Low permittivity epoxy nanoporous composites filled with hollow nanosilica

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Abstract: An epoxy nanoporous composite (NPC) filled with hollow nanosilica exhibits lower permittivity than unfilled epoxy resin. The hollow nanosilica is a silica nanoparticle containing a nanometric closed pore. To investigate the effect of the closed pore of hollow nanosilica, the particle porosity and permittivity of NPC filled with hollow nanosilica and NPC filled with mesoporous silica, the pores of which were open at the particle surface, were compared. The nanometric pores of hollow nanosilica and mesoporous silica were unfilled and partially filled with epoxy resin, respectively. The relative permittivity of NPC filled with hollow nanosilica was lower than that of NPC filled with mesoporous silica mainly owing to the closed pore of the hollow nanosilica. Moreover, the existence of the nanometric pore in hollow nanosilica negligibly affected the breakdown strength. These results indicate that the hollow nanosilica is applicable to insulating composites as a filler that can lower the permittivity of the epoxy composites even to a value lower than that of unfilled epoxy resin.

1 Introduction

To achieve compactness and high reliability of a gas/solid-insulated system, such as gas-insulated switchgears and rotating machines, solid insulators play an important role in the insulation design [1–3]. The permittivity of solid insulators is much higher than that of gas ones. This difference enhances in the electric field around the insulators in the gas/solid insulated systems. The decrease in the permittivity of solid insulators reduces the enhancement of electric field, facilitating the insulation design easier and improving the compactness and reliability.

Epoxy composites, particularly epoxy resin filled with ceramic particles such as alumina or silica, are used as the solid insulating materials. Since the relative permittivity of the ceramic fillers is higher than that of unfilled epoxy resin, the reduction in the filler permittivity is one of the solutions for obtaining a low permittivity solid insulator.

Porous ceramic particles have been used as low permittivity fillers because they are filled with gas, the permittivity of which is 1.0. The permittivity of micrometric porous fillers, such as syntactic foam [4] and hollow glass microspheres [5], has been reported to be lower than that of the epoxy composites [6]. However, void discharges may occur inside the micrometric pores when a high voltage is applied to the pores [7, 8], which limits the design voltage of high-voltage power equipment. However, it is expected that electron avalanches do not grow inside the nanometric pores even under a high voltage and that these pores do not act as insulation defects [9–11]. Nanometric porous fillers are expected to be used as low-permittivity fillers for high-voltage applications.

Typical nanoporous fillers include mesoporous ceramics [12–14] and zeolites [15]. The nanoporous fillers have open nanoporous structures, the pores of which are open at the particle surface. The permittivity of the epoxy composites filled with mesoporous ceramics was found to be lower than that of unfilled epoxy resin [16–18]. However, the pores inside mesoporous ceramic composites are partially filled with epoxy resin, which decreases the pore volume of the mesoporous ceramics [19] and thus reduces the extent of permittivity reduction [20]. However, hollow nanosilica is expected to be free of the above-mentioned partial-filling effect. The same effect on relative permittivity as seen in the hollow micrometric filler is expected in the case of hollow nanosilica. However, when the filler size decreases, the ratio of surface area to volume increases; this may enhance effects arising from the dielectric property of the surface region such as the adsorption of high-permittivity foreign substances (e.g. water). Therefore, it is important to experimentally investigate the effect of the hollow nanosilica on the permittivity reduction [21–23]. This study discusses the permittivity reduction of epoxy nanoporous composites (NPCs) filled with hollow nanosilica.

2 Experimental

2.1 Polymer NPC filled with hollow nanosilica

Fig. 1 shows an illustration of a polymer NPC filled with hollow nanosilica. The matrix material is a polymer, such as epoxy or polyimide. The particle diameter of hollow nanosilica is <100 nm. The hollow nanosilica, the pore of which remains unfilled with epoxy resin, can be used as a filler to lower the permittivity of the epoxy composite for use in high-voltage applications.

2.2 Materials and sample preparation

Fig. 2 shows a transmission electron microscopy (TEM) image of the hollow nanosilica used in this study. The TEM observation showed that the diameter of the hollow nanosilica particle and silica shell thickness was 70–200 and 8–10 nm, respectively. The pore diameter was 50–184 nm. The silica material was similar to fused silica. Table 1 lists the specifications of the nanoporous composites filled with hollow nanosilica.
fillers used in this work. To investigate the effect of the closed pore structure of the hollow nanosilica on the permittivity of the NPC, mesoporous silica, with an open pore structure as shown in Fig. 3 [20], was used for comparison. The porosity of the nanoporous filler (particle porosity) is defined as the ratio of the pore volume inside the particles to the total volume of the particles. The particle porosities of both hollow nanosilica and mesoporous silica were ∼70 vol%. The volume fractions of nanoporous fillers differ before and after being filled into the epoxy resin owing to the partial intrusion of epoxy resin into the pores. Therefore, the filling ratio of the fillers is expressed in wt%.

To eliminate the water absorbed on the surface of the nanoporous fillers, the particles were heated at 100°C. The epoxy resin we used was a bisphenol-A type, and the hardener was an anhydride type. The nanoporous fillers were mixed with the epoxy resin by using a planetary mixer. Then, the epoxy resin was first cured at 60°C for 6 h and then at 100°C for 10 h. The cured sample was circular in shape with a diameter of ∼40 mm. The sample thicknesses were 0.4 and ∼10 mm for the permittivity and specific-gravity measurements, respectively. As listed in Table 2, the NPCs filled with hollow nanosilica having different filler contents are denoted as closed NPC1 and closed NPC2, whereas the NPCs filled with mesoporous silica are denoted as open NPC1 and open NPC2. The filler content of the mesoporous silica was 15.8 wt% or 21.4 wt%, which produced the same volume ratio as the hollow nanosilica, i.e. 4.9 wt% or 10.0 wt% [20].

### 2.3 Measurement methods

The pore structure of the hollow nanosilica inside the NPC may be broken or filled with epoxy resin during the mixing process. The nanometric pores of the hollow nanosilica inside the closed NPC were evaluated by observing the internal cross section of the sample by using a field-emission scanning electron microscope. The cut section was polished through the ion polishing method so that the nanometric pores were not filled with shavings or polishing powders.

The specific gravity was measured to evaluate the proportion of nanometric pores in the NPCs. The specific gravity of each sample (ρ [g/cm³]) was determined from its weight in air and its volume as measured using an electronic balance and a density determination kit (Metter–Toledo, Japan). The capacitance and dielectric loss tangent of a plate sample with a thickness of ∼0.4 mm were measured at room temperature using an LCR meter. Aluminium electrodes (with 30 mm diameter) with a guard ring were formed on both sides of the sample through vacuum deposition. The measurement frequency was in the range of 100 Hz to 1 MHz.

### 3 Experimental results

Fig. 4 shows the scanning electron microscopy (SEM) image of closed NPC2. The white part, grey and black parts represent the silica shell, epoxy resin and air pore inside the hollow nanosilica, respectively. Nanometric pores with sizes of ∼100 nm each were evident inside the NPC. The thickness of the silica shell was approximately several nanometres. The nanometric pores of the hollow nanosilica inside closed NPC remained unfilled with the epoxy resin.

Fig. 5 shows the specific gravity of the NPCs. The specific gravities of the closed NPC were lower than those of the open NPC or unfilled epoxy. With the increasing weight fraction of the hollow

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### Table 1 Specifications of nanoporous fillers

| Material          | Particle diameter | Pore morphology | Pore diameter | Porosity before mixing with epoxy [vol%] |
|-------------------|-------------------|-----------------|---------------|-----------------------------------------|
| hollow nanosilica | silica 70–200 nm  | hollow          | 50–180 nm     | 70                                      |
| mesoporous silica | silica 1 μm on average | hexagonal   | 3 nm on average | 70                                      |

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### Table 2 Specifications of epoxy NPCs

| Filler type | Weight fraction of nanoporous filler [wt%] |
|-------------|-------------------------------------------|
| unfilled epoxy | 0                                          |
| closed NPC1  | hollow nanosilica 4.9                     |
| closed NPC2  | hollow nanosilica 10.0                    |
| open NPC1    | mesoporous silica 15.8                    |
| open NPC2    | mesoporous silica 21.4                    |
nanosilica, the specific gravities of the closed NPC decreased whereas those of the open NPC increased.

The frequency dependence of the relative permittivity of the NPCs is shown in Fig. 6. The relative permittivity of the closed NPC was lower than that of the open NPC or unfilled epoxy. The frequency dependence of the dielectric loss tangent of NPCs is shown in Fig. 7. The dielectric loss tangents of NPCs are almost the same as those of the unfilled epoxy, showing only a slight increase of those of NPCs around 100 Hz.

4 Discussions

4.1 Particle porosity of hollow nanosilica inside epoxy NPC

To evaluate the proportion of nanometric pores in the hollow nanosilica after being incorporated into epoxy composites, the particle porosity (\( P \) [vol%]) and the volume fraction of the filler (\( V_f \) [vol%]) in the NPC samples were calculated from the specific gravity of the NPCs using the following equations:

\[
\rho_f = \frac{w_f}{(100 + w_f)/\rho_e - 100/\rho_e}, \quad (1)
\]

\[
V_f = (\rho_e - \rho_f)/(\rho_f - \rho) \times 100, \quad (2)
\]

\[
P = (1 - \rho/\rho_{SiO_2}) \times 100, \quad (3)
\]

where \( \rho_f \) (g/cm\(^3\)) is the specific gravity of the hollow nanosilica, \( w_f \) [g] is the weight of hollow nanosilicas mixed with 100 g of the epoxy matrix, \( \rho_e \) (g/cm\(^3\)) is the specific gravity of the unfilled epoxy resin, \( \rho_f \) (g/cm\(^3\)) is the specific gravity of the NPCs, and \( \rho_{SiO_2} \) (g/cm\(^3\)) is the specific gravity of the non-porous silica material (2.0 g/cm\(^3\)).

Fig. 8 shows the relation between the filler-volume fraction and specific gravity of the NPCs. The filler-volume fraction was obtained from (2). The specific gravity of the closed NPC was lower than that of the unfilled epoxy and decreased by increasing the volume fraction of fillers; this result indicates that the specific gravity of the hollow nanosilica was lower than that of the unfilled epoxy. In the filler-volume fraction range of 10–16 vol%, the specific gravities of closed NPC were lower than those of open NPC, suggesting that the specific gravity of hollow nanosilica in closed NPC is considered to be higher than that of mesoporous silica in open NPC by assuming that the specific gravity of the silica shell of each filler is the same. The calculated specific gravity of the NPC when the particle porosity was 70% is indicated by the broken line in Fig. 8. Since the measured specific gravity of closed NPC is almost the same as the calculated specific gravity, the porosity of the hollow nanosilicas incorporated into the epoxy composites must be close to 70%.

The NPC particle porosity obtained from (3) is shown in Fig. 9. The particle porosities of hollow nanosilica inside NPC were ~70 vol%, which are almost the same as that of hollow nanosilica itself before being mixed with the epoxy resin. This result indicates that the nanometric pores inside the hollow nanosilica remain unfilled.
with epoxy resin owing to the closed pore structure. On the contrary, the particle porosities of mesoporous silica inside NPC were lower than those of the mesoporous silica before being mixed with the epoxy resin, which indicates that the nanometric pores of mesoporous silica were partially filled with epoxy resin.

### 4.2 Relation between pore volume and permittivity of epoxy NPC

Fig. 10 shows the relationship between the volume fraction of the filler and the relative permittivity at 1 MHz for the NPCs and unfilled epoxy. The relative permittivity of the closed NPC was lower than that of the unfilled epoxy and decreased as the volume fraction of the hollow nanosilica increased. This indicates that the filling of hollow nanosilica can reduce the permittivity of epoxy composites even to a value lower than that of an unfilled epoxy resin. The reduction of permittivity from 3.5 to 3.2 can cause the relaxation of the electric field strength around the gas-insulated substation (GIS) spacer by 3–5% [10]. Further field relaxation could be achieved by increasing the volume fraction of hollow nanosilica through the filler-surface treatment, by using NPC in the permittivity graded GIS spacer [3] and so on.

It has been already reported that relative permittivity of epoxy resin filled with hollow silica particles with micrometric pore sizes is lower than that of unfilled epoxy [4–6]. The same effect is expected in the case of hollow nanosilicas. However, as the size of the silica particles decreases, the ratio of the surface area to volume increased, which may enhance the effects arising from the surface region such as high permittivity foreign substances (e.g. water). However, our experimental results show that the relative permittivity of epoxy resin filled with hollow nanosilica, the pore size of which was nanometric, was lower than that of unfilled epoxy. This result implies that the effect of air inclusion predominates over the surface effect even in the case of nanosilicas.

The permittivity decrease in open NPCs is less than that in closed NPCs. This relationship seems to correlate with the particle porosity, as shown in Fig. 9. To investigate the influence of the nanometric pore volume that remains inside NPCs on the low-permittivity characteristics of NPCs, the total volume of the nanometric pores relative to the total volume of the NPC ($P_{\text{total}}$) was calculated using the following equation:

$$P_{\text{total}} = V_f \times P.$$  \hspace{1cm} (4)

Fig. 11 shows the relationship between $P_{\text{total}}$ and the relative permittivity at 1 MHz. The permittivity of the NPC decreased as $P_{\text{total}}$ increased, indicating that the main cause for the low permittivity of NPCs was the total pore volume inside the NPCs.

The permittivity of the closed NPC calculated from the volume ratio of the pore, silica and epoxy resin and their permittivities [20] is lower than the experimental permittivity [17]. The electric field distortion in and around the hollow nanosilica was not considered in the calculation of permittivity. To quantitatively explain the experimental permittivity of the closed NPC, the electric field distortion caused by particle shapes and agglomeration should be taken into consideration. This requires finite element method modelling and will be described in our next paper.

### 4.3 Effect of nanometric pore on AC breakdown strength

In order to confirm that the nanometric pore does not act as a defect that reduces the breakdown strength, we measured the AC

Fig. 8 Relationship between volume fraction of fillers $V_f$ and specific gravity $\rho_c$ of epoxy NPC filled with hollow nanosilica (closed NPC), epoxy NPC filled with mesoporous silica (open NPC) and unfilled epoxy

Fig. 9 Particle porosity $P$ of hollow nanosilica and mesoporous silica before and after filling epoxy NPC

Fig. 10 Relation between relative permittivity at 1 MHz and volume fraction of fillers

Fig. 11 Relation between relative permittivity at 1 MHz and the total volume of nanopores relative to the total volume of NPC ($P_{\text{total}}$)
Conclusions

Applicable to insulating composites as fillers that can reduce the composite and unfilled epoxy resin permittivity of epoxy composites even to a value lower than that of a 50–70 μm thick sheet was sandwiched between two sphere electrodes (with diameters of 10 mm); then, they were sealed with an isolating resin. The corresponding results are shown in Fig. 12. The breakdown tests were conducted using the McKeown electrode system [11], wherein a 50–70 μm thick sheet was sandwiched between two square electrodes (with diameters of 10 mm); then, they were sealed with an isolating resin. The corresponding results are shown in Fig. 12. The breakdown strength of NPC was almost the same as that of the non-porous-silica/epoxy composite, which suggests that the nanometric pores inside NPC did not act as a defect.

5 Conclusions

In NPC, the nanometric pores of hollow nanosilicas remained unfilled with epoxy resin, whereas the nanometric pores of mesoporous silica were partially filled with epoxy resin. The relative permittivity of NPC filled with hollow nanosilicas (closed NPC) is lower than that of unfilled epoxy or NPC filled with mesoporous silica (open NPC). The extent of the decrease in the permittivity of the NPC’s depends mainly on the total volume of the pores remaining inside the NPCs. Moreover, the existence of nanometric pores in hollow nanosilica did not affect the breakdown strength. These results indicate that the hollow nanosilica can be applicable to insulating composites as fillers that can reduce the permittivity of epoxy composites even to a value lower than that of an unfilled epoxy resin.

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Fig. 12 AC breakdown strength of closed NPC, non-porous-silica epoxy composite and unfilled epoxy resin