Influence of Hydrophobic Silica on Physical Properties of Epoxy Nanocomposites for Epoxy Molding Compounds


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ABSTRACT: In this work, the effect of hydrophobic treated silica on the water absorption, thermal stabilities, and mechanical properties of the epoxy nanocomposites were investigated as a function of the silica content. As filler, fumed silica treated by dimethyldichlorosilane was used. It was found that the silica was well dispersed in the epoxy resins by the melt-mixing method with the addition of a silane coupling agent. The water absorption of the nanocomposites decreased with an increase of the silica content due to the effect of hydrophobic treated silica. The thermal properties, such as thermal degradation temperature, glass transition temperature (Tg), and coefficient of thermal expansion (CTE), of the nanocomposites were improved by the addition of silica. Furthermore, the mechanical properties of the nanocomposites, that is, the tensile strength and modulus, were enhanced with increasing silica content. This was attributed to the physically strong interaction between silica and epoxy resins.

KEYWORDS: hydrophobic silica, water absorption, thermal behaviors, mechanical properties.

I. Introduction

Organic nanocomposites with nanometer sized inorganic particles represent a new class of materials that combine the desirable physical and chemical properties of both organic and inorganic components.1,2 As an inorganic filler, silica has been widely used to create high-performance or high-function materials over the last few decades. Silica particles can be used for reinforcement of polymer matrices to lower shrinkage upon curing, as well as for decreasing thermal expansion coefficients and improving adhesion properties, abrasion resistance, and corrosion resistance.4,5

Generally, epoxy molding compounds (EMCs) are organic and inorganic hybrid composites and a number of research groups have worked on silica/organic composites based on epoxy resins. These researchers have reported significant improvements in material properties, such as high thermal stability, glass transition temperature, and mechanical properties. Accordingly, silica/epoxy composites have been widely used...
in functional electronic device applications, such as in adhesives, coatings, electrical cable insulation, and matrix materials for EMCs in semi-conductor chips and printed circuit boards.\textsuperscript{8-10}

Currently, EMCs are used for protecting and packaging materials of semiconductors, based on their low cost, light weight, and ease of processing. It is designed to provide good thermal and mechanical properties, coefficient of thermal expansion (CTE), and water resistance and to protect against delamination between the die pad and EMC.\textsuperscript{11,12}

In terms of package reliability, delamination is one of the critical issues and is related to water absorption of the EMC and mismatch between the die-pad and EMC. Hence, a great deal of research has focused on improving package reliability, such as through the synthesis of new resins, increasing the filler content, and modification of the filler surface, as well as using silane coupling agents to enhance the interfacial interaction between fillers and epoxy resins.\textsuperscript{13}

In the present study, fumed silica treated by dimethyldichlorosilane is used to improve the water resistance of EMCs and silica/epoxy nanocomposites are prepared using melt-mixing with the addition of a coupling agent. The effects of surface treated silica on the water absorption, thermal stabilities, and mechanical properties of nanocomposites are discussed.

2. Experimental

2.1 Materials

The multi-functional epoxy (M-EP, EEW: 167) and crystalline epoxy (C-EP, EEW: 195) were supplied from Meiwa Plastics and Tohto Kasei, respectively. Acryl binder (Mw: 750,000) was obtained from Fujikura Kasei. Glycidoxypropyl trimethoxysilane (GPTS, ShinEtsu) was used as a silane coupling agent. Hydrophobic fumed silica treated by dimethyldichlorosilane (R 972) was supplied by Degussa. As a curing agent, Xylok type phenol+TPP-K (6:1) and Bisphenol A (EEW: 114) were obtained from Meiwa Plastics and Kukdo Chem. (Korea). As an imidazole catalyst, 2-phenyl-4,5-dihydroxymethylimidazole was supplied by Shikoku Chemicals.

2.2. Sample preparation

M-EP, C-EP, and acryl binder were mixed under stirring after melting at 80 °C. 1.0 wt.% GPTS and silica were added from 0 to 15 wt.% to the resin mixtures and then mixed via melt-mixing at 80 °C. The curing agents and catalyst were added and mixed with the silica/epoxy mixtures and the final mixture was then degassed using a vacuum oven at 80 °C. The mixtures were poured into a mold and cured at 100 °C for 1 h and 200 °C for 1 h. The samples are named as M/C-EP-S0, M/C-EP-S5, M/C-EP-S10, and M/C-EP-S15.

2.3 Characterization and measurements

The characterization of surface treated fumed silica and nanocomposites with and without silica was confirmed using a Fourier transform infrared spectrophotometer (FT-IR 4200, Jasco).

The structure of the nanocomposites was determined with X-ray diffraction (XRD, Rigaku D/Max 2200V) at 40 kV and 40 mA using Cu K\alpha radiation. The XRD patterns were obtained in 2\(^{\circ}\) ranges between 10° and 70° at a scanning rate of 2°/min.

The thermal stability of the nanocomposites was measured via a thermogravimetric analysis (TGA, STA 409 PC, NETZSCH) from 30 to 850 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The glass transition temperature was measured by DSC (DSC200F3, NETZSCH) over a temperature range of 30 to 300 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The coefficient of thermal expansion was obtained by a thermal mechanical analysis (RDS-II, Rheometrics Co.) at a heating rate of 5 °C/min under a nitrogen atmosphere.

The mechanical properties of the nanocomposites were measured via a tensile strength test. This test was conducted on a universal test machine (UTM) according to the ASTM D-790 specifications.

3. Results and discussion

3.1 Structure of the nanocomposites

Figure 1 shows FT-IR spectra of hydrophobic silica and nanocomposites with and without silica. It is observed that the IR spectra show notable differences for the characteristic peaks. The silica treated by dimethyldichlorosilane shows a
Figure 2. X-ray diffraction patterns of the silica, M/C-EP-S0, and M/C-EP-S15.

Figure 3. TGA thermogram of M/C-EP-S0 and M/C-EP-S15.

Table 1. Water Absorption of the Nanocomposites as a Function of Silica Content

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<td>0.119</td>
<td>0.102</td>
<td>0.075</td>
<td>0.071</td>
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Water absorption (%) = \( \frac{\text{Wet weight} - \text{Conditioned weight}}{\text{Conditioned weight}} \) \( \text{(1)} \)

The water absorption of the nanocomposites decreases as the silica content is increased. The water absorption of M/C-EP-S15 is about 40 % lower, as compared with pure epoxy resins. It is clear that the hydrophobic properties of silica are increased with the surface treatment by dimethyldichlorosilane due to induction of a methyl group on the silica surface.

3.3 Thermal properties of the nanocomposites

Thermal degradation of pure epoxy resins and nanocomposites is shown in Figure 3. The thermal stability parameters, such as the initial decomposed temperature (IDT) and the temperature of maximum rate of weight loss (T_max), are listed in Table 2.

The thermal degradation temperature of the nanocomposites is observed to be shifted to a higher temperature than that of the pure epoxy resins, and the IDT and T_max increase with
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Figure 4. DSC thermograms of the nanocomposites as a function of silica content.

Figure 5. Coefficient thermal expansion of the nanocomposites as a function of silica content.

The addition of silica. It could be concluded that the thermal stability of the nanocomposites is enhanced by the addition of silica. Also, no significant weight change is observed at temperature exceeding roughly 530 °C and the total weight loss is lower than that of the pure epoxy resins. These results indicate that the difference of the total weight loss can be attributed to the excellent thermal stability of silica dispersed in epoxy resins.16

Figure 4 shows the change of the glass transition temperature (T_g) according to the silica content. Generally, the T_g of an epoxy resin used under the same conditions is dependent on the cross-linking density after curing. The T_g of the nanocomposites increases with the addition of silica, whereas it decreases with the addition of 15 wt.% silica. It is suggested that silica is well dispersed in the epoxy resins, leading to an increase of the T_g by increasing the cross-linking density via strong interactions between silica and epoxy resins.17

Table 3. CTE of the Nanocomposites as a Function of Silica Content

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<tr>
<th>Silica Content</th>
<th>CTE (ppm)</th>
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<tbody>
<tr>
<td>M/C-EP-S0</td>
<td>4.94</td>
</tr>
<tr>
<td>M/C-EP-S5</td>
<td>3.80</td>
</tr>
<tr>
<td>M/C-EP-S10</td>
<td>3.00</td>
</tr>
<tr>
<td>M/C-EP-S15</td>
<td>2.98</td>
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</tbody>
</table>

Figure 5 shows the dimension change of the nanocomposites as a function of silica content at a heating rate of 10 °C/min in a nitrogen atmosphere, and the obtained coefficient of thermal expansion (CTE) values are listed in Table 3. The results indicate that the CTE of the nanocomposites decreased with increasing silica content and the M/C-EP-S10 and M/C-EP-S15 show similar CTE values. It is clear that silica binds the epoxy resins well and prevents thermal expansion, resulting from good interaction between silica and epoxy resins. Furthermore, this leads to a decrease in the segment motion of the macromolecules of the epoxy resins.18

3.4 Mechanical properties of the nanocomposites

Figure 6 shows the tensile strength and modulus of the nanocomposites as a function of silica content. The tensile strength and modulus of the nanocomposites increase with the addition of silica, as compared with pure epoxy resins. The maximum value is shown at 10 wt.% silica and it was about 75% higher relative to the pure epoxy resins. This indicates that in the silica/epoxy system, the use of a coupling agent leads to strong interfacial interactions between the silica and epoxy resins. However, the tensile strength and modulus of the nanocomposites decrease at 15 wt.% silica due to the accumulation of silica during processing. The aggregates of silica result in weak interaction between the silica and epoxy resins.19

Figure 6. Tensile strength and modulus of the nanocomposites as a function of silica content.
4. Conclusion

Silica/epoxy nanocomposites were prepared by a melt-mixing method and the water absorption and thermal and mechanical properties of the nanocomposites were investigated as a function of silica content. The water absorption of the nanocomposites decreased with the addition of silica due to the hydrophobic features of the surface treated silica. The thermal properties, i.e. thermal degradation temperature, glass transition temperature, and coefficient of thermal expansion, as well as the mechanical properties of the composites were improved by the addition of silica. This could be understood on the basis of the interfacial interaction between silica and epoxy resins increasing as a result of the addition of a coupling agent, resulting in increased cross-linking density.

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References