



Mechanical and Water Repellent Properties of Cycloaliphatic Epoxy/Microsilica/Nanosilica Composite

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The effect of the content of microsilica and nanosilica continuously modified with hydroxy silane and epoxy-modified silicone in cycloaliphatic epoxy/microsilica/nanosilica composites (EMNCs) on the mechanical and water repellent properties was evaluated. Surface-modified micro- and nanosilica was well-mixed with a cycloaliphatic epoxy resin in the presence of polyester-modified polydimethylsiloxane (PEM-PDMS) as a dispersing agent using an ultrasonicator. Tensile and flexural tests were carried out using a universal testing machine (UTM). The water repellent property was evaluated by contact angle measurements of water on the composite surface. Tensile strength of the composite could be enhanced by 32.2% up to 91.4 MPa, and the flexural strength was raised to 122.0 MPa, which is 38.8% higher than that of neat epoxy. The contact angle of water on the composite was as high as 104.1°.

Keywords : Outdoor insulating material, Epoxy composite, Cycloaliphatic epoxy, Epoxy/silica composite, Silicone-modified silica

1. INTRODUCTION

Various polymer systems have been used as electrical insulators for electrical equipment, such as mold-type transformers, current transformers (CT), potential transformers (PT), metering outfit (MOF), and gas switching gears. In particular, epoxy resins were the first and most widely used polymers in the field of solid electrical insulators which have been substituting conventional ceramic materials since the mid-1940s, and are still used today to make electrical insulators for indoor and outdoor applications [1-3]. The reasons for the continuous use of epoxy resins are their good mechanical and thermal properties as well as the excellent electrical properties [4,5].

Polymers from the family of cycloaliphatic epoxies have been used for outdoor applications because their resistance to UV radiation, carbon formation and surface discharges is far superior to that of aromatic bisphenol structures. Furthermore, the inherent low

viscosity of cyclic aliphatic epoxies allows the addition of high levels of inorganic fillers, such as silica, alumina, or mica [6]. Generally, the loading level of micro-sized inorganic fillers is 65-80 wt% in order to satisfy the dimensional stability of heavy electric equipment.

There are many types of curing agents, such as carboxylic acid anhydrides, amines, polyamides, imidazoles, polymercaptans, or polyols [7-9]. Carboxylic acid anhydrides are commonly used for outdoor applications of epoxy electrical insulators because of their long working time, low processing viscosities and low exothermic heat. In order to control the working time during reactions, tertiary amines are commonly used as accelerating agent.

The insulation performance of epoxy/silica composites for outdoor applications is greatly limited by environmental humidity and pollutant levels, because a conductive pollutant layer on the insulator surface can lead to a serious reduction in the insulation performances; in detail, the surface leakage current, flashover and arcing characteristics are considerably decreased. Therefore, it will be beneficial to minimize the wettability of humidity and pollutants on the insulator surface by realizing an insulator surface with a high water repellency. Commonly, in order to increase water repellency, water repellents, such as silicone oils, are introduced into epoxy systems [9,10].

In this study, the surface of microsilica and nanosilica was continuously modified with hydroxy silane and epoxy-modified

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silicone to investigate the effects of these modifications on the mechanical and water repellent properties in cycloaliphatic epoxy/microsilica/nanosilica composites (EMNCs).

2. EXPERIMENTS

2.1 Materials

Diglycidyl 1,2-cyclohexanedicarboxylate (Araldite CY 184, Huntsman Co., USA) was used as a cycloaliphatic epoxy resin. Its equivalent weight was 164–172 g/eq and the viscosity was 700–900 mPa·s at 25 °C. 4-Methyl-1,2-cyclohexanedicarboxylic anhydride (Araldur HY 917, Huntsman Co., USA) was used as a cycloaliphatic anhydride type curing agent. Its anhydride content was $\geq 98\%$ and the viscosity was 50–100 mPa·s at 25 °C. Benzyl dimethyl amine (a tertiary amine; DY 062, Huntsman Co., USA) was used as an accelerating agent.

To modify the surface characteristics of micro and nanosilica, bis(2-hydroxyethyl)-3-aminopropyltriethoxysilane (SIB1140.0, Gelest Inc., USA) was used as a hydroxy silane coupling agent and 1,3-bis(glycidoxypropyl)tetramethyl-disiloxane (SIB1115.0, Gelest Inc., USA) as a silicone-modified epoxy. Polyester-modified polydimethylsiloxane (PEM-PDMS) was used as a dispersing agent (BYK-310, BYK-Gardner GmbH, Germany).

Microsilica (MILLISIL® M10) was purchased from Sibelco, Korea. Its silica content was 95.5 wt% and the average diameter of the silicon particles was 21.1 μm . Nanosilica was purchased from Nanostructured & Amorphous Materials Inc., USA. In this case, the average particle diameter was 15 nm. Before use, samples of micro- and nanosilica were dried at 110 °C for 24 h in a vacuum oven.

Silicone-modified microsilica was prepared by the following procedures: first, the surface of the microsilica particles (5 g) was modified with SIB 1140.0 (5 g) in the presence of a H^+ catalyst (acetic acid) in a toluene/acetone (7/3 wt%) mixture solution at 80 °C. The microsilica was rinsed with toluene. Next, the hydroxyl group of SIB 1140.0 on the microsilica was each reacted with an epoxy group of the epoxy-modified silicone (5 g) in the presence of triethylamine (TEA) in a toluene/acetone (7/3 wt%) mixture solution at 80 °C. Finally, the modified microsilica was rinsed with toluene.

Nanosilica was modified in an analogous procedure. In the first step, 0.5 g of SIB1140.0 and 5 g of nanosilica were combined; and in the second step, 0.5 g of SIB1115.0 and 5 g of the silane-modified nanosilica were used.

2.2 Preparation of EMNC

In order to prepare EMNCs, CY 184 (epoxy base resin, 100 g), surface-modified nanosilica (0, 0.5, 1, 2 and 3 phr) and PEM-PDMS (0.5 times of the nanosilica weight) were homogeneously mixed for 30 min by an ultrasonic processor (phr stands for one part per one hundred gram of epoxy base resin). Next, surface-modified microsilica (50, 55, 60 and 65 wt%) was added and mixed for 30 min using a mechanical stirrer. Finally, HY 917 (curing agent, 90 phr) and DY 062 (accelerating agent, 0.6 phr) were added and mixed for 5 min using again a mechanical stirrer. Afterwards, the mixture was injected into a mold, cured at 100 °C for 2 h, and post-cured at 140 °C for 2 h. The sample were named as EMNC-x-y, where x denotes the content of microsilica in wt% and y the content of nanosilica in units of phr.

2.3 Instrumental analyses

Fourier Transform infrared (FTIR) spectroscopy with a Nicolet iS 10 (Thermo Fisher Scientific Inc., USA) and thermogravimetric analysis (TGA) with a TG-121 (Thermo Fisher Scientific Inc., USA)

were carried out in order to confirm the modification of the silica surfaces. Field emission scanning electron microscopy (FE-SEM; JMS-6701E, JEOL, Japan) was used at an acceleration voltage of 10 kV in order to confirm that the microsilica particles are well-dispersed and to study the interfacial morphology between epoxy and the microsilica. The fractured surface was gold sputter-coated after tensile tests. Tensile and flexural tests were carried out by a universal testing machine (SHM-C-500, Shamhan Tech, Korea). Specimens for tensile tests were prepared following the recommendation JIS B7502, and they were tested at a crosshead speed of 10 mm/min at 23 °C and 50% relative humidity. Following the recommendation JIS B7507, specimens for flexural test were prepared by the three-point bending method with a size of 70×10×4 mm. The span length was 50 mm and crosshead speed was 10 mm/min at the same temperature and humidity in the tensile test. Water repellency was estimated by contact angle analysis (Phoenix-multi, SEO, Korea).

3. RESULTS AND DISCUSSION

In our experiments [12], FTIR and TGA analyses indicated that the surface of micro- and nanosilica was modified with hydroxyl silane and epoxy-modified silicone compounds in a way the loading weight of hydroxyl silane and epoxy-modified silicone compounds for microsilica was 9.2 wt% and that for nanosilica was 6.8 wt%. Figure 1 shows the effect of the surface-treated microsilica content on the tensile strength of the EMNC system. Weibull analysis was applied to study the experimental data statistically [11,12]. For this kind of analysis, the nanosilica content was fixed to 1 phr and the microsilica contents was varied in the range of 0–65 wt%: (●) 0 wt%, (■) 50 wt%, (▲) 55 wt%, (▼) 60 wt%, and (◆) 65 wt%. The resulting Weibull parameters, such as scale and shape parameters and B10 value, are listed in Table 1. Specifically, the scale parameter relates to the value of tensile strength at which a sample would fail with a cumulative probability of 63.2%. Further, the B10 value relates to the tensile strength value at which the cumulative probability for failures is 10% (i.e., 90% of the samples would survive). Eventually, the shape parameter relates to the distribution of the data and can be calculated from the slope of linear fits shown in Fig. 1. The tensile strength of the EMNC-60-1 was 91.4 MPa, which was 32.3% higher than that of neat epoxy (69.1 MPa). However, an excess amount of microsilica could not increase the tensile strength, instead the tensile

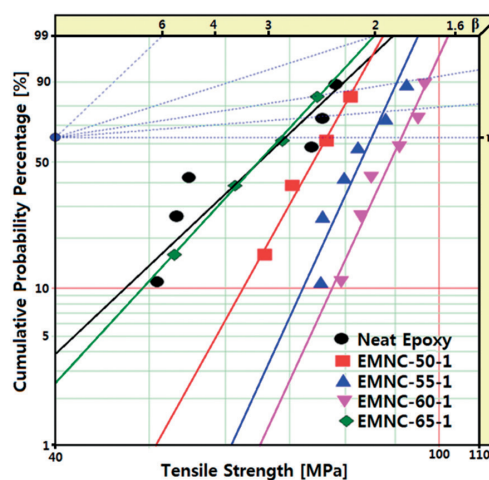


Fig. 1. Effect of the microsilica content on the Weibull statistical tensile strength of EMNC systems: (●) neat epoxy, (■) EMNC-50-1, (▲) EMNC-55-1, (▼) EMNC-60-1, and (◆) EMNC-65-1, where the ratio of nanosilica to PEM-PDMS was 2 : 1.

Table 1. Weibull parameters for tensile strength in EMNC systems obtained from data in Fig. 1 by statistical analysis.

System	Scale parameter (kV/2 mm)	B10 value (kV/2 mm)	Shape parameter
Neat Epoxy	69.1	47.1	5.9
EMNC-50-1	76.4	62.8	11.3
EMNC-55-1	85.1	72.2	13.7
EMNC-60-1	91.4	77.5	13.6
EMNC-65-1	68.6	49.5	6.8

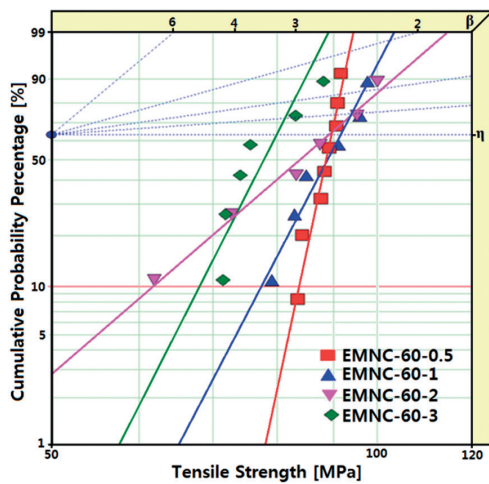


Fig. 2. Effect of the nanosilica content on the Weibull statistical tensile strength of EMNC systems: (■) EMNC-60-0.5, (▲) EMNC-60-1, (▼) EMNC-60-2, and (◆) EMNC-65-3, where the ratio of nanosilica to PEM-PDMS was 2 : 1.

Table 2. Weibull parameters for tensile strength in EMNC systems obtained from data displayed in Fig. 2.

System	Scale parameter (kV/2 mm)	B10 value (kV/2 mm)	Shape parameter
EMNC-60-0.5	89.6	83.8	33.4
EMNC-60-1	91.4	77.5	13.6
EMNC-60-2	89.0	61.7	6.1
EMNC-60-3	80.0	68.0	14.0

strength greatly decreased. The excessive amount of the microsilia is considered to result in an incomplete curing reaction of the epoxy, causing the observed significant decrease in tensile strength. When silane-silicone-treated microsilia was mixed with the epoxy resin and the curing reaction was allowed to proceed, the interfacial characteristics were enhanced by the hydrogen bonding between the silanol on the surface of the silica and the hydroxyl group of the epoxy resin and thus, the tensile strength was improved. However, when silica was added in an excess amount, the mobility of the epoxy resin was lowered and the curing reaction was interrupted, so that the crosslinking density was lowered and therefore, the tensile strength decreased.

Figure 2 shows the effect of the surface-treated nanosilica content on the tensile strength of EMNC systems. The data were also statistically studied by Weibull analysis. In this case, the microsilia content was fixed to 60 wt% and the nanosilica contents was varied in the range of 0.5~3 phr: (■) 0.5 phr, (▲) 1 phr, (▼) 2 phr, and (◆) 3 phr. The Weibull parameters are listed on Table 2. As the nanosilica content increased, the tensile strength increased as well up to a content of 1 phr; afterwards, for higher contents of nanosilica, it decreased. This observation can also be explained by the effects of an excessive amount of the nanosilica on the composite system.

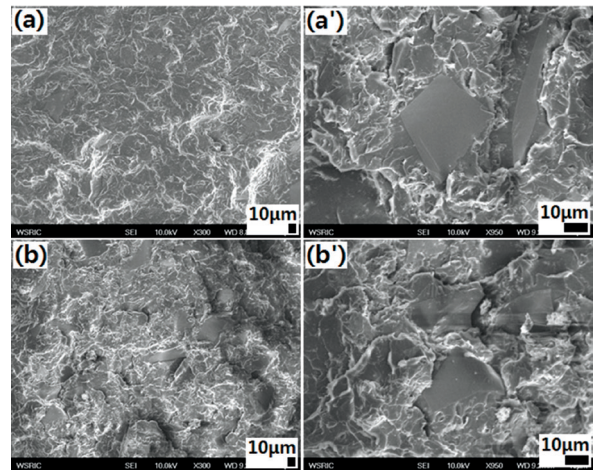


Fig. 3. SEM images of the EMNC systems: (a) EMNC-60-1 and (b) EMNC-65-1, showing the fractured surface after tensile test and (a' and b') images showing the interface between the epoxy matrix and microsilia.

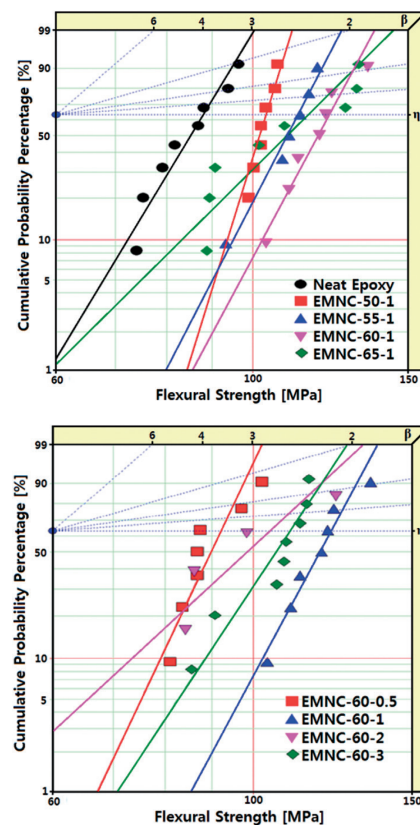


Fig. 4. Flexural strength for EMNC systems. The upper graph displays the effect of the microsilia content, while the lower one shows the effect of the nanosilica content.

In order to observe the interface between the epoxy and microsilia, SEM observation was carried out as shown in Fig. 3. In detail, the investigated systems were (a) EMNC-60-1 and (b) EMNC-65-1. The fractured surface after tensile tests and the interface between the epoxy matrix and microsilia (a' and b') are shown for both systems. In the case of the EMNC-60-1 system, the silica content was optimal, while for the EMNC-65-1 system, the silica content was excessive. As shown in the micrograph, when the silica content was optimal, the fracture surface of the tensile specimen was uniform without cracks

Table 3. Weibull parameters for the flexural strength in EMNC systems obtained from data in Fig. 4.

System	Scale parameter (kV/2 mm)	B10 value (kV/2 mm)	Shape parameter
Neat Epoxy	87.9	72.2	11.5
EMNC-50-1	103.6	93.6	22.2
EMNC-55-1	112.6	95.1	13.4
EMNC-60-1	122.0	102.5	12.9
EMNC-65-1	115.6	83.1	6.8
EMNC-60-0.5	92.2	79.0	14.5
EMNC-60-1	122.0	102.5	12.9
EMNC-60-2	104.4	73.4	6.4
EMNC-60-3	109.9	88.6	10.4

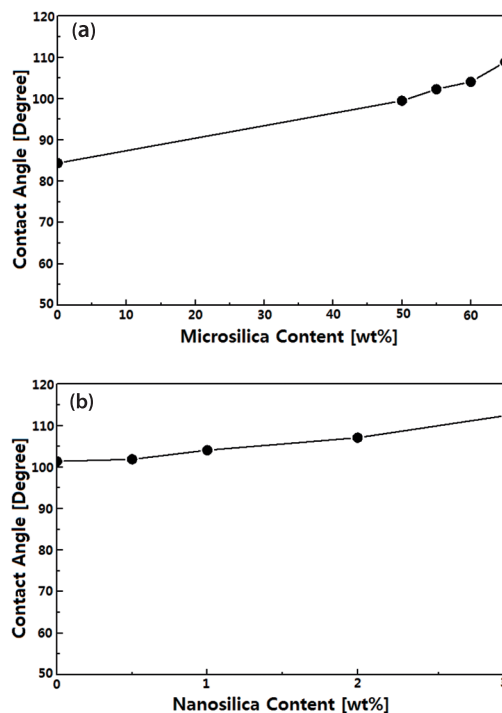


Fig. 5. Effect of the microsilica and nanosilica contents on the contact angle of water on EMNC systems. (a) The microsilica content was fixed at 60 wt% and nanosilica contents were varied in the range of 0.5–3 phr and (b) the nanosilica content was fixed to 1 phr and the microsilica contents were varied in the range of 50–65 wt%.

and the interface was smooth, whereas, when the silica content was excessive, the fracture surface of the tensile specimen was very rough and large gaps were visible at the interface.

Additionally, the effects of the silane-silicone-treated microsilica or nanosilica content on the flexural strength of EMNC systems were investigated. The data were also treated with Weibull statistical analysis, as shown in Fig. 4. The resulting Weibull parameters are listed in Table 3. The effect of microsilica and nanosilica on the flexural strength exhibited the same tendency as has been observed for the tensile strength. The flexural strength of EMNC-60-1 was 122.0 MPa, which was 38.8% higher than that of neat epoxy (87.9 MPa). However, in analogy to the previous results, an excess amount of microsilica or nanosilica greatly decreased the flexural strength.

As shown in Fig. 4, the contact angle increased with increasing contents of silane-silicone treated microsilica or nanosilica. The contact angle of EMNC-60-1 was 104.1°, which was 35.2% higher than that of neat epoxy (77°).

4. CONCLUSIONS

Microsilica and nanosilica were treated with silane-silicone compounds and used for the preparation of epoxy/microsilica/nanosilica composites employed as electrical insulator material in outdoor applications. It was found that, as either the microsilica or nanosilica contents were increased, the tensile and flexural strength increased up to an optimal micro- or nanosilica content; however, any excess amount of microsilica and nanosilica beyond the optimal content greatly decreased the mechanical strength of the composite. The tensile strength of the EMNC-60-1 system reached 91.4 MPa, which was 32.3% higher than that of neat epoxy, while its flexural strength exceeded that of neat epoxy by 38.8%. However, an excess amount of microsilica could not increase the tensile strength but instead led to a decrease. Likewise, excess amounts of microsilica and nanosilica greatly decreased the flexural strength. The contact angle of the EMNC-60-1 system was enhanced by 35.2% and amounted to 104.1°.

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