Influence of Nanopore Diameter on Dielectric Permittivity of Epoxy/Open Nanoporous Silica Microcomposites

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ABSTRACT

The purpose of this study was to obtain epoxy/open nanoporous silica (ONPS) microcomposites whose permittivity was lower than that of the unfilled epoxy resin. The ONPS filler comprised silica particles containing nanometric pores that were open at the particle surface. The particle size of the ONPS filler used in this study was on the order of micrometers. If air pores inside the ONPS filler remain unfilled with epoxy resin, the ONPS filler can be used as a low-permittivity filler for epoxy composites. In this study, we investigated the appropriate pore diameter of the ONPS filler for lowering the permittivity of epoxy/ONPS microcomposites. The permittivities of the epoxy/ONPS microcomposites were compared for ONPS fillers with the average pore diameters in the range from 0.6 nm to 15 nm. The permittivity of the epoxy/ONPS microcomposite whose average pore diameter was 3 nm was found to be lower than that of the unfilled epoxy resin. This low-permittivity characteristic can be explained quantitatively in terms of the pore volume. These results are expected to be useful for selecting ONPS fillers for epoxy/ONPS microcomposites that can be used as low-permittivity insulating materials.

Index Terms — **Open-nanoporous silica filler, nanometric pore, epoxy composite, low permittivity**

1 INTRODUCTION

EPOXY composites comprising epoxy resin filled with ceramic particles are widely used as solid insulating materials for electric power apparatus [1]. Generally, epoxy composites have higher permittivity than the unfilled epoxy resin because the permittivity of the ceramic particles, such as alumina or silica, is higher than unfilled epoxy. To reduce the size of the apparatus in a gas-solid insulation system, which typically appears in gas-insulated switchgears and rotating electrical machines, the electric field stress due to the difference in permittivity between the solid insulator and the gas insulator must be reduced [2-5]. Therefore, the development of epoxy composites whose permittivity is closer to that of the gas [6-9] is desirable.

A number of studies have investigated the feasibility of low-permittivity epoxy composites formed by filling epoxy resin with open nanoporous ceramic particles [10-17]. An open nanoporous ceramic filler consists of ceramic particles containing nanometric pores that are open at the particle surface. If air pores inside the particles remain unfilled with epoxy resin, the open nanoporous ceramic filler can be used as a low-permittivity filler for epoxy composites. Typical open nanoporous ceramic filler materials are mesoporous particles [18-20] and zeolite particles [21]. Since the pore size of the fillers is on the order of nanometers, it is expected that electron avalanches will not grow inside the nanometric pores even under a high voltage and that these pores will not act as insulation defects [22-25]. We have already revealed that the permittivity of an epoxy composite filled with an open nanoporous alumina filler having an average pore diameter of 3.8 nm was

Manuscript received on 9 June 2017, in final form 19 February 2018, accepted 20 February 2018. Corresponding author: M. Kurimoto.

lower than that of an epoxy composite having the nonporous alumina filler but higher than that of the unfilled epoxy resin [13]. The breakdown strength of the epoxy/open nanoporous alumina composite was almost the same as that of the epoxy/nonporous alumina composite under DC voltage application [26].

In this study, to obtain an epoxy/open nanoporous ceramic composite whose permittivity was lower than that of the unfilled epoxy resin, we used an open nanoporous silica (ONPS) filler composed of silica, which has lower permittivity (ε_r=4.5) than alumina(ε_r=10). The particle size of the ONPS filler used in this study was on the order of micrometers. We investigated the influence of the pore diameter of the ONPS fillers on the permittivity of the epoxy/ONPS microcomposites. The permittivity and porosity of the epoxy/ONPS microcomposites were compared for ONPS fillers with average pore diameters in the range from 0.6 nm to 15 nm. From the results, the pore diameter of the ONPS filler appropriate for lowering the permittivity of epoxy/ONPS microcomposites is discussed.

2 SAMPLES AND EXPERIMENTS

2.1 MATERIALS AND PREPARATION OF EPOXY/ONPS MICROCOMPOSITE

An epoxy/ONPS microcomposite (ONPS-MC) was prepared by combining an ONPS filler and an epoxy material. Four types of ONPS filler were used in this study, which are denoted as Type 1 to Type 4. The specifications of the ONPS fillers are shown in Table 1. The average particle diameter of the ONPS fillers varied from submicrometer to micrometer. The average pore diameter of the ONPS fillers varied from 0.6 nm to 15 nm. Type 1 had a pore morphology with an orthorhombic cross section. Type 2 and Type 3 had a pore morphology with an hexagonal cross section. Type 4 pores were cellular foams. Although these structures were different, it was assumed that the pore diameter of the ONPS filler mainly determined whether the nanopores of the ONPS filler was filled with epoxy resin. The material of Type 1 was aluminosilicate. Since the molar ratio of silica to alumina in the aluminosilicate was 1500, its permittivity was almost the same as that of silica. The material of the other fillers was silica. The porosity of the ONPS fillers (particle porosity) was defined as the ratio of the pore volume inside the particles to the total volume of the particles. The particle porosity was 25 vol% for Type1 and 70 vol% or more for the other fillers. For comparison, a nonporous silica filler was used, denoted as Type 0. The amount of ONPS filler in the ONPS-MC was varied from 6.4 wt% to 21.8 wt% as shown in Table 2. The filler amounts in the present study are the maximum amount achieved in our experiment. The ONPS-MC samples with the four different types of ONPS filler (Type 1 to Type 4) are denoted as ONPS-MC1 to ONPS-MC4. The epoxy/nonporous silica microcomposite sample with the Type 0 filler is denoted as S-MC.

The ONPS fillers were dried at 100 ℃ for 1 h. They were then dispersed in a mixture of bisphenol-A epoxy resin and an anhydride hardener by planetary stirring (THINKY, ARE-400TWIN). After degassing the mixture under a vacuum environment, it was formed into a sheet whose thickness was 0.4 mm and diameter was 50 mm. The samples were then thermally cured at 60 °C for 6 h then at 100 °C for 10 h.

Table 1. Specifications of Silica Fillers Used.

	Material	Average particle diameter [μm]	Average pore diameter [nm]	Porosity before mixing with epoxy [vol%]	Pore morphology
Type 0	Fused silica	2.2	No pores		
Type 1	Aluminosilicate (silica/alumina =1500 mol/mol)	10	0.6	25	Ortho-rhombic
Type 2	Silica	1	3	70	Hexagonal
Type 3		0.3	4		
Type 4		1-100	15	84	Cellular Foam

Table 2. Specifications of Silica/Epoxy Composites.

	Filler type	Weight fraction of filler [wt %]
Unfilled epoxy	No filler	0
S-MC	Type 0	20.1
		32.9
ONPS-MC1	Type 1	17.2
		21.8
ONPS-MC2	Type 2	15.8
		21.4
ONPS-MC3	Type 3	17.3
		17.6
ONPS-MC4	Type 4	6.4
		9.3

2.2 MEASUREMENTS

The internal cross section of the samples was observed by field emission scanning electron microscope (SEM) to examine the particle dispersion state of the ONPS fillers in the epoxy resin. The specific gravity of the samples was measured to ascertain the existence of pores in the ONPS fillers inside the ONPS-MC. The specific gravity of each sample (ρ [g/cm^3]) was determined from its weight in air, w_a (g) and its weight in ethanol w_b (g), as measured by an electronic balance (METTLER TOLEDO, XS205),

$$\rho_{sample} = \frac{w_a}{w_a - w_b}(\rho_0 - d) + d \quad (1)$$

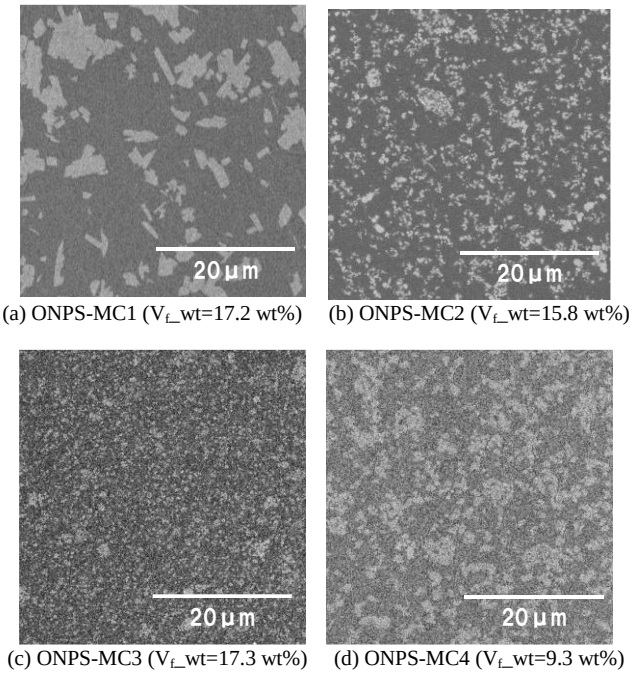
where ρ_0 [g/cm^3] is the specific gravity of ethanol and d is the density of air.

After depositing an aluminum electrode (with a guard electrode) with a diameter of 40 mm on a sheet sample, the capacitance and dissipation factor were measured using an LCR meter (Agilent E4980A). The measurement frequency was from 100 Hz to 1 MHz and the measurement temperature was between 22 and 26 ^{0}C.

3 RESULTS

3.1 SEM OBSERVATION IMAGES OF EPOXY/ONPS MICROCOMPOSITES

Figure 1 shows SEM images of the ONPS-MCs. The bright part is the ONPS filler and the dark part is the epoxy resin. It was confirmed that the ONPS fillers were well dispersed inside the epoxy resin.



(a) ONPS-MC1 (V_{f}_wt=17.2 wt%) (b) ONPS-MC2 (V_{f}_wt=15.8 wt%)

(c) ONPS-MC3 (V_{f}_wt=17.3 wt%) (d) ONPS-MC4 (V_{f}_wt=9.3 wt%)

Figure 1. SEM images of epoxy/open nanoporous silica microcomposites (ONPS-MC1-4). Vf_wt is the weight fraction of the filler.

3.2 SPECIFIC GRAVITY OF EPOXY/ONPS MICROCOMPOSITES

If the air pores of the ONPS filler remain unfilled with epoxy resin, the specific gravity of the ONPS-MCs is expected to be lower than that of S-MC. Figure 2 shows the specific gravity of the unfilled epoxy, S-MC, and ONPS-MCs. The broken line is the specific gravity of S-MC calculated from the density of the nonporous silica filler and the weight fraction of the filler. It was confirmed that the measured values of the specific gravity of S-MC agree with the calculated values. The specific gravity of the ONPS-MCs tends to be lower than that of S-MC. This investigation indicates that the air pores of the ONPS filler inside the ONPS-MCs can remain unfilled with epoxy resin.

3.3 DIELECTRIC PROPERTIES OF EPOXY/ONPS MICROCOMPOSITES

Figure 3 shows the frequency dependence of the relative permittivity (ε_r) of the unfilled epoxy, S-MC, and ONPS-MCs. ε_r decreases as the frequency increases in all of the samples. This is explained by the dielectric relaxation of the epoxy resin. ε_r for S-MC is higher than that for the unfilled epoxy. This is because ε_r for the nonporous silica particles (ε_r =4.5) is higher than that for the epoxy resin (ε_r =3.5). ε_r for the ONPS-MCs is less than or equal to that of the unfilled epoxy. This indicates

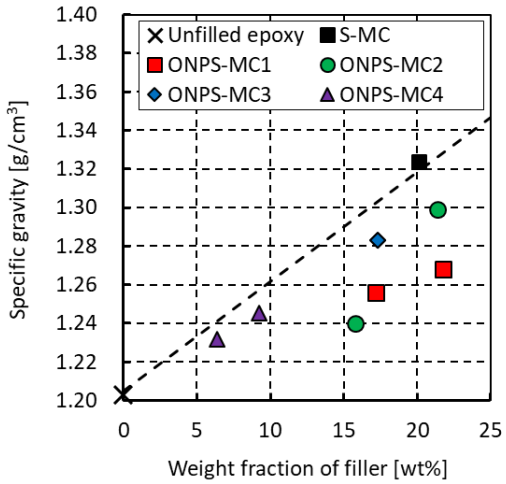


Figure 2. Specific gravity of unfilled epoxy, S-MC, and ONPS-MCs for different silica filler contents by weight.

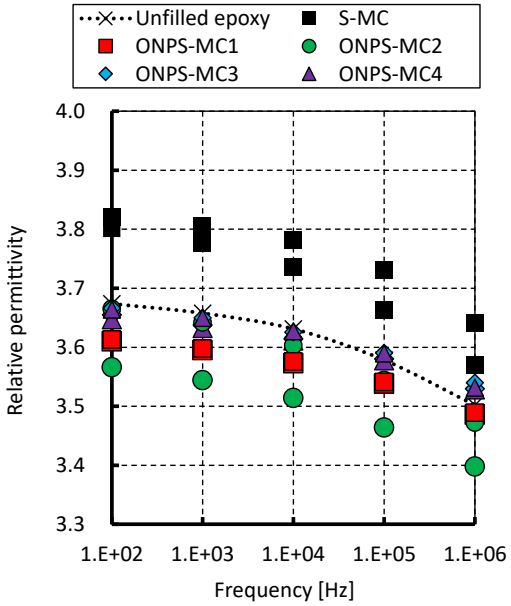


Figure 3. Frequency dependence of relative permittivity ε_r of unfilled epoxy, S-MC, and ONPS-MCs.

that ε_r for the ONPS fillers inside the ONPS-MCs is less than or equal to that of the epoxy resin.

The frequency dependence of the dielectric tangent of the unfilled epoxy, S-MC, and ONPS-MCs is shown in Figure 4. The dielectric loss tangent increases with the frequency. This involved a motion of the epoxy chains [27]. No differences among the samples were observed at the dissipation tangent in this experiment.

The relationship between ε_r at 1 MHz and the weight fraction of the filler is shown in Figure 5. ε_r for ONPS-MC1 is almost the same as that for the unfilled epoxy. ε_r of ONPS-MC2 is significantly lower than that for the unfilled epoxy. The permittivity of the unfilled epoxy and nonporous silica/epoxy composites fabricated in our fabrication process is consistent with the permittivity of the bubble-free epoxy composites [16]. These results indicates that ε_r for the ONPS Type 2 filler inside ONPS-MC2 is lower than that for the epoxy resin.

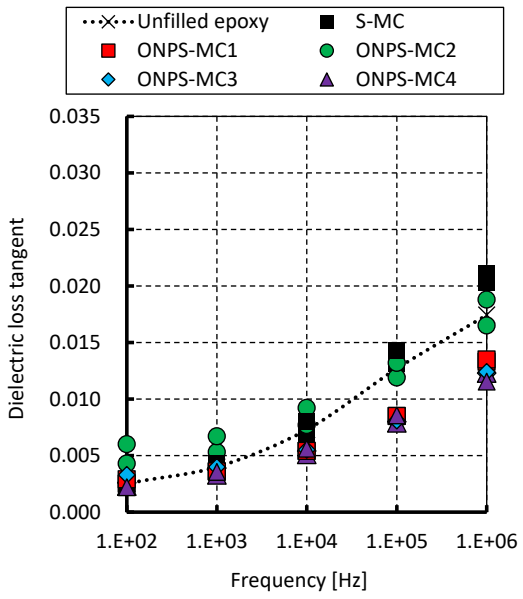


Figure 4. Frequency dependence of dielectric loss tangent of unfilled epoxy, S-MC, and ONPS-MCs.

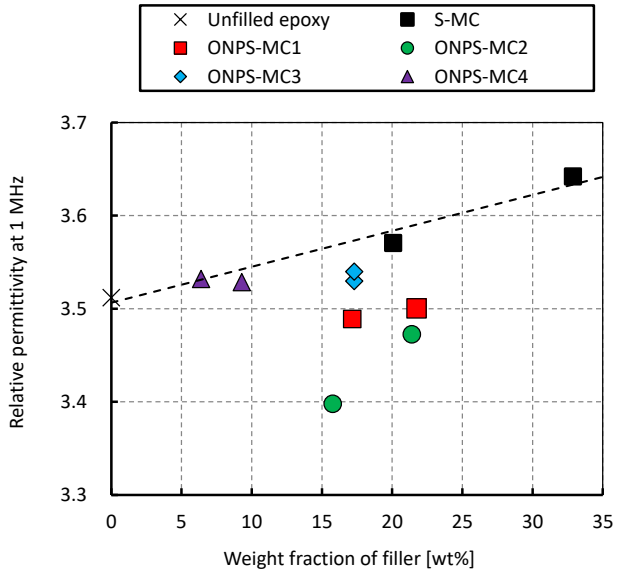


Figure 5. Relative permittivity at 1 MHz of unfilled epoxy, S-MC, and ONPS-MCs with different silica filler contents by weight.

4 DISCUSSION

4.1 PARTICLE PORE

The specific gravities of the ONPS-MCs were lower than that of S-MC. There are a few cases in which nanopores inside the open nanoporous silica particles filled in epoxy resin are observed by TEM [28] and by specific gravity measurement [29]. Since the particle material of our research is almost the same as that in these references, our investigation suggests that the air pores of the ONPS filler inside the ONPS-MCs can remain unfilled with epoxy resin. It is a future task to directly show the exsistence of pores inside ONPS filler. This may be achieved by TEM observation or electron energy loss spectroscopy (EELS). The specific gravity measurement is an indirect method for evaluating the existence of pores inside ONPS filler of the ONPS-MCs but is an effective method to clarify the pore volume required for realizing low-permittivity composite.

4.2 PARTICLE POROSITY

The particle porosity of the ONPS fillers inside the ONPS-MCs was estimated to investigate how much of the pores inside the ONPS fillers can remain unfilled with epoxy resin. Using the following equations, the particle porosity P (vol%) of the ONPS fillers inside the ONPS-MCs was calculated from the measured values of the specific gravity of the samples.

$$P = (1 - \rho_f/\rho_{SiO2}) * 100 \quad (2)$$

$$\rho_f = \frac{w_f}{(100 + w_f)/\rho_c - 100/\rho_e} \quad (3)$$

$$V_f = (\rho_c - \rho_e)/(\rho_f - \rho_e) * 100 \quad (4)$$

where ρ_f (g/cm^3) is the specific gravity of the ONPS filler, ρ_{SiO2} (g/cm^3) is the specific gravity of the nonporous silica material (2.26 g/cm^3), ρ_e (g/cm^3) is the specific gravity of the unfilled epoxy resin, ρ_c (g/cm^3) is the specific gravity of the ONPS-MC, and V_f (vol%) is the volume fraction of the filler.

Figure 6 shows the particle porosity of the ONPS fillers. The particle porosity of the ONPS fillers inside all the ONPS-MCs is lower than that of the ONPS fillers before filling them with epoxy resin as shown in Table 1. It is considered that the pores were partially filled with epoxy resin or that the pore structure was partially broken. The particle porosity of Type 1 and Type 2 inside the ONPS-MCs was about 20 vol%, whereas the particle porosity of Type 3 and Type 4 inside the ONPS-MCs was less than 6 vol%.

Figure 7a shows the relationship between the average pore diameter and the particle porosity of the ONPS fillers inside the

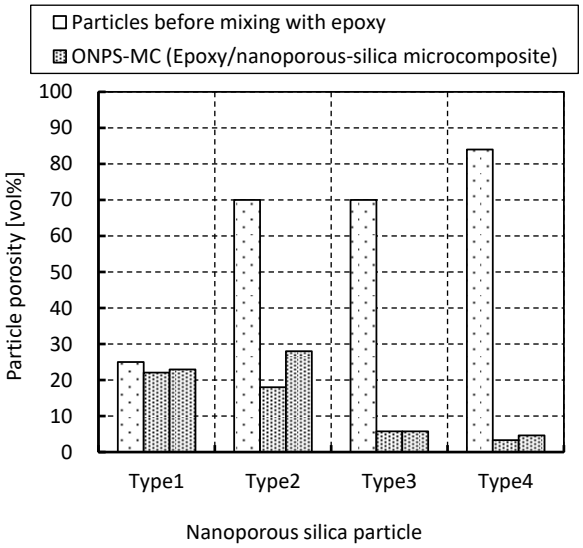
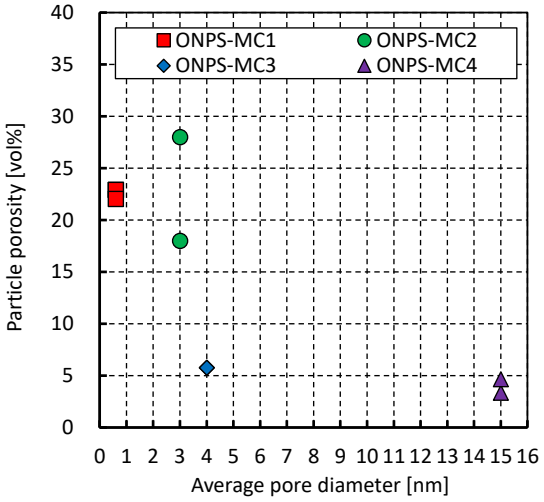
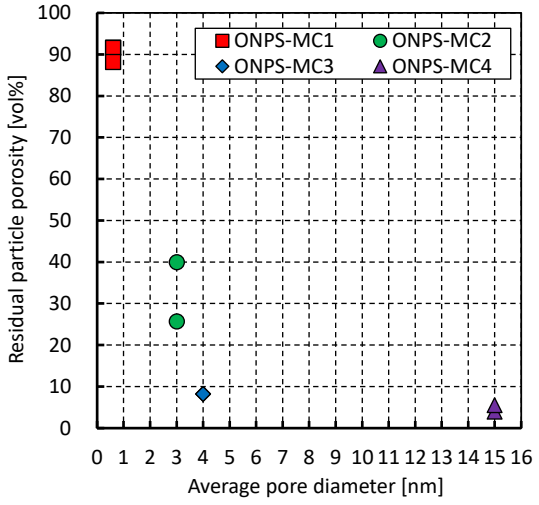


Figure 6. Porosity of open nanoporous silica fillers (Types 1-4) before mixing with epoxy and those filled with ONPS-MCs.

ONPS-MCs. It was found that the porosity of the ONPS filler whose pore diameter was 3 nm or less is more than 18%, whereas that of the ONPS filler whose pore diameter was 4 nm or more is less than 6 %. Figure 7b shows the residual particle porosity, which was obtained by dividing the particle porosity of the ONPS fillers inside the ONPS-MCs by the particle porosity of the ONPS fillers before filling with epoxy resin. The ONPS filler whose pore diameter was 3 nm or less had a residual particle porosity of more than 25%, whereas the ONPS filler whose pore diameter was 4 nm or more had a residual particle porosity of less than 8%. The above results may be related to the fact that the length distribution of the bisphenol A epoxy molecule is about 2 nm. That is, it is considered that the pores with a similar or smaller diameters than the length of the epoxy molecules are not filled with the epoxy molecules and that the pores with a diameter larger than the length of the epoxy molecules are partially filled with the epoxy molecules.



(a) Porosity of nanoporous silica filler

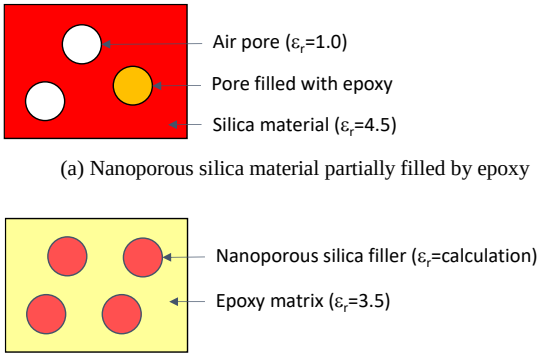


(b) Remaining porosity

Figure 7. Porosity of nanoporous silica filler and remaining porosity of ONPS-MCs with different pore diameters.

4.3 DIELECTRIC MODEL OF EPOXY/ONPS MICROCOMPOSITES

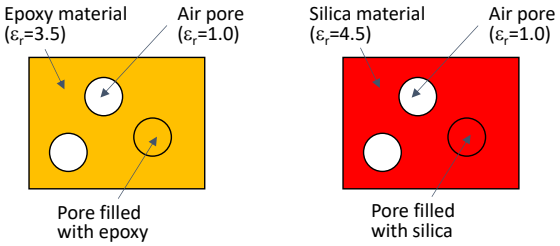
To quantitatively investigate the cause of the low permittivity of the ONPS-MCs, we constructed a model for estimating ε_r for the ONPS-MC that used the particle porosity and volume fraction of the filler. The pores of the ONPS fillers are considered to be partially filled with epoxy molecules as shown schematically in Figure 8. However, since it is unknown how the pores of the ONPS filler are partially filled with the epoxy resin, it is difficult to model ε_r for the ONPS filler inside the ONPS-MC. Therefore, we modeled the lower and upper limit values of ε_r for the ONPS filler as shown in Figure 9. Figure 9a shows the particle model with a lower limit of ε_r, where it is assumed that the parts other than the air pores are made of epoxy resin. Figure 9b shows the particle model with an upper limit of ε_r, where it is assumed that the parts other than the air pores are made of silica. Using these particle models, ε_r for the ONPS-MC was calculated.



(a) Nanoporous silica material partially filled by epoxy

(b) Nanoporous silica/epoxy composite

Figure 8. Schematics of epoxy composite with nanoporous silica filler whose nanopores are partially filled with epoxy resin.



(a) Nanoporous silica material with lower limit of ε_r

(b) Nanoporous silica material with upper limit of ε_r

Figure 9. Assumptions of lower and upper limits of permittivity for nanoporous silica material whose nanopores are partially filled with epoxy resin.

ε_r for the models in Figure 9a and b were calculated from a random arrangement model to obtain the permittivity of a composite material made of two materials (ε_c). ε_r in the random arrangement model is given by [29]

$$\varepsilon_c = \sqrt{\frac{(\varepsilon_f - \varepsilon_m) * V_f/100 + \varepsilon_m}{(1/\varepsilon_f - 1/\varepsilon_m) * V_f/100 + 1/\varepsilon_m}}\ , \qquad (5)$$

where ε_f is ε_r for the filler (pores or particles), ε_m is ε_r for the matrix (silica or epoxy), and V_f is the volume fraction (particle porosity or volume fraction of filler). This equation is geometric mean value of the parallel capacitor and the series capacitor.

Firstly, ε_r for the ONPS filler was calculated from equation (5). To obtain the upper limit of ε_r for the ONPS filler, the epoxy resin inside the pores was substituted with the silica material. To obtain the lower limit of ε_r for the ONPS filler, all the silica material was replaced with the epoxy resin. In this case, ε_c in equation (5) is ε_r for the ONPS filler, ε_f is ε_r for the pores, ε_m is ε_r for the silica or epoxy, and V_f is the particle porosity. The value of ε_r for air, epoxy resin and silica were 1.0, 3.48, and 4.5, respectively.

Secondly, ε_r for the epoxy/ONPS microcomposites was calculated from equation (5). In this case, ε_c is ε_r for the epoxy/ONPS microcomposites, ε_f is the upper limit or lower limit of ε_r for the ONPS filler, ε_m is ε_r for the epoxy resin, and V_f is the volume fraction of the filler.

4.4 LOW PERMITTIVITY DUE TO PARTICLE POROSITY

Figure 10 shows the relationship between the volume fraction of the filler and ε_r for the unfilled epoxy, S-MC, and the ONPS-MCs. The frequency of ε_r was 1 MHz and the volume fraction of the filler was obtained from equation (4). The measured values of ε_r for ONPS-MC2, ONPS-MC3, and ONPS-MC4 are within the range of the calculated values. Therefore, these measured values can be explained by the pore volume remaining inside the ONPS fillers. In particular, it was suggested that the lower permittivity of ONPS-MC2 than that of the unfilled epoxy resin is due to the existence of nanopore volumes remaining unfilled with epoxy resin.

On the other hand, the measured value of ε_f for ONPS-MC1 is higher than the calculated value. This cannot be explained by the fact that the material of the ONPS Type 1 filler used for ONPS-MC1 is aluminosilicate, which is different from silica. It is mainly because ε_f for aluminosilicate is 4.51, which is almost the same as that of silica (ε_f =4.5). Another possible reason is the influence of high permittivity impurity remaining inside the nanopores. Figure 11 shows the particle surface area dependence of ε_f for the ONPS-MCs. The particle surface area is calculated as the total pore volume inside the ONPS-MCs divided by the average pore diameter, which is considered to be correlated with the area of the silica walls inside the pores. It was confirmed that the particle surface area of ONPS-MC1 is the largest among the ONPS-MCs. The investigation indicated that the high permittivity impurity could remain on the particle surface including the inner surface of the nanopores. The impurity may be water. It will be necessary to investigate the cause such as the water adhering to the particle surface.

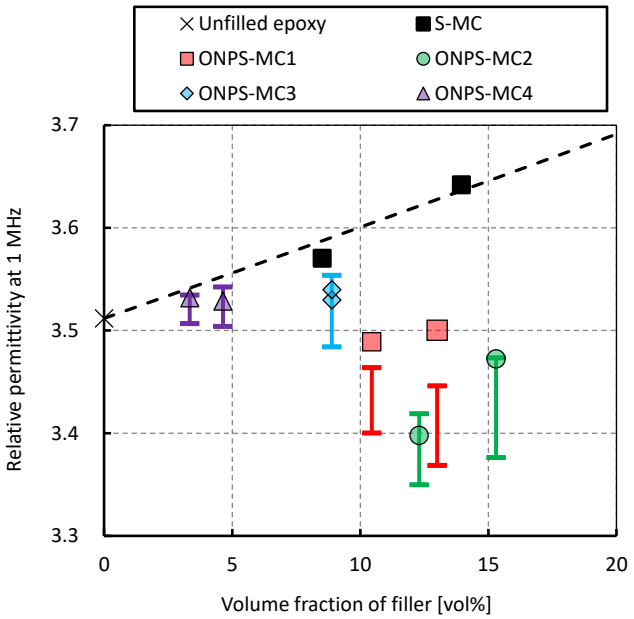


Figure 10. ε_r at 1 MHz with different silica filler content by volume for unfilled epoxy, S-MC, and ONPS-MCs. The two horizontal marks indicated on the vertical lines are calculated values obtained from the model with the estimated lower and upper limits of permittivity for mesoporous silica material with the nanopores partially filled with epoxy.

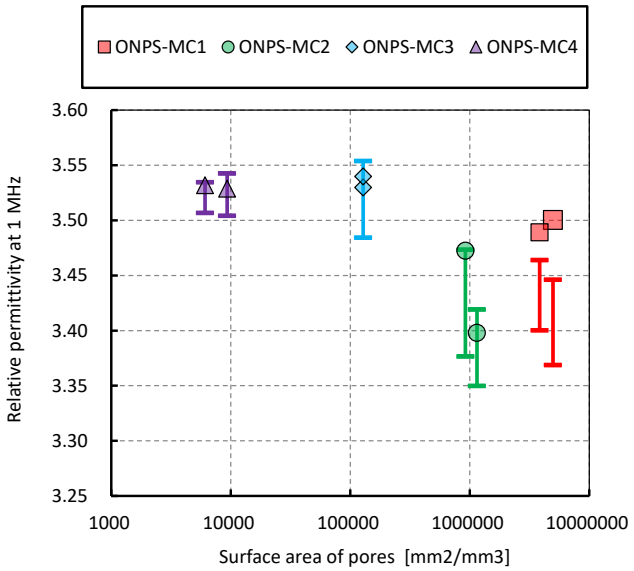


Figure 11. ε_r at 1 MHz with different surface areas of pore. The two horizontal marks indicated on the vertical lines are calculated values obtained from the model with the estimated lower and upper limits of permittivity for mesoporous silica material with the nanopores partially filled with epoxy.

5 CONCLUSIONS

To obtain epoxy/ONPS microcomposites whose permittivity was lower than the unfilled epoxy resin, the influence of the pore diameter of the ONPS fillers on the permittivity of epoxy/ONPS microcomposites was investigated. The epoxy/ONPS microcomposites were prepared using ONPS fillers with an average pore diameter ranging from 0.6 nm to 15 nm, and their permittivity and particle porosity were measured. The main results are as follows.

(1) The permittivity of the epoxy/ONPS microcomposites whose average pore diameter was 3 nm (ONPS-MC2) was found to be lower than that of the unfilled epoxy resin. This low permittivity can be explained quantitatively in terms of the nanopore volume.

(2) In the ONPS filler whose pore diameter was 3 nm or less (Type 1 and Type 2), more than 18% of the nanopore volume (particle porosity) could remain unfilled with epoxy resin.

(3) In the ONPS filler whose pore diameter was 4 nm or more (Type 3 and Type 4), the nanopore volume did not remain unfilled. It is considered that the pores were completely filled with epoxy resin or the pore structure was broken.

(4) The permittivity of the epoxy/ONPS microcomposite whose average pore diameter was 0.6 nm (ONPS-MC1) was found to be almost the same as that of the unfilled epoxy resin. This may be explained not by the particle porosity but by the high permittivity impurity remaining inside the ONPS-MC1 to increase the permittivity.

These results are expected to be useful for selecting ONPS fillers for epoxy/ONPS microcomposites that can be used as a low-permittivity insulating materials.

ACKNOWLEDGMENT

This research work was partly supported by JSPS Grants-in-Aid for Scientific Research Grant Number JP17H04917, JP16K14213.

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