Effects of interaction between filler and resin on the glass transition and dielectric properties of epoxy resin nanocomposites

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Abstract: Polymer nanocomposites are known to exhibit superior insulation performance. As a reason for this, interactions at the filler/polymer interfaces are widely believed to take an important role. To obtain information on this, the glass transition temperature ($T_g$), complex permittivity ($\epsilon^*$), and conductivity ($\sigma$) were measured in various epoxy resin nanocomposites. As a result, all the parameters ($T_g$, $\epsilon^*$, and $\sigma$) decrease when the filler is MgO, whereas $T_g$ decreases and $\epsilon^*$ and $\sigma$ increase when the filler is TiO$_2$. This fact clearly indicates that the filler exerts significant influences on various properties such as molecular motions in the host epoxy resin, and that these influences differ profoundly depending on the filler material.

1 Introduction

Polymer nanocomposites are attracting our attention as emerging insulating materials with superior dielectric properties [1–7]. As a reason for the superior properties, interactions between the filler and the polymer are widely believed to take an important role. For example, the influence of the dispersion of guest nano-metric fillers in the host polymer on the dielectric property is explained by assuming the ‘multi-core model’. In this model, the interaction zone between the guest and the host is assumed to have a layered structure, typically consisting of three layers [3]. However, the evidence of the presence of such interactions has scarcely been reported. In this research, we made various epoxy resin nanocomposites using TiO$_2$ and MgO with differing sizes as their fillers and measured the glass transition temperature ($T_g$), complex permittivity ($\epsilon^*$), and conductivity ($\sigma$) as three typical properties that should reflect and depend on the properties of the host polymer.

As a result, all the three physical quantities ($T_g$, $\epsilon^*$, and $\sigma$) decrease when MgO is added to epoxy resin. However, when the filler is TiO$_2$, $\epsilon^*$ and $\sigma$ increase obviously although $T_g$ decreases similarly. These results seem to be convincing evidence of the occurrence of a certain interaction at the interfaces between the filler and the resin. However, the effect of such interaction differs profoundly depending on the filler material.

2 Experimental method

As mentioned above, we used TiO$_2$ and MgO as nanofillers added to epoxy resin. Fig. 1 shows typical transmission electron micrographs (TEM) observed for TiO$_2$ and MgO particles. The two fillers are apparently of a nearly cubic shape and the average side length of the cube is around 35 nm for the TiO$_2$ fillers shown in Fig. 1a, while it is around 200 nm for the MgO fillers shown in Fig. 1b.

The samples used in this experiment are listed in Tables 1 and 2. In these tables, the first capital letters T and M in the composite names stand for TiO$_2$ and MgO, respectively, whereas EF and EA represent bisphenol A and F epoxy resins, respectively. The numbers before and after the dash stand for the filler content in vol % and average filler size, respectively. Note that the filler size is shown in nm and μm in Tables 1 and 2, respectively.

In the case of TiO$_2$, we prepared five kinds of epoxy resin nanocomposites listed in Table 1. The host resin is bisphenol F epoxy resin (jER806, Mitsubishi Chemical) cured with acid anhydride curing agent (HN2000, Hitachi Chemical). The filler

![Fig. 1 TEM images of TiO$_2$ and MgO particles. The black horizontal bar in each figure represents the length of 100 nm. (By the courtesy of the manufacturing companies of the two fillers)](image-url)
Table 1: Samples of epoxy/TiO$_2$ nanocomposites and their compositions in vol%

| Sample   | EF | T5-35 | T10-35 | T20-35 | T5-15 | T5-140 |
|----------|----|-------|--------|--------|-------|--------|
| TiO$_2$ (15 nm) | —  | —     | —      | —      | —     | —      |
| TiO$_2$ (35 nm) | —  | —     | —      | —      | —     | 5      |
| TiO$_2$ (140 nm) | —  | —     | —      | —      | —     | 5      |

Table 2: Samples of epoxy/MgO nanocomposites and their compositions in vol%

| Sample   | EA M 1.7–10 | M 3.6–10 | M 9.7–10 | M 1.7–3 | M 3.6–3 | M 9.7–3 | M 1.7–0.2 | M 3.6–0.2 | M 9.7–0.2 | M 3.6–0.05 |
|----------|--------------|----------|----------|----------|----------|----------|------------|------------|------------|------------|
| MgO (4–10 μm) | —  | 1.7      | 3.6      | 9.7      | —        | —        | —          | —          | —          | —          |
| MgO (3 μm) | —  | —        | —        | —        | 1.7      | 3.6      | 9.7        | —          | —          | —          |
| MgO (200 nm) | —  | —        | —        | —        | —        | 1.7      | 3.6        | 9.7        | —          | —          |
| MgO (50 nm) | —  | —        | —        | —        | —        | —        | —          | —          | 1.7        | 3.6        | 9.7        | —          | —          | 3.6        |

Fig. 2: Frequency spectra of complex permittivity, $\varepsilon_r'(a)$ and $\varepsilon_r''(b)$, observed for sample T5-35, measured at temperatures of 20 (white circle), 40 (black circle), 60 (yellow up-pointing triangle), 80 (yellow open up-pointing triangle), 100 (green square), 140 (blue down-pointing triangle), 160 (open blue down-pointing triangle), 180 (open red diamond), and 200 (red diamond) °C.

(a) Real part, (b) Imaginary part

was dispersed in the epoxy resin as uniformly as possible using mixer (Filmix 40-L, Primix). The filler content is also listed in Table 1. The resin was first cured at 120°C for 2 h and then cured second for 4 h at 180°C in air.

In the case of MgO, we prepared ten kinds of epoxy resin nanocomposites listed in Table 2. The host resin is bisphenol A epoxy resin (JEER828, Mitsubishi Chemical) cured with acid anhydride curing agent (HN5500, Hitachi Chemical). The resin was first cured at 100°C for 5 h and then cured second for 5 h at 150°C in air. Since some fillers are 4 to 10 μm in size, such samples would be better to be called micro-composites.

For both TiO$_2$ and MgO fillers, the sample thickness was adjusted to about 100 or 500 μm using a stainless steel mould. The 100-μm samples were mainly used to measure electric currents, while the 500-μm samples were used to measure complex permittivity.

The thermal property, especially the glass transition temperature ($T_g$), was measured by a differential scanning calorimeter (DSC, DSC8500, Perkin Elmer) using a sample fragment of about 10 mg put on an aluminium pan. In addition, electrical conductivity $\sigma$ was calculated using the DC current values measured during the last 100 s of voltage application as mentioned above, and its real part $\sigma'$ and imaginary part $\sigma''$ of complex relative permittivity were also measured in a frequency range from $10^{-2}$ to $10^6$ Hz by applying ac $V_{rms}$ using an impedance analyser (SI126096W, Solartron).

3 Results

Fig. 2 shows $\varepsilon_r'$ and $\varepsilon_r''$ as a function of frequency, measured at various temperatures for the sample T5-35 containing 35 nm TiO$_2$ fillers at the content of 5 vol%. It is clearly demonstrated that both $\varepsilon_r'$ and $\varepsilon_r''$ become very high at low frequencies when the sample temperature exceeds a certain critical temperature. The reason for this increase in $\varepsilon_r'$ and $\varepsilon_r''$ is carrier transport and the above-mentioned critical temperature is related to $T_g$, as will be discussed later. Note that especially $\varepsilon_r'$ exhibits very similar values at a certain frequency regardless of the temperature when it is below 140°C. Therefore, the $\varepsilon_r'$ values measured at 120°C or below are omitted from Fig. 2a to avoid congestion.

Although the differences in $\varepsilon_r'$ and $\varepsilon_r''$ at such low frequencies are obvious, Fig. 3 shows $\varepsilon_r'$ and $\varepsilon_r''$ measured for samples EF, T5-35, T10-35, and T20-35 at industrially important 50 Hz. Both $\varepsilon_r'$ and $\varepsilon_r''$ increase with the increase in content of TiO$_2$ fillers with the average size of 35 nm.

Fig. 4 shows the measurement result of conductivity $\sigma$. First, $\sigma$ was calculated using the DC current values measured during the last 100 s of voltage application as mentioned above, and its dependence on the content of TiO$_2$ fillers is shown in Fig. 4 using solid symbols. Then, $\sigma$ was estimated by substituting the values of $\varepsilon_r''$ at 0.01 Hz measured at 160 and 200°C into the equation [8, 9],

$$\sigma = 2\pi\varepsilon_0\varepsilon_r''f,$$

where $\varepsilon_0$ is the permittivity of vacuum and $f$ is the frequency. These values are shown using open symbols. The conductivity calculated from the DC current and that estimated based on $\varepsilon_r''$ can be regarded as similar to each other, if we take account of the fact that the two values were derived from completely different physical variables. Therefore, it is clear that the dominant factor governing the dielectric loss is the charge transport. Although several exceptions are seen, as a general trend, $\sigma$ becomes higher with the increase in filler content.
In order to examine the effect of fillers on the bulk properties of epoxy resin, $T_g$ was measured for the samples and its filler content dependence and filler size dependence are shown in Figs. 5a and 5b, respectively. Here, $T_g$ is plotted in Fig. 5a for all the samples listed in Tables 1 and 2, including the MgO fillers, the properties of which will be mentioned later. On the other hand, in Fig. 5b with the objective to show the reciprocal size dependence among the samples with similar filler contents, $T_g$ is plotted only for the samples with the TiO$_2$ fillers with the content of 5 vol% and those with the MgO fillers with the contents of 3.6 and 9.7 vol%.

It is clear in Fig. 5a that $T_g$ decreases with the increase in filler content. In our previous paper [10], we added nano-sized clay in bisphenol A epoxy resin with a content of 3 vol% and measured $T_g$ by DSC and by a dynamic mechanical analyser. While $T_g$ was measured to be about 10°C higher by the mechanical analyser than by DSC, both $T_g$s showed a significant decrease by the addition of nanoclay. Since $T_g$ in epoxy resin is closely related positively to its cross-linking degree [11], the addition of nanofillers decelerates the formation of cross-linked structures. Therefore, Fig. 5a indicates that the addition of TiO$_2$ nanofillers gives its effect on the epoxy resin in a way that activates the molecular motion in the bulk of epoxy resin.

It is also clear in Fig. 5b that $T_g$ decreases with the increase in reciprocal average filler size. The interaction between the filler and
epoxy bulk should originate from their interfaces. Although both fillers are not truly cubic, we assume that all the fillers are cubic with the same side length $L$ for the sake of simplicity. Then, their total surface area in a sample with a fixed filler content is inversely proportional to $L$. In this regard, $T_g$ is shown as a function of $1/L$ in nm$^{-1}$. As the fillers become smaller, $T_g$ becomes lower.

For continuing the investigation of the effect of filler addition on electrical conduction, complex electric modulus $M^*$ was calculated. Here, $M^*$ was defined as the inverse of complex permittivity and is expressed by the following equation [12],

$$\frac{1}{\epsilon^*} = \frac{\epsilon'}{\epsilon'} + \frac{i\epsilon''}{\epsilon''} \quad \text{(2)}$$

In general, spectra of the imaginary part, $M''$, give clearer results than those of the real part, $M'$. As an example, frequency spectra $M''$ measured for the samples with TiO$_2$ fillers with different size at 200°C are shown in Fig. 6a. A clear peak is seen around 3 Hz in the sample with no fillers, which shifts towards a higher frequency with the decrease in $L$ of the fillers added to the sample. In Fig. 6b, this frequency shift can be seen clearly at temperatures from 120 to 200°C. Note that the peak is not seen in the measurement frequency range at temperatures below 120°C. In addition, the peak frequencies at 120 and 140°C observed with the fillers with $L = 35$ nm are very similar and they lie over each other. These $M''$ peaks that appear at relatively high temperatures are thought to reflect the carrier transport in polymers [12, 13]. Therefore, Fig. 6b indicates that the carrier transport is activated when $L$ becomes smaller.

As in the case of samples with different contents of fillers, electrical conductivity $\sigma$ was calculated by measuring the currents flowing through the samples. This time, the average current observed during the last 100 s in the total of dc voltage application of 1 h at 200°C was used for comparison. As a result, $\sigma$ is found to increase monotonically with the increase in $1/L$ when the filler is TiO$_2$ as shown in Fig. 7. This in turn means that $\sigma$ becomes higher in the sample with lower $T_g$ in the case of TiO$_2$. Note that the $1/L$ dependence of $\sigma$ in the MgO composites will be mentioned later, as in the case of Fig. 5.

Ions, most probably Na$^+$ ions, are considered to be dominant carrier species in epoxy resins, especially at high temperatures [14, 15]. If this is the case in the present samples, $\sigma$ corresponds to the activity of molecular motions that facilitate the ionic conduction. In this sense, the fact that $T_g$ becomes lower with the decrease in $L$ shown in Fig. 5b and the results shown in Figs. 6a and b are in good agreement.

Similar analyses mentioned above were conducted using similar epoxy nanocomposites with MgO fillers. Since some details were already reported elsewhere [16–18], only the important results are shown. The glass transition temperatures ($T_g$s) measured in samples EA, M3.6-10, M3.6-3, M3.6-0.2, M3.6-0.05, M9.7-10, M9.7-3, and M9.7-0.2 are plotted in Fig. 5b. It is obvious that $T_g$ decreases with the addition of fillers. As $L$ of the filler becomes smaller, $T_g$ decreases more.

Fig. 7 shows the conductivity $\sigma$ measured at 200°C for the same eight kinds of samples with MgO fillers mentioned in relation to Fig. 5b. The conductivity $\sigma$ decreases, as a general trend, with the increase in $1/L$ or as the fillers become smaller, although its dependence on $1/L$ is not monotonic. This dependence is opposite to that of TiO$_2$ seen in the same figure. Regarding this, comparison of the results shown in Figs. 5b and 7 indicates that $\sigma$ changes in the MgO composites almost in accord with $T_g$. That is, $\sigma$ is low in the sample with a low $T_g$ in the case of MgO. This is exactly opposite to what is expected from the results shown in Figs. 2–6 obtained for the composite samples with TiO$_2$.

In addition, the conductivity $\sigma$ becomes lower when we add smaller MgO fillers more abundantly. The $\sigma$ values of eleven kinds of samples with MgO fillers are shown in Fig. 8 as a function of $T_g$ of each sample. Although the data scatter to some extent, a strong positive relation can be seen between $T_g$ and $\sigma$. Although not described here, Mg(OH)$_2$ shows a similar effect to MgO when its nanofiller is added in epoxy resin [19].

As a summary of Figs. 5, 7, and 8, the addition of MgO fillers to epoxy resin lowers $T_g$ similarly to the case of TiO$_2$ fillers. However, it suppresses the carrier transport, which is apparently opposite to what is induced by the addition of the TiO$_2$ fillers. These apparently contradictory effects of TiO$_2$ and MgO are strong indications that inorganic fillers, especially those with small sizes, exert strong filler-dependent influences to various properties of the host polymer. One thing to note is that we already reported the possibility of gathering information on the interaction between the filler and the polymer by terahertz absorption spectroscopy [4].
Fig. 8 DC conductivity $\sigma$ at 160°C measured for various epoxy resin composites with MgO nanofillers as a function of $T_g$. Samples EA (black circle), M1.7-10 (yellow open up-pointing triangle), M3.6-10 (yellow up-pointing triangle), M9.7-10 (black up-pointing triangle), M1.7-3 (blue open square), M3.6-3 (blue square), M9.7-3 (black square), M1.7-0.2 (green open down-pointing triangle), M3.6-0.2 (green down-pointing triangle), M9.7-0.2 (black down-pointing triangle), and M3.6-0.05 (red diamond).

4 Conclusion

Many kinds of epoxy resin nanocomposites with TiO$_2$ or MgO fillers with different sizes and different contents were prepared and the glass transition temperature, complex permittivity and electrical conductivity were measured. As a result, it has become clear that TiO$_2$ and MgO give apparently similar effects on the glass transition of the host epoxy resin, although they seemingly show opposite effects on the carrier transport. Although the mechanism behind this would be an important task to be solved, all the results obtained in this research indicate the existence of strong interactions between guest nanofiller and host epoxy resin.

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6 References

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