisture at the surface of the bulk state sample may increase the dielectric constant and decrease the dielectric breakdown strength. Also the physical defects such as cracks and micro voids can affect the dielectric properties of electrical insulation filled with natural zeolite. All the concerned results will be presented in the next paper.

4. Conclusions

The effects of moisture absorbing deteriorated epoxy resin composite with natural zeolite under high thermal stress on the thermal properties were observed by using DSC and TG and the followings were concluded. The moisture absorption results showed a weight increase during hygrothermal aging at 120℃. The prolonged environmental aging under high humidity and temperature leaded the discoloration of specimen and lowering the T_g. The absorbed moisture was detected by TG thermogram. The moisture may be considered as the defects in the dielectric properties of natural zeolite filled epoxy resin system.

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