Preparation and characterization of isotactic polypropylene/MgO composites as dielectric materials with low dielectric loss

Susumu TAKAHASHI, Yusuke IMAI,* Akinori KAN,[†] Yuji HOTTA* and Hirotaka OGAWA

Graduate School of Science and Technology, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 4688502, Japan

*National Institute of Advanced Industrial Science and Technology (AIST),
2268-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan

The dielectric and thermal properties of isotactic polypropylene/magnesium oxide (0–30 vol %) composites were investigated. The dielectric constant of the composite material increased from 2.3 to 3.2 on increasing the MgO content and the observed variation of the dielectric constant with the MgO fraction was in good agreement with the Bruggeman mixing model. Low dielectric losses at microwave frequencies, on the order of 10^{-4} , were obtained using highly crystalline MgO as the filler, and it was also found that the use of larger MgO particle sizes led to further reductions in the dielectric loss. The absolute value of temperature coefficient of the dielectric constant as well as the coefficient of thermal expansion decreased with increasing MgO content, while thermal conductivity increased with increasing MgO content in a manner which could be predicted using the Maxwell-Garnett mixing model.

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1. Introduction

In recent years, communications systems such as high-speed wireless and collision avoidance radar have increasingly utilized the high-frequency region above 10 GHz, since this region has high capacity and allows high speed information transfer. Dielectric materials composed of polymers and inorganic compounds have been widely used as resonators, antennae, and substrates within these wireless communications systems. Dielectric substrates intended for high-speed information transfer applications are required to have a low dielectric constant (ϵ_r) in order to reduce the propagation delay time, which is proportional to the square root of the dielectric constant. In addition, it is also necessary for the dielectric substrate to exhibit low dielectric loss ($\tan \delta$), a quantitative measure of the dissipation of energy resulting from the interaction of electromagnetic waves with the material.¹⁾ The dielectric attenuation coefficient (α_d), a measure of the attenuation of an electromagnetic wave during propagation, is proportional to the multiplication of $\tan \delta$ and the square root of ϵ_r , and hence low values of both ϵ_r and $\tan \delta$ result in a small α_d coefficient at high frequencies. For practical applications, it is also important that these dielectric properties are stable over temperature variations. The temperature coefficient of the dielectric constant ($TC\epsilon$) is the parameter which indicates how much the dielectric constant changes with temperature, and thus smaller absolute values of $TC\epsilon$ are desirable. In addition to optimal dielectric properties, high thermal conductivity and a low coefficient of thermal expansion are also required to have high device heat dissipation and good conductor adhesion, respectively.

The fabrication of composites consisting of a polymer matrix filled with ceramic particles is considered to be one of the most promising approaches to producing suitable dielectric materials. To date, a variety of polymer/ceramic composites, including

polystyrene/MgTiO₃, polyethylene/Sm₂Si₂O₇, and polytetrafluoroethylene/TeO₂, have been investigated for high-frequency applications.^{2)–4)} These composites exhibit ϵ_r values in the range of 2 to 8 and $\tan \delta$ values on the order of approximately 10^{-3} . Such polymer/ceramic materials, however, require further reductions in dielectric loss before they are suitable for high-frequency applications. Isotactic polypropylene (iPP) is a thermoplastic polymer which has a low dielectric constant ($\epsilon_r = 2.3$) and a low dielectric loss ($\tan \delta < 2 \times 10^{-4}$), while the filler MgO has an ϵ_r of 9.6, which is relatively low compared to other inorganic materials, and its $\tan \delta$ can be as low as 0.5×10^{-4} .⁵⁾ In addition to these useful dielectric properties, MgO also possesses high thermal conductivity (60 W/m·K) and therefore is considered an attractive candidate as a dielectric filler. The aim of this study was therefore to develop polymer/ceramic composites based on the application of iPP and MgO as the matrix polymer and filler. These iPP/MgO composites were prepared by a melt mixing method, and the effects of processing conditions and composition on their dielectric and thermal properties were studied. Moreover, the classification of MgO was carried out and the effects of filler particle size on dielectric properties were also characterized in this study.

2. Experimental procedures

iPP (Japan Polypropylene Corp., NOVATEC-PP MA3) and MgO (Ube Material Industries, Ltd., MgO-2000A) were used as the matrix polymer and particulate filler, respectively. MgO-2000A is a high-purity monocrystalline powder manufactured by the vapor phase oxidation of magnesium. Since MgO-2000A was found to contain particles with a fairly wide range of sizes, the classification of MgO-2000A was carried out into two different particle size portions, based on the controlled centrifugation of a dispersion in ethanol. Both as-received and classified MgO fillers were used for composite preparation in order to study the effects of particle size on the dielectric properties.

[†] Corresponding author: A. Kan; E-mail: akan@meijo-u.ac.jp

iPP/MgO composites were prepared by melt mixing at 200°C using a kneading machine (HAAKE MiniLab Rheomex CTW5), and pelletized. The number of mixing cycles and the mixing atmosphere (either with or without a nitrogen gas flow of 10 L/min) were varied in order to clarify the effects of processing conditions on the dielectric properties of the resulting composites. The pelletized composites were subsequently molded into plate samples with dimensions of 50 mm × 50 mm × 1 mm at 200°C using a simple injection molding machine (Imoto Machinery Co., Ltd.). The thermal conductivity of each sample was determined using the heat flow method (Eko-HC-110) and coefficients of thermal expansion (CTE) were measured by the differential thermal expansion method (Bruker axs TD 5200SA-S16). The relative densities of composites were measured by Archimedes method.

The dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) values of the composites were estimated from the resonant frequency of the TE₀₁₁ mode at approximately 12 GHz, employing the circular cavity resonance method^{6,7)} and a network analyzer (Agilent 8720 ES). Measurements were carried out in a temperature controlled chamber over the temperature range of 0–80°C. The coefficients of thermal expansion of both the composites and the copper cavity were measured in order to allow calculation of the ϵ_r and $\tan \delta$ values, and the relative surface resistivity of the cavity at each temperature was also determined before the measurement of resonant frequency. Unless otherwise noted, ϵ_r and $\tan \delta$ values at 23–25°C are reported in the following results. The temperature coefficient of the dielectric constant (TC ϵ) was calculated from the dielectric constants at 0 and 80°C. The MgO particles and the fracture surfaces of iPP/MgO composites were

observed via field emission scanning electron microscopy (Hitachi FE-SEM S-4300). Samples for Fourier transform infrared spectroscopy (FT-IR) were prepared as 0.3 mm films by hot pressing at 200°C and FT-IR spectra were obtained in the transmission mode using a Perkin-Elmer Spectrum GX FT-IR instrument.

3. Results and discussion

3.1 Effects of mixing conditions on dielectric properties

Several different mixing conditions were initially applied to determine the optimal composite manufacturing procedure. In this section, iPP/MgO composites were prepared using either one or two mixing cycles and either with or without the application of a nitrogen flow. All these sections used the as-received MgO as the filler. The dielectric properties of a series of composites produced in this manner, all containing 20 vol% MgO, are provided in **Table 1**. From these data, it is evident that the ϵ_r values of the composites are almost constant over the various mixing conditions, within the accuracy of the measurement. The FE-SEM images of the fractured surfaces, shown in **Fig. 1**, also demonstrate that a single mixing cycle is sufficient to disperse MgO particles uniformly throughout the matrix. Conversely, the value of $\tan \delta$ appears to be significantly affected by the mixing conditions. The dielectric loss of the composite prepared using two mix cycles and without nitrogen flow is drastically increased compared to the composites produced using a single mix cycle, although the dielectric loss is slightly improved by the application of nitrogen flow. These results suggest that the observed change in dielectric loss may be due to thermal degradation of

Table 1. Dielectric properties of iPP/MgO composites for different mixing conditions

Composition	Mixing times	Atmosphere	f_0 (GHz)	ϵ_r	$\tan \delta$ ($\times 10^{-4}$)	Relative density (%)
iPP/MgO–20 vol %	1	N ₂	10.66	3.117 ± 0.004	1.93 ± 0.06	97.3
	1	Air	10.57	3.208 ± 0.003	2.05 ± 0.05	99.1
	2	Air	10.73	3.155 ± 0.009	4.90 ± 0.19	98.5

Fig. 1. FE-SEM photographs of fractured surface of iPP/MgO composites with different volume fraction.

the iPP during mixing. **Figure 2** shows the FT-IR spectra of iPP samples produced using the same conditions as described above. In these spectra, the iPP processed using two mix cycles exhibits increased absorption at 1720 cm^{-1} compared with the other two samples. The absorption at 1720 cm^{-1} can be assigned to the C=O stretching bond of a carboxylic acid,⁸⁾ indicating that oxidation of iPP takes place during processing in air. It is known that polar group in polymer increases dielectric loss of polymers.^{8),9)} Thermal oxidation during mixing under air atmosphere caused the increased dielectric loss. Based on these results, a single mix cycle under a nitrogen flow was employed in the following study.

3.2 Dielectric and thermal properties with different MgO concentrations

In this section, the dielectric and thermal properties of iPP/MgO composites prepared using different volume fractions of MgO filler are discussed. As-received MgO filler was again used in this section.

The FE-SEM photographs in Fig. 1 show that MgO added to the composite up to 30 vol% is uniformly distributed in the iPP matrix under the optimized mixing conditions. **Figure 3(a)** plots the ϵ_r values of the iPP/MgO composites as a function of the MgO volume percent. The ϵ_r increased with increasing the volume fraction of the MgO filler, since the ϵ_r of MgO is higher than that of the iPP matrix. These experimental results are compared with two well-known theoretical mixing rules: the Maxwell-Garnett and Bruggeman models. These models are expressed respectively by the equations

Fig. 2. FT-IR spectra of iPP with different mixing conditions.

Fig. 3. Variation of (a) dielectric constant and (b) dielectric loss of iPP/MgO composites as a function of volume fraction of MgO.

$$\frac{\epsilon_c - \epsilon_m}{\epsilon_c + 2\epsilon_m} = V_f \frac{\epsilon_f - \epsilon_m}{\epsilon_f + 2\epsilon_m} \quad (1)$$

and

$$V_f \frac{\epsilon_f - \epsilon_c}{\epsilon_f + 2\epsilon_c} + (1 - V_f) \frac{\epsilon_m - \epsilon_c}{\epsilon_m + 2\epsilon_c} = 0, \quad (2)$$

where ϵ_c , ϵ_f , and ϵ_m are the dielectric constants of the composite, filler, and matrix, respectively, and V_f is the volume fraction of the filler. Both models assume that filler particles are dispersed in isolation, and connection between particles is not taken into account. Also, no consideration was included for effects from interfacial region between matrix and filler. The difference between these two models is based on the designation of the host medium in which the filler is embedded; the Maxwell-Garnett model assumes that the matrix material is the host medium, while the Bruggeman model assumes that the composite itself is the host.¹⁰⁾ For the dielectric constants of the composites, the result in Fig. 3(a) indicated that Bruggeman model gave better estimation especially in the higher filler concentration region.

Figure 3(b) plots the dielectric loss values of the composites. The $\tan \delta$ values evidently increase with increasing volume fractions of the MgO filler, but remain in the order of 10^{-4} even at the highest MgO concentration. These values are quite low as compared with the dielectric composites reported so far.¹¹⁾ It is considered that the high crystallinity of vapor phase synthesized MgO filler allowed the limited increment of the dielectric loss. The increase of $\tan \delta$ can be attributed to the increase of the interfacial polarization between the polymer and filler with increasing the filler amount.¹²⁾

The temperature coefficient of dielectric constant ($TC\epsilon$) and the coefficient of thermal expansion (CTE) of iPP/MgO composites are shown in **Fig. 4**. By the addition of MgO filler up to 30 vol%, the $TC\epsilon$ reduced from -260 to $-160\text{ ppm}/^\circ\text{C}$. CTE also decreases from 160 to 80 $\text{ppm}/^\circ\text{C}$ with increase in MgO filler.

The variation of thermal conductivity of iPP/MgO composites as a function of MgO concentration is shown in **Fig. 5**. Thermal conductivity of iPP/MgO composites was increased with MgO concentration, since thermal conductivity of MgO is higher compared to that of iPP. A comparison of these experimental data with the aforementioned two mixing models was again carried out. The Maxwell-Garnett and Bruggeman models were applied to thermal conductivity by replacing the dielectric constants ϵ_c , ϵ_f , and ϵ_m in Eq. (1) and (2) with thermal conductivities k_c , k_f , and k_m , respectively. In the case of thermal conductivities, the Maxwell-Garnett model shows a better correspondence with the observed experimental values, while the Bruggeman equation

predicts much higher thermal conductivity than those observed, especially at higher filler concentrations.

The dielectric constant describes the interaction between an electromagnetic wave and the composite material, whereas thermal conductivity is related to the transfer of thermal vibrations within the material. It is not clear a priori which model gives better estimation for different properties. In the iPP/MgO system, it was found that Bruggeman model was applied better for the dielectric constant, while thermal conductivity was described well by Maxwell-Garnett model.

3.3 Effects of MgO particle size on dielectric properties

It was found the as-received MgO filler have fairly large size distribution [Fig. 6(a)]. As mentioned earlier, it is considered that the major origin of the increase in dielectric loss in composite materials is the interface between matrix and filler. Therefore, it is expected that larger particle size results in reduction of interface area and smaller dielectric loss deterioration. Thus, the classification of as-receive MgO was performed to confirm this hypothesis.

Fig. 4. Variation of temperature coefficient of dielectric constant (TCε) and coefficient of thermal expansion (CTE) of iPP/MgO composites as a function of volume fraction of MgO.

Fig. 5. Variation of thermal conductivity of iPP/MgO composites as a function of volume fraction of MgO.

Classification of the as-received MgO filler was successfully carried out by the controlled centrifugation from the ethanol dispersion into two classes [Figs. 6(b) and 6(c)]. Smaller portion had average particle size of 73 ± 27 nm, while it was 1.1 ± 0.3 μm for larger one. These samples were assigned the label MgO-nano and MgO-micro, respectively.

Composites with iPP containing 20 vol % of each classified MgO filler were prepared, and the dielectric properties were evaluated. The results are summarized in Table 2. Dielectric constants were found to be almost identical. In contrast, remarkable differences were observed between the dielectric loss values of the samples. $\tan \delta$ of 2.0×10^{-4} was obtained for the composite when 20 vol % MgO without classification was loaded. Utilization of MgO-micro decreased the $\tan \delta$ to 1.3×10^{-4} , while MgO-nano resulted in the increase of $\tan \delta$ to 2.9×10^{-4} . This result clearly indicates that it is the iPP-MgO interface area that governs the change in the dielectric loss in the composites. Thus, utilization of larger particle size filler is the effective way to obtain dielectric composites with lower dielectric loss.

4. Conclusions

The iPP/MgO composites manufactured in this work exhibited low ϵ_r and low $\tan \delta$ values when tested at high frequencies. The variation of ϵ_r with the composition of the material could be estimated with reasonable accuracy using the Bruggeman mixing rule. $\tan \delta$ values in the order of 10^{-4} are quite low as composite dielectrics. Utilization of MgO with high crystallinity and large particle size was important to maintain low dielectric loss. Small absolute values of TCε and CTE were also achieved by increasing MgO fraction. The compositional dependence of thermal conductivity could be successfully estimated by using Maxwell-Garnett model. It is considered that the composites approach is promising for developing dielectric materials for high frequency applications.

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Fig. 6. FE-SEM photographs of (a) as-received MgO, (b) MgO-nano and (c) MgO-micro.

Table 2. Dielectric properties of iPP/MgO composite used different MgO filler size at 20 vol % loading

Composition	f_o (GHz)	ϵ_r	$\tan \delta$ ($\times 10^{-4}$)	Relative density (%)
iPP/as-received MgO	10.66	3.117 ± 0.004	1.93 ± 0.06	97.3
iPP/MgO-micro	10.65	3.180 ± 0.004	1.34 ± 0.05	98.2
iPP/MgO-nano	10.64	3.162 ± 0.001	2.93 ± 0.05	98.4

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