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DGEBA/MDA/SN/천연 제올라이트계의 절연파괴현상에 미치는 흡습의 영향

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Effect of Moisture Absorption on Dielectric Breakdown Phenomena of DGEBA/MDA/SN/Natural Zeolite System

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Abstract - Hygrothermal aging at the elevated temperature induces the long-term degradation of the epoxy resin. We investigated the effects of hydrothermal stress on the dielectric breakdown phenomena of epoxy composite filled with natural zeolite. The cured specimens absorbed the moisture in the autoclave at 120 ℃. T_g of the deteriorated composite by moisture absorption decreased. The dielectric breakdown strength decreased with the moisture absorption cycle. It was concluded that the thermal stress and the high water-vapour-pressure deteriorated the natural zeolite filled epoxy resin system, consequently and the tree growth rate increased.

1. Introduction

Epoxy resin composites have been used in the field of electrical insulation like power generator and electrical distribution equipment. They are used in the harsh conditions where the high thermal stress, the high humidity, and many outdoor environmental stresses exist. These factors cause the deterioration of epoxy resin matrix and the dielectric breakdown of electrical insulation. But the exact mechanisms of this deterioration is not well defined. Epoxy resin matrix has polar groups, -OH, that relates to the absorption of water molecules. And the epoxy matrix has free volume that make the water molecule to penetrate through the matrix [1,2]. To describe the water absorption process, a diffusion model following Fickian was proposed by G. Z. xiao, et al. [3]. In this study, the dielectric breakdown test and the weighing the mass were conducted to evaluate the effect of zeolite on the moisture absorption and the dielectric breakdown phenomena in the specimens which absorbed water molecules in the autoclave at 120℃.

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 as curing agent. SN(10 phr) as a new reactive additive was purchased from Fluka Chemie AG[4]. Natural zeolite (clinoptilolite type) [5] from Kampo area in Korea was used in 60 phr content after sieving with #270 mesh and drying at 120℃ vacuum oven for 5 hrs. The average diameter of zeolite particle was 64.86 ㎛.

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 mixtures were cured on the plate mold for moisture absorption rate test and in the mold with the needle electrode for the dielectric breakdown test at 150℃ for 1 hr after curing at 80℃ for 1.5 hr, respectively. After curing, it was sliced to the specimen for the moisture absorption rate test with the dimensions of 10(W)×20(L)×2(T) mm and to the needle electrode specimen for the dielectric breakdown test with the dimensions of 35(L)×8(W)×50(H) mm, respectively. Before moisture absorption, samples were dried in a vacuum oven at 80℃ for 2 hrs and weighed to ㎍ scale. The weight of the dried specimen was then recorded as the initial weight of the resin(W_0).

2-3. Forced moisture absorption experiment

The samples for moisture absorption rate test

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 drying for 1 hr in room condition, the samples were placed again in an autoclave. This procedure was set as a cycle. It was proceeded to 7th cycle. The absorption rate of epoxy resin was obtained by using the following equation

$$absorption\ rate(\%) = \frac{W - W_0}{W_0} \times 100$$

where, W: the weight of specimen after treatment. W_0: the initial weight of the cured specimen.

2-4. DSC analysis

The cured sample(5~7 mg) was tested by DSC to investigate the effect of moisture absorption on T_g. 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. Dielectric breakdown test

The needle-plane electrode specimen deteriorated by absorbing water molecules was immersed into the electrical insulating silicon oil to prevent surface flashover under high electrical stress. High voltage of 60 Hz was applied to the specimen until dielectric breakdown at the voltage rising rate of 500 V/sec and the breakdown voltage was measured. The dielectric breakdown step was detected by the breakdown sound or the flashover at the tip of needle electrode.

3. Results and discussion

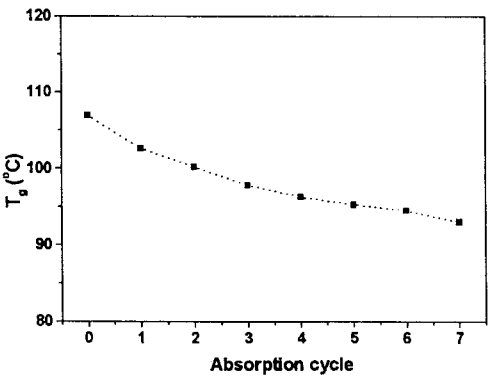

Fig. 1 T_g variation with absorption cycle

The effects of moisture absorbing cycle on the glass transition temperature(T_g) of the system is shown in Fig. 1. 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 it is clear that the absorbed moisture under high thermal stress decreases the thermal properties of the epoxy-zeolite composite consequently, plasticizing the resin.

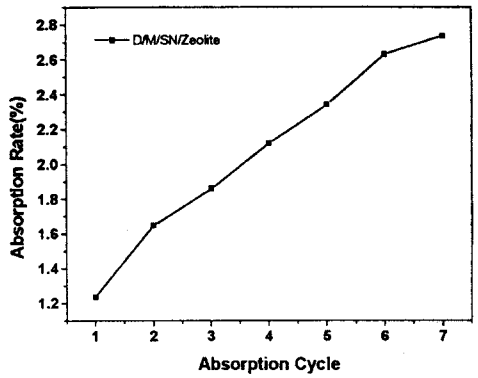

Fig. 2 Moisture absorption rate of epoxy resin composite filled with and without zeolite.

Fig. 2 shows the absorption rate of epoxy composite filled with zeolite at various cycle. Zeolite particle has a hygroscopic characteristics and absorbing serious amount of moisture when it is opened to the atmosphere. As shown in Fig. 2, weight of epoxy composite with zeolite particle increased with increasment of the cycle. In other words, the zeolite absorbed the water molecules which penetrated through the epoxy resin and took part a role of decreasing the electrical properties.

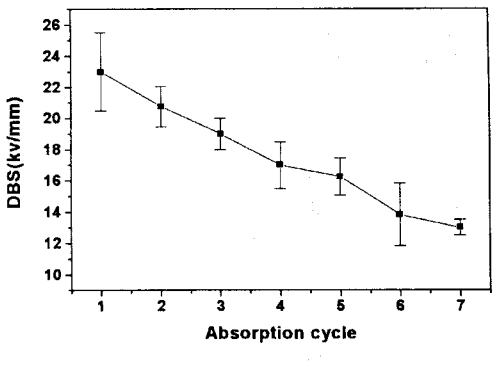

Fig. 3 The dielectric breakdown strength vs. moisture absorption cycle.

Fig. 3 shows the decrease of dielectric breakdown strength by moisture absorption. It is due to the degradation leaded by the attacks of moisture and thermal stress. Tree initiation under high electrical stress is followed by the growth of fine channels driven by partial discharge activity between two electrodes [6]. It grows to be the puncture of epoxy resin.

4. Conclusions

The effects of moisture absorption on dielectric breakdown phenomena of epoxy resin filled with zeolite were observed by using DSC and dielectric breakdown test 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 to degradation of specimen and lowering the T_g. The absorbed moisture lowered the dielectric breakdown strength. The moisture acts as the defects in the dielectric properties of natural zeolite-filled epoxy resin system.

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