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Effect of Amino Silane Coupling Agent on the AC Electrical Breakdown Phenomena of Epoxy/Layered Silicate Nanocomposite in Needle-plate Electrodes

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The effects of amino silane coupling agent on the AC electrical treeing and breakdown behaviors in an epoxy/layered silicate (1 wt%) were examined in needle-plate electrode geometry. A layered silicate was exfoliated in an epoxy base resin by using our AC electric field apparatus. To measure the tree initiation and propagation and the breakdown rate, an alternating current (AC) of 10 kV (60 Hz) was applied to the specimen in needle-plate electrode arrangement with a 30℃ insulating oil bath. In the epoxy/amino silane system, the tree initiation time was 11.5 times higher and the breakdown time was 17.9 times higher than those of the neat epoxy resin. The tree initiation time in the epoxy/layered silicate (1 wt%) system with the amino silane was 2.0 times higher, and the breakdown time was 1.5 times higher than those of the epoxy/layered silicate (1 wt%) system.

Keywords: Electrical treeing, Epoxy nanocomposites, Layered silicate, Amino silane coupling agent

1. INTRODUCTION

Multilayered silicates such as montmorillonite, hectorite, mica, etc. have been introduced to polymer matrixes as a nano-sized filler in order to give them some special characteristics such as electrical insulation, modulus, hardness, thermal stability, etc [1-3]. However, they exist as micro-sized multilayered bulk shapes prior to being used in a polymer matrix. Therefore, in order to prepare polymer/layered silicate nanocomposites, they should be separated into nano-sized sheet-like monolayers ose dimensions are 20~1,000 nm (length) × 20~1,000 nm (width) × 1 nm (thick). The driving force to separate them from each other is given by polymer penetration into the intergalleries between the silicate monolayers [4,5]. The polymer chains are presented in the intergalleries forming A coil-like conformation which leads to intercalated or exfoliated nonocomposites [2,3].

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There are five synthetic methods to prepare polymer/layered silicate nanocomposites [6-9]: (1) In-situ polymerization is the conventional process to synthesize thermoset/layered silicate or addition polymer/layered silicate nanocomposites. (2) Direct melt intercalation is a simple process which consists of blending a molten thermoplastic with a layered silicate at a temperature above the glass transition temperature of the polymer. (3) Solution intercalation is carried out in a polar solvent such as toluene or N, N-dimethylformamide. (4) Direct layered silicate method is conducted under the sol-gel process,where molecular level layered silicates are directly synthesized from the clay precursor of gel shape in the polymer solution. And, (5) dispersion and aggregation method consists of the mixing of clay solution and polymer latex. In this study, a new electric field method was used to prepare an epoxy/layered silicate nanocomposite [10,11].

Many suudies have been done on electrical treeing phenomena in order to estimate the insulation characteristics of neat polymers or polymer/filler composites, and it was often been referred to as the most important mechanism for the deterioration of polymeric insulators (e.g. high voltage polymeric cables) [12-14]. The tree growth mechanism is divided into three processes: (1) incubation process, (2) initiation process, and (3) propagation process [15]. When an electrical tree is initiated, it propagates rapidly until breakdown finally occurs. Ideally the initiation time should be delayed and the propagation rate be retarded in order to achieve excellent polymeric insulation materials.

In this study, an epoxy/layered silicate nanocomposite for the insulation of heavy electric equipment was prepared by our electric field method and the effects of amino silane coupling agent on the electrical treeing phenomena were studied in needle-plate electrodes.

2. EXPERIMENTS

2.1 Materials

A commercial DGEBA (diglycidyl ether of bisphenol A) type epoxy resin, YD 128 (Kukdo Chem. Co.) was used. The equivalent weight was 184~190 and the viscosity was 11,500~13,500 cps at 25℃. The curing agent was Me-THPA (3- or 4-methyl-1,2,3,6-tetrahydrophthalic anhydride) whose grade name was HN-2200 (Hitachi Chem. Co.). It is widely used in the field of electric insulation. The accelerator was BDMA (benzyl-dimethyl amine, Kukdo Chem. Co.). The amino silane coupling agent was 3-aminopropyl-triethoxysilane (KBE-903, ShinEtsu Co.). Cloisite® 10 A (Southern Clay Products, Inc., USA) was used as a multilayered silicate, and is a natural montmorillonite modified with 2MBHT (dimethyl-benzyl-hydrogenated tallow quaternary ammonium) as a sort of quaternary ammonium salt. It was also dried at 110℃ for 24 h in a vacuum oven and stored in a desiccator before use.

2.2 Specimen preparation for AC treeing test

To prepare the epoxy/layered silicate nanocomposite, DGEBA (100g) and Cloisite 10 A (1.83 g) were mixed with an ultrasonic homogenizer (20 kHz) for 30 min and put into an AC electric field apparatus as shown in Fig. 1 [11]. An AC electric field was generated by a high voltage (HV) generator in the following conditions; (1) inter-electrode distance: 50 mm,(2) application voltage:11 Kv, (3) frequency: 1 kHz, and (4) application time: 60 min. During the AC application time, epoxy resin penetrated into the interlayer making the layered silicate swollen. And then, the mixture was mixed with THPA (80 g), BDMA (0.9 g), and silane coupling agent (3 g) for 5 min. The weight percent of nano-silicate in the epoxy nanocomposite was 1.0 wt%.

The mixture was poured into a mould with a cavity of 15×15 mm^2 and 30 mm height. A needle electrode was arranged in the mold beforehand at a needle-plate electrodes distance of 2.7 mm, as shown in Fig. 2. Then the mold was cured at 120℃ for 2 hr and postcured at 150℃ for 2 hr, and then it was cooled slowly at a rate of -0.5 ℃/min to room temperature to avoid internal stress. Finally, the opposite-side of the needle electrode in the epoxy specimen was coated with the conductive silver paste. The specimen shape is shown in Fig. 2 [16].

2.3 AC treeing test

To measure the tree initiation and propagation and the breakdown rate, an alternating current (AC) of 10 kV (60 Hz) was applied to the specimen in the needle-plate electrode arrangement in a 30℃ insulating oil bath. It was monitored by a video microscope system (ICS-305B, SOMETECH Inc.). High voltage (HV) was applied by an AC Endurance Voltage Tester (Haefely, Germany) at a rising speed of 1 kV/s until 10 kV and kept at the test voltage until electrical breakdown took place. The tree images were collected every 1 min.

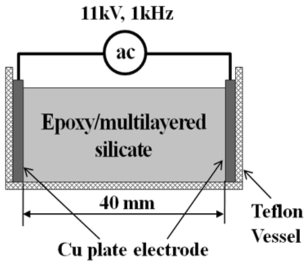

Fig. 1. AC electric field apparatus for nanocomposite [11].

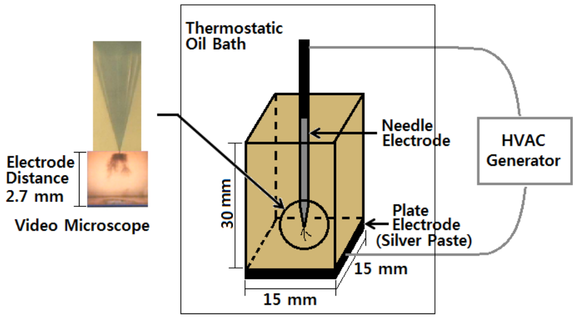

Fig. 2. Arrangement of needle-plate electrode in a specimen [16].

3. RESULTS AND DISCUSSION

In order to study the retarding effect of amino silane coupling agent on the electrical tree behaviors, tree growth rate curves of the neat epoxy with or without the coupling agent were compared, as shown in Fig. 3. When 10 kV was applied to the specimen in needle-plate electrode arrangement, the electrical field at the needle tip, E_{tip}=520.9 kV/mm, was calculated by Masons formula [17], $E_{tip}=2V/(r\cdot\ln(1+4x/r))$, where r is the needle tip radius, 5 μm, V is the applied voltage, 10 kV, and x is the needle-plate distance, 2,700 μm.

In the neat epoxy system, an electrical tree was initiated in 650 min and propagated rapidly at the speed of 6.89 μm/min.

and finally breakdown took place in 1,042 min after applying 520.9 kV/mm. Meanwhile in the epoxy/amino silane system, the tree initiation time in needle-plate electrode geometry was 7,465 min, which was 11.5 times higher, and the breakdown time was 18,616 min, which was 17.9 times higher than those of the neat epoxy resin. The average propagation rate was 0.24 μm/min, which was 28.7 times slower. This implied that the amino silane coupling agent might have acted as a tree retardant.

The morphology of the electrical tree for the epoxy systems with or without amino silane was compared. Typical behaviors of branch type electrical trees were obtained from the morphology observation of Figs. 3(a) and 3(b). That is to say, charges injected and extracted at the needle tip initiated a small electrical tree from the needle tip, as clearly shown in Fig. 3(a), and then charges injected and extracted at the newly generated conductive tree tip were carbonized so that several branches had newly appeared (Fig. 3(b)). They grew rapidly and became fatter and darker with new branches, and finally,penetration breakdown took place.

As was expected, the retarding effect of the amino silane coupling agent was shown in Figs. 3(c)~3(e): the amino silane blocked the tree growth, so the tree should have developed a new root. This was a time-consuming process. Many branches were generated (Fig. 3(c)), and each branch also formed many new secondary branches (Fig. 3(d)), andthe trees became bush type trees (Fig. 3(e)).

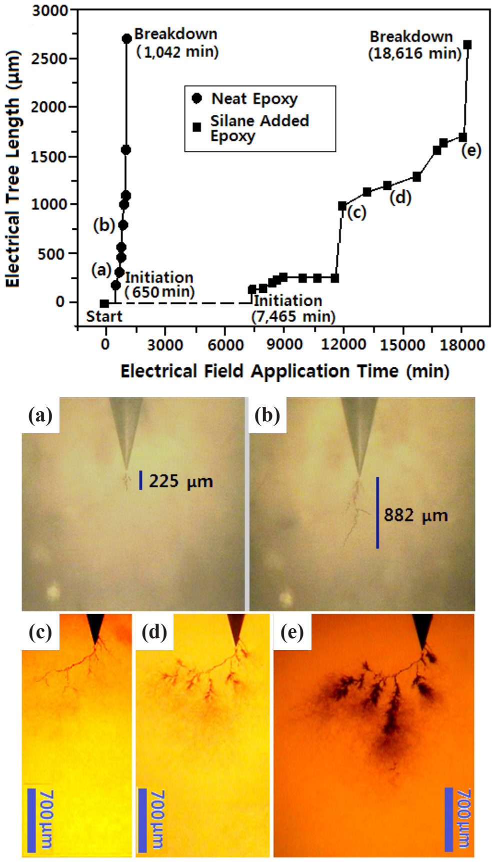

Fig. 3. Tree growth rate in the neat epoxy resin with or without amino silane coupling agent (1.0 wt%) tested in the constant electric field of 520.9 kV/mm (60 Hz) at 30℃. The morphology of electrical tree corresponding to (a) 680 min and (b) 860 min in the neat epoxy resin, and (c) 12,140 min, (d) 14,360 min and (e) 18,230 min in the epoxy/amino silane system.

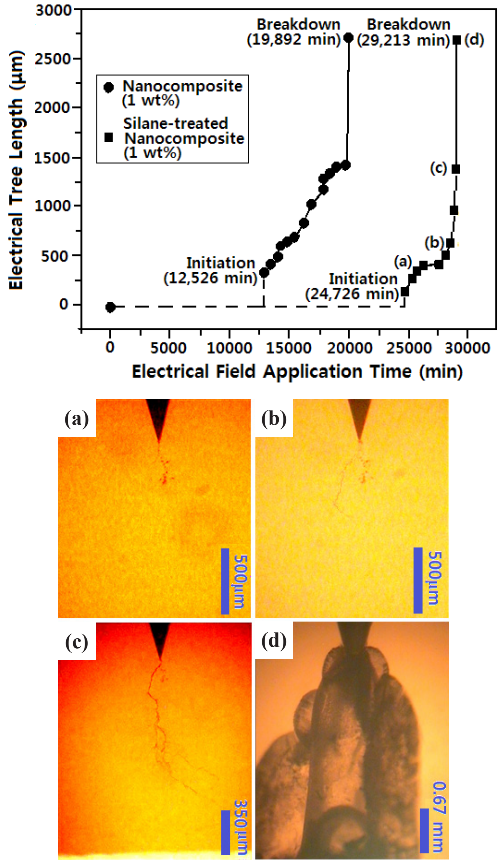

Fig. 4. Tree growth rate in the epoxy/layered silicate (1 wt%) nanocomposite with or without amino silane coupling agent (1.0 wt%) tested in the constant electric field of 520.9 kV/mm (60 Hz) at 30℃. The morphology of an electrical tree corresponding to photos (a) 27,760 min, (b) 28,722 min, (c) 29,204 min and (d) 29,213 min in the epoxy/layered silicate (1 wt%)/amino silane nanocomposite.

In our previous works [10,11], the exfoliated nano-sized silicate monolayers were well dispersed in the epoxy matrix, and it was confirmed by a wide-angle X-ray scattering diffractometer (WAXS) and a high-resolution transmission electron microscope (HR-TEM).

As shown in Fig. 4, in the epoxy/layered silicate (1 wt%) nanocomposite, an electrical tree was initiated in 12,526 min and propagated relatively slowly at the speed of 0.37 μm/min, and finally breakdown took place in 19,892 min after applying 520.9 kV/mm. The initiation time compared to the neat epoxy system was 19.3 times higher, and the breakdown time was 19.1 times higher. This meant that well-dispersed nano silicates blocked the tree progress in the initiation and propagation processes.

To improve the electrical tree behaviors of the epoxy/layered silicate (1 wt%) nanocomposite, an amino silane coupling agent was employed and the resulting tree growth rate was monitored and displayed in Fig. 4. The tree initiation time in needle-plate electrode geometry was 24,726 min, which was 2.0 times higher, and the breakdown time was 29,213 min, which was 1.5 times higher than those of the epoxy/layered silicate (1 wt%) nanocomposite. The average propagation rate was 0.60 μm/min, which was 1.62 times faster. These results meant that the amino silane coupling agent retarded the tree initiation,but the tree growth rate in the propagation became faster.

Typical behaviors of branch type electrical trees as shown in Figs. 4(a)~4(d)appeared regardless of the treatment of amino silane, although the growth speed was changed compared to the neat epoxy resin. The morphology of the epoxy/layered silicate (1 wt%) without amino silane was not shown. These implied that if an electrical tree was blocked by a sheet-like silicate, the tree should develop a new root. So many short branches would be generated.

4. CONCLUSIONS

The effects of amino silane coupling agent on the AC electrical treeing and breakdown behaviors in epoxy/layered silicate (1 wt%) were examined in needle-plate electrode geometry. In the epoxy/amino silane system, the tree initiation time was 7,465 min, which was 11.5 times higher, and the breakdown time was 18,616 min, which was 17.9 times higher than those of the neat epoxy resin. This implied that the amino silane coupling agent might have acted as a tree retardant. The tree initiation time in the epoxy/layered silicate (1 wt%) nanocomposite with the amino silane was 24,726 min, which was 2.0 times higher, and the breakdown time was 29,213 min, which was 1.5 times higher than those of the epoxy/layered silicate (1 wt%) nanocomposite. These results meant that the amino silane coupling agent retarded the tree initiation, but the tree growth rate in the propagation became faster.

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