

Dielectric property of Cu powder/polymer composites*

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Dielectric property of Cu/polymer thermoplastic composites was measured in high frequencies up to 1 GHz. Generally relative permittivity and dielectric loss of the composites increased as the increasing metal inclusion loading as the percolation theory predicts. The incorporation of the copper inclusion with surface antirust layer raised relative permittivity of the composite from 2.3 to 21.3 at the loading level of 39.3 vol. % at 500 MHz. When copper oxide layer was introduced to the filler surface, estimated increase of relative permittivity was ca. 25 %. Since metal composites with ordered structure would raise the relative permittivity of the composites, the cause of this increase in relative permittivity in the present study can be attributable to reduced compatibility of the filler surface and the polymer matrix which lowers randomness of particle distribution. On the other hand, dielectric loss of the composite with surface oxidized Cu powder was increased by ca. 50 % compared to that of the anti-rusted powder composite. This would be caused by skin effect that part of the induced current flows through the less conductive surface oxide layer.

Keywords: *Metal-polymer composite Dielectric property Surface modification.*

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1. Introduction

There has been a huge interest in 0-3 inorganic material-polymer composites recently, because they enable inexpensive industrial level realization of 3-D microwave devices and packages with advanced electric and mechanical properties in comparison to those counterparts made of pure ceramics or metals [1]. Particularly, composites using thermoplastic polymers attract industrial and academic interest because they have the additional advantage of simple, 3-D fabrication processes, such as injection moulding of electronic components. However, due to growing demands for composites with higher electrical and physi-

cal properties, such as relative permittivity, electrical or thermal conductivity, magnetic permeability, piezoelectric coefficient and so forth, filler loadings of such inorganic-polymer composites tend to exceed 50 vol. % to achieve the properties of required level [2–4]. Accordingly, processing of such composites becomes more difficult due to their extremely high melt viscosity to be realised industrially.

In the case of dielectric composites, insulator-conductor composites near the percolation threshold has been focused to solve this difficulty in production since it is anticipated that it can reduce the filler loading compared to the ceramic-polymer counterparts with relative permittivity of similar level, thus resulting in ease of fabrication. It is reported that molybdenum filled ceramic-metal composites (cermets) show an extremely high relative permittivity of 80 000 experimentally, although it needs to be sintered to be formed thus

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does not meet the industrial requirement described above [5]. In the case of thermoplastic insulator-conductor composites, poly(vinylidene fluoride)-nickel composites show high relative permittivity of 400 or even higher [6, 7].

It has been reported that the percolation threshold of a metal-insulator composite depends on various parameters such as size, shape and spatial distribution of the metal inclusion, adhesiveness between the inclusion and matrix and process condition employed [8, 9]. On the other hand, the authors reported earlier that surface modification of filler will affect the dielectric behaviour of ceramic-polymer composites [10, 11]. It is supposed that compatibility of surface of the fillers and the polymer matrices controls the dielectric nature and thickness of interphase at filler-polymer interface and also affect on dispersion state of the filler within the matrix thus affecting total dielectric property of the composites. Therefore, it can be anticipated that the surface chemical structure will affect the dielectric property even in the case of metal-polymer composites.

Copper is a potent metal inclusion suitable for such metal-polymer dielectric composites applicable in high frequency usage due to its low loss nature derived from excellent high conductivity, low cost from abundance in nature and high availability in industry. Generally, commercially available copper powders are antirust-treated to avoid corrosion or surface oxidation during distribution and use.

In this work, 0-3 metal-polymer composites using copper powders having anti-rusted and oxidized surfaces and polypropylene-graft-poly(styrene-*stat*-divinylbenzene) thermoplastic polymer alloy were fabricated and the effects of the surface structure of the metal inclusion on dielectric property of the composites up to 1 GHz were investigated.

2. Experimental section

2.1. Materials

Cu powders with a nominal diameter of 10 μm (denoted as Cu₁₀) were purchased from Thiokol/Ventron Division (Danvers, MA, USA). It

shows reddish metallic lustre therefore it is coated with antirust on the surface. Polypropylene-graft-poly(styrene-*stat*-divinylbenzene) (Dammondex® ER182, hereafter ER) with a density of 0.93 g/cm³ were supplied from NOF Co. (Tokyo, Japan). Concentrated hydrochloric acid was purchased from Alfa-Aesar. Ethanol (A grade) was purchased from Altia Oyj (Helsinki, Finland). All the materials and reagents were used as received. Deionised water was used for thinning the acid and washing after treatments of Cu₁₀ powder.

2.2. Introduction of copper oxide layer on Cu₁₀ powder

Cu₁₀ powder had surface antirust layer to avoid tarnishing. To clarify the effect of surface nature of the powders on dielectric property of the composites, the antirust layer of Cu₁₀ was removed and surface oxide layer was introduced instead (hereafter Cu_{10,OX}).

First, 50 g of Cu₁₀ powder was weighed into an Erlenmeyer flask. Then surface antirust layer was removed by 50 ml of 2 M HCl aqueous solution under magnetic stirring. The acid waste was discarded by decantation. Then resulting Cu powder was washed with ethanol for 2 times then with deionised water for 3 times. Waste solutions were discarded by decantation. The cleaned powder was collected by filtering over a membrane filter and dried in an oven for overnight at 70 °C. Finally, surface oxide layer was introduced by heating at 250 °C for 1 h in a furnace under air atmosphere. Since diluted HCl aqueous solution does not dissolve copper, change in particle size and specific surface area of copper powder by the treatment is expected as minimum.

2.3. Compounding of the composites and sample fabrication for measurements

Composites of copper powders and ER were fabricated using a small-scale twin-screw extruder (HAAKE MiniLab Rheomex CTW5, Thermo Scientific, Inc., USA). During compounding, the barrel temperature was set at 220 °C. Cu powder and ER pellets were supplied to the compounding machine in portions at a rotation rate of 60 rpm. After

the addition of the powder and the polymer pellets was completed, the mixture was mixed under circulation for further 20 min to render it as homogeneous as possible. Finally, the composite melt was extruded from the die of the extruder. Also the composite melt remaining in the circulation bypass was collected.

Samples for dielectric measurement were fabricated by an injection moulding machine (HAAKE MiniJet, Thermo Scientific, Inc., USA). The temperature of the cylinder and the mould were maintained at 230 °C and 40 ~ 100 °C, respectively, depending on the viscosity of the composite melts. Circular shaped samples with 18 mm diameter and ca. 1.3 mm thickness were prepared for the measurement. Surfaces of the samples were polished before the measurement to assure better contact with the electrodes of the measurement fixture.

2.4. Characterisation and testing methods

The surface structure of the as-received and surface treated Cu powders were characterised using an FT-IR spectrometer (IFS66, Bruker Optic GmbH, Germany) by the KBr disk method in transmission mode. Morphology of polished surface of obtained composites was observed using optical microscope (BX51, Olympus Co., Tokyo, Japan). Dielectric properties of the samples were measured using an RF Impedance/Material Analyzer (E4991A equipped with a 16453A fixture, Agilent Technologies, Inc., USA). The measurement temperatures were 20 ~ 23 °C. Densities of the composite samples were measured by Archimedes method. Filler loadings of the composite samples were calculated out from the density of each composite together with copper (8.96 g/cm³) and the polymer alloy (0.93 g/cm³).

3. Experimental results

A list of fabricated Cu/ER composites is shown in Table 1. Samples were named as *x*/ER*y*, where *x* indicates which Cu powder was used (Cu₁₀ and Cu_{10,ox}), and *y* represents volumetric filler loading in feed.

Table 1. A list of fabricated anti-rusted and oxidized Cu/ER composites.

Sample name	Powder used	Designed Cu loading/ vol.%	Measured Cu loading/ vol.%
Cu ₁₀ /ER10	Cu ₁₀	10	8.7
Cu ₁₀ /ER20		20	18.4
Cu ₁₀ /ER30		30	28.0
Cu ₁₀ /ER40		40	39.3
Cu _{10,ox} /ER10	Cu _{10,ox}	10	9.5
Cu _{10,ox} /ER20		20	18.6
Cu _{10,ox} /ER30		30	27.2
Cu _{10,ox} /ER40		40	36.6

3.1. Characterisation of the surface chemical structure of Cu powders

The transmission FT-IR spectra of the as-received Cu₁₀ powder and Cu_{10,ox} powder on which surface oxide layer was introduced are shown in Fig. 1. In the spectrum of Cu₁₀, we don't see any trace of copper oxide which is anticipated to appear as a peak at 620 cm⁻¹ [12], which is attributable to Cu₂O, therefore it can be concluded that Cu₁₀ powder is effectively anti-rusted. However, we could not acquire the chemical detail of the antirust layer since its peaks are quite weak. From the spectrum of Cu_{10,ox} powder, we can easily find a peak at 620 cm⁻¹. Therefore it can be concluded that the surface oxide layer was successfully introduced onto the Cu surface. Broad peaks around 3500 cm⁻¹ are attributable to surface absorbed water or surface hydroxyl groups.

3.2. Optical observation of the Cu composites

Optical micrographs of polished surfaces of Cu₁₀/ER10 and Cu_{10,ox}/ER10 composites with Cu loading of ca. 10 vol. % are shown in Fig. 2. It is clear that Cu particle in this study is consisted of large agglomerated particles with diameter of several tens of μm and small primary crystallites with diameter of micrometer order, despite of its nominal diameter of 10 μm. However from these figures, it seems that the Cu particles are dispersed almost uniformly in both Cu composites with surface antirust and oxide layers.

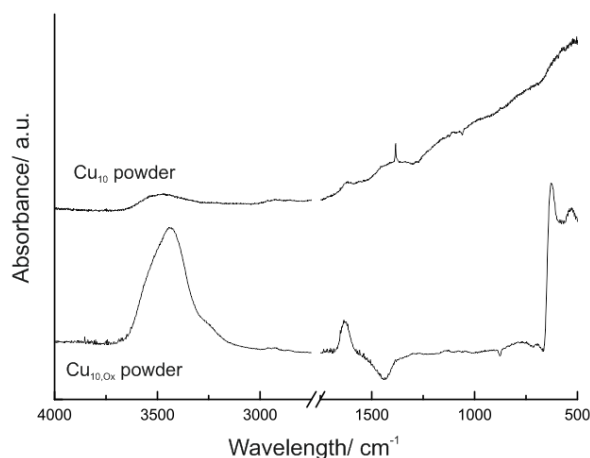


Fig. 1. Transmission FT-IR spectra of Cu_{10} and $\text{Cu}_{10,\text{Ox}}$ powders

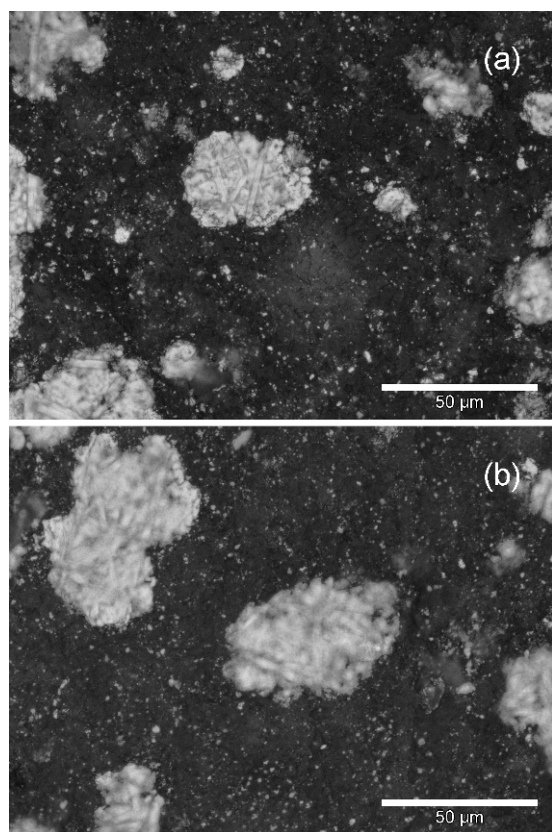


Fig. 2. Optical micrographs of (a) $\text{Cu}_{10}/\text{ER}_{10}$ and (b) $\text{Cu}_{10,\text{Ox}}/\text{ER}_{10}$ composites with filler loadings of ca. 10 vol. %. The white bars correspond to 50 μm .

3.3. Dielectric properties of the composites

Relative permittivity (ϵ') and dielectric loss tangent ($\tan \delta$) of the composites at 100 and 500 MHz as functions of measured filler loading are summarized in Figs. 3 and 4. Comparison of estimated ϵ' and $\tan \delta$ of Cu_{10} and $\text{Cu}_{10,\text{Ox}}$ composites at filler loading of 35 vol. % is shown in Fig. 5. Estimation of ϵ' and $\tan \delta$ was done by reading values from the guide lines in Figs. 3 and 4.

As we can see from Figs. 3 and 4, it is clear that both ϵ' and $\tan \delta$ of the composites increases with accelerating rate with increasing filler loading. Also it can be easily seen that ϵ' of $\text{Cu}_{10,\text{Ox}}/\text{ER}$ composites are almost the same level as that of Cu_{10}/ER composites when the filler loading is less than 30 vol. %. However, in the range above 30 vol. %, ϵ' of $\text{Cu}_{10,\text{Ox}}/\text{ER}$ composites are obviously higher than that of Cu_{10}/ER composites. The increase of ϵ' of $\text{Cu}_{10,\text{Ox}}/\text{ER}$ composite with filler loading of 35 vol. % is estimated as ca. 25 % in comparison to that of Cu_{10}/ER composite with the same loading. $\tan \delta$ of $\text{Cu}_{10,\text{Ox}}$ composites is larger than that of Cu_{10} composites in all the loading levels up to 40 vol. %.

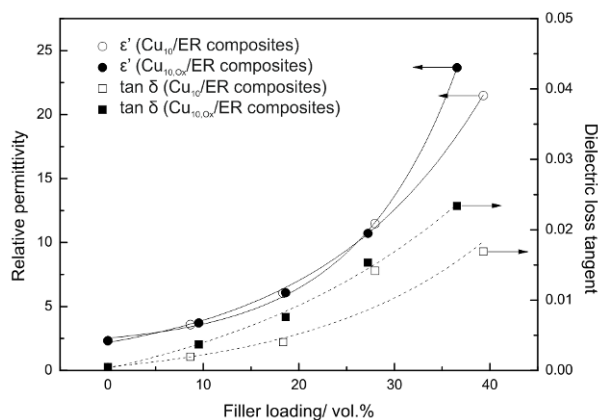


Fig. 3. Dependence of relative permittivity and dielectric loss tangent of Cu/ER composites on Cu filler loading at 100 MHz. The lines are guides for the eyes.

Frequency dependence of ϵ' of both the composites was found to be quite small in the frequency range of 100 to 500 MHz, but $\tan \delta$ shows consid-

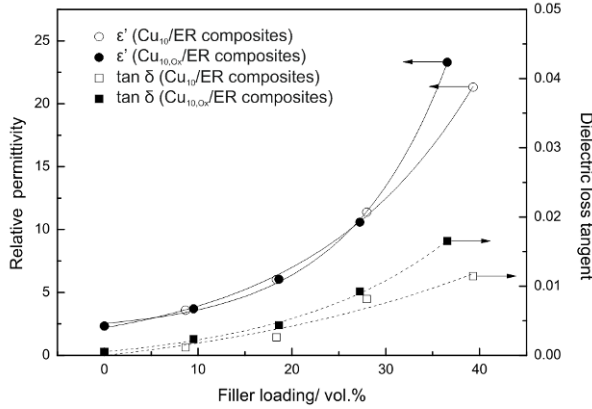


Fig. 4. Dependence of relative permittivity and dielectric loss tangent of Cu/ER composites on Cu filler loading at 500 MHz. The lines are guides for the eyes.

erable dependence (Fig. 5). As frequency increases, estimated $\tan \delta$ of Cu_{10} and $\text{Cu}_{10,0x}$ composites with 35 vol. % filler decrease from 0.014 to 0.010 and 0.022 to 0.015, respectively.

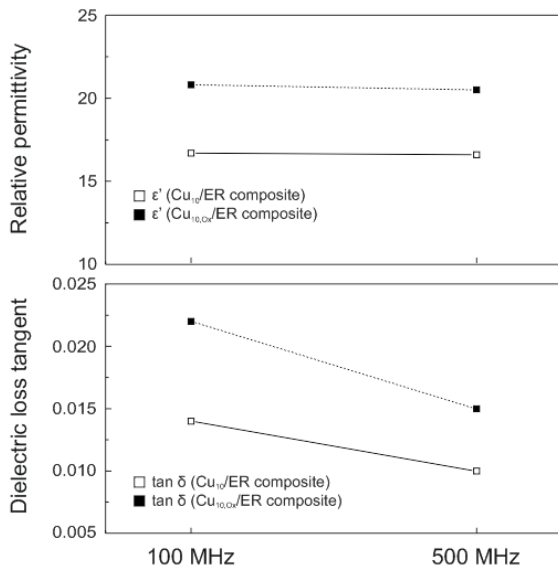


Fig. 5. Comparison of estimated relative permittivity and dielectric loss of Cu_{10}/ER and $\text{Cu}_{10,0x}/\text{ER}$ composites with filler loading of 35 vol. % at 100 and 500 MHz. The lines are guides for the eyes.

4. Discussion

It is well known that metal-insulator composites show metal-insulator transition as the metal concentration increases. The metal-insulator transition is generally characterised by an abrupt increase in electrical conductivity and a deviation of the real part of the relative permittivity. This behaviour is well explained by the percolation theory. When the metal concentration is low enough, each particle is isolated within the insulator matrix. Therefore the composite does not show electrical conductivity. When the metal concentration becomes higher, the particles start to form conductive network within the composite. Finally when the metal concentration is high enough, the particle network develops throughout the composite thus the composite become to show conductivity. This development of metal particle network occurs at certain narrow metal concentration region. This critical concentration is referred as the percolation threshold. According to the theory, ϵ' and $\tan \delta$ should obey the following power laws [7–9].

$$\epsilon' \propto (P_c - P)^{-s}, \text{ for } P < P_c \quad (1)$$

$$\tan \delta \propto (P_c - P)^{-r}, \text{ for } P < P_c \quad (2)$$

where s and r are the dielectric permittivity and the dielectric loss tangent critical exponents, respectively.

From the view point of dielectric property, a metal-insulator composite can be treated as a huge network of tiny capacitors connected in series or in parallel with each other. As the metal concentration increases, distance between close neighbours become shorter and shorter to increase the local capacitance higher since capacitance of a capacitor is inversely proportional to the electrode gap. Thus results in rapid increase of relative permittivity.

We could not see any abrupt increase in relative permittivity of both Cu_{10} and $\text{Cu}_{10,0x}$ composites, therefore it can be concluded that the percolation threshold of these composites may be located at certain filler loading higher than 40 vol. %. It is not strange since it is reported that percolation

threshold can locate above 50 vol. % in some composite system with high randomness of filler [7]. But the increase of relative permittivity of $\text{Cu}_{10,\text{Ox}}$ composites containing more than 30 vol. % of the filler indicates that the percolation threshold of $\text{Cu}_{10,\text{Ox}}$ /ER composite exists on some concentration not so higher than 40 vol. %, while it is obvious that the percolation threshold of Cu_{10} /ER composite is expected to be on higher filler concentration than that of $\text{Cu}_{10,\text{Ox}}$ composite.

Why this difference in percolation threshold occurs? The surface of $\text{Cu}_{10,\text{Ox}}$ is covered by Cu_2O layer introduced by heating in air atmosphere as it can be seen from Fig. 2. Cu_{10} is covered by organic antirust layer although detailed chemical structure of the coating layer is not known. As the authors indicated in the earlier report, compatibility of filler and polymer matrix increases when surface organic layer is introduced to the filler surface. As a result, filler with organic surface can be dispersed better than filler with inorganic surface in a polymer matrix [11]. In the case of this study, $\text{Cu}_{10,\text{Ox}}$ powder has less compatibility compared to Cu_{10} powder to the modified polypropylene matrix. Consequently, randomness of filler dispersion would be lower in the case of $\text{Cu}_{10,\text{Ox}}$ composites. Reduced randomness of filler dispersion means that the conductive filler network develops easier and local capacitors with smaller gap increases. As a result, the percolation threshold of $\text{Cu}_{10,\text{Ox}}$ composites can be lowered compared to Cu_{10} composites.

The cause of increment in $\tan \delta$ of $\text{Cu}_{10,\text{Ox}}$ composites can be attributable to conductivity of the surface oxide layer. At higher frequencies, when AC current is applied to a conductor, electric current is concentrated toward the surface of the conductor. This is well known as skin effect. The surface of $\text{Cu}_{10,\text{Ox}}$ powder is covered by Cu_2O , which has far lower conductivity than that of bulk Cu although it is categorised as semi-conductive. On the other hand, the surface of Cu_{10} powder is covered by antirust layer, which might behave as an insulator layer. When AC electric field is applied to the Cu_{10} composites, induced current flows through the surface of the Cu phase which has quite low resistivity. In the case of $\text{Cu}_{10,\text{Ox}}$ composites, part of

induced current flows through more resistive oxide layer, resulting in higher ohmic loss. Consequently, the dielectric loss of $\text{Cu}_{10,\text{Ox}}$ composites would be increased compared to that of Cu_{10} composites.

5. Conclusion

In this study, dielectric property of copper-polymer thermoplastic composites was investigated. It is observed that use of copper filler covered by oxide will raise the relative permittivity of the metal-polymer composites in comparison to the use of organic antirust coated copper powder. It is also suggested that introduction of oxide instead of organic antirust would lower the percolation threshold of the composite. The cause of these phenomena can be attributable to reduced randomness of the filler due to difference in compatibility of the two copper powders with different surface structure. Dielectric loss of the composites with the oxide covered Cu powder was higher than that of the composites from anti-rusted powder. This would be caused by the skin effect under AC electric field that part of induced current flows through semi-conductive oxide layer.

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References

- [1] SEBASTIAN M. T., JANTUNEN H., *Int. J. Ceram. Technol.*, 7 [4] (2010), 415.
- [2] HU T., JUUTI J., JANTUNEN H., VILKMAN T., *J. Eur. Ceram. Soc.*, 27 (2007), 3997.
- [3] KONG L. B., LI Z. W., LIN G. Q., GAN Y. B., *IEEE Trans. Magn.*, 43 [1] (2007), 6.
- [4] YAO J. L., XIONG C. X., DONG L. J., CHEN C., LEI Y. A., CHEN L., LI R., ZHU Q. M., LIU X. F., *J. Mater. Chem.*, 19 (2009), 2817.
- [5] PECHARROMAN C., MOYA J. S., *Adv. Mater.*, 12 [4] (2000), 294.
- [6] DANG Z. M., LIN Y. H., NAN C. W., *Adv. Mater.*, 15 [19] (2003), 1625.
- [7] PANDA M., SRINIVAS V., THAKUR A. K., *Appl. Phys. Lett.*, 93 (2008), 242908.

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- [8] LI Y. J., XU M., FENG J. Q., DANG Z. M., Appl. Phys. Lett., 89 (2006), 072902.
- [9] ZOIS H., APEKIS L., MAMUNYA YE. P., J. Appl. Polym. Sci., 88 (2003), 3013.
- [10] SONODA K., HU T., JUUTI J., MORIYA Y., JANTUNEN H., J. Eur. Ceram. Soc., 30 (2010), 381.
- [11] SONODA K., JUUTI J., MORIYA Y., JANTUNEN H., Compos. Struct., 92 (2010), 1052.
- [12] BALAMURUGAN B., MEHTA B. R., Thin Solid Films, 396 (2001), 90.

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