



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

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### 에폭시 몰딩 컴파운드를 위한 에폭시 나노복합재료의 소수성 실리카의 영향

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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 ( $T_g$ ), 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.

**요약** : 본 연구에서는 에폭시 나노복합재료의 수분 흡수, 열적 안정성 및 기계적 특성에 대한 소수성 실리카의 효과에 대해 고찰하였고, 에폭시 수지의 필러로는 디메틸디클로로실란에 의해 소수성으로 처리된 실리카를 사용하였다. 실험 결과, 실리카는 실란 커플링제의 첨가후 용융혼합법에 의하여 에폭시 수지내에서 균일하게 분산되었으며, 나노복합체의 수분 흡수율은 소수성으로 처리된 실리카의 함량 증가와 함께 감소하는 것을 확인하였다. 열분해 온도, 유리전이 온도, 그리고 열팽창 계수를 통한 나노복합재료의 열안정성은 실리카의 첨가와 함께 향상되는 것을 확인하였다. 또한, 인장강도 및 탄성율을 통한 나노복합재료의 기계적 특성은 실리카 함량 증가와 함께 증가하였고, 이는 에폭시 수지내에 고르게 분산된 실리카와 에폭시 수지 간의 강한 물리적 상호작용에 기인하는 것으로 판단된다.

**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.<sup>1-3</sup> 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.<sup>4-7</sup>

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

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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.<sup>8-10</sup>

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.<sup>11,12</sup>

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.<sup>13</sup>

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  $2\theta$  ranges between 10° and 70° at a scanning rate of 2°/min.

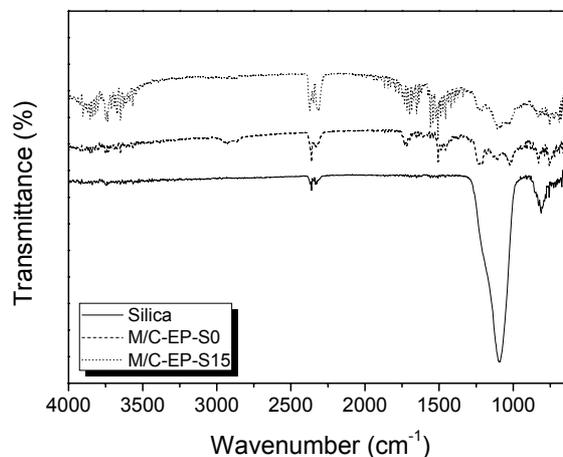
The thermal stability of the nanocomposites was measured via a thermogravimetric analysis (TGA, STA 409 PC, NETZSCH) from 30 to 850 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The glass transition temperature was measured by DSC (DSC200F3, NETZSCH) over a temperature range of 30 to 300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

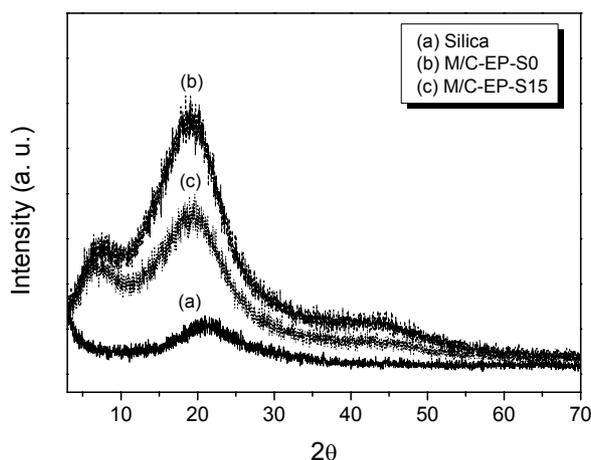
## 3. Results and discussion

### 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 1.** FT-IR spectrum of the silica, M/C-EP-S0, and M/C-EP-S15.



**Figure 2.** X-ray diffraction patterns of the silica, M/C-EP-S0, and M/C-EP-S15.

good hydrophobic property. The absorption peaks at  $1110$  and  $820\text{ cm}^{-1}$  are attributed to Si-O-Si stretching vibration. In the silica/epoxy nanocomposites, the vibration intensity of the carboxyl group (C=O) at about  $1720\text{ cm}^{-1}$  increases after curing, as compared with pure epoxy composites, suggesting the generation of product. It is likely due to the interaction between silica and epoxy resins.<sup>14</sup>

Figure 2 shows XRD patterns of silica and nanocomposites with and without silica. No intensive crystalline peaks are observed, indicating the samples have a homogeneous structure. They all show an amorphous peak at about  $2\theta=26^\circ$ . However, the intensity of the nanocomposites is higher than that of the silica due to the use of crystalline epoxy resins. Also, the results imply that the crystallinity is influenced by the surface properties and the interaction between silica and epoxy resins. The silica particles are reacted with the epoxy resin molecules by the functional group of silica and the addition of the coupling agent. This causes a decrease of the degree of crystallinity of the nanocomposites (M/C-EP-S15), leading to the reduction of the diffraction peak intensity.<sup>15</sup>

### 3.2 Water absorption of the nanocomposites

In the electronic device packing industry, protection against delamination between the EMC and the die pad is very important. Delamination can be initiated by a number of factors, one of which is water absorption of the EMC.

In this work, to improve the water resistance of the EMC, fumed silica treated by dimethyldichlorosilane is used as inorganic fillers. The water absorption of the nanocomposites is measured as a function of silica content and is listed in Table 1. It is determined by the following equation:

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

SA	M/C-EP-S0	M/C-EP-S5	M/C-EP-S10	M/C-EP-S15
%	0.119	0.102	0.075	0.071

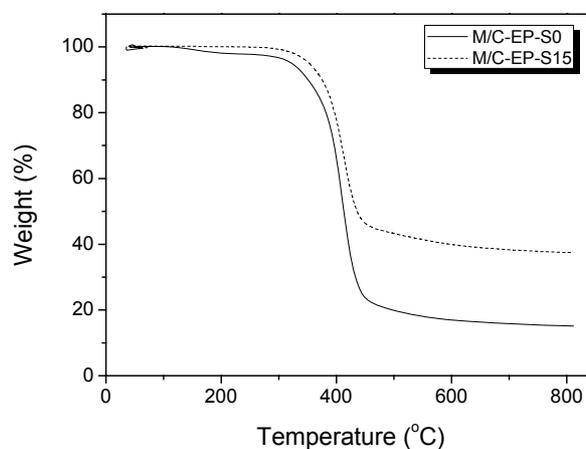
$$\text{Water absorption (\%)} = \frac{\text{Wet weight} - \text{Conditioned weight}}{\text{Conditioned weight}} \quad (1)$$

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.

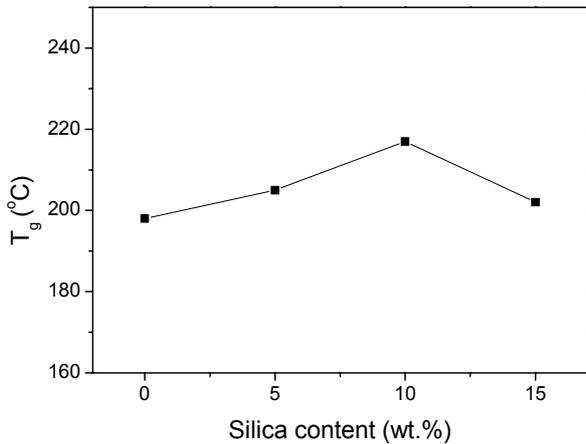
The thermal degradation temperature of the nanocomposites is observed to be shifted to a higher temperature than that of the pure epoxy resins, and the IDT and  $T_{\max}$  increase with



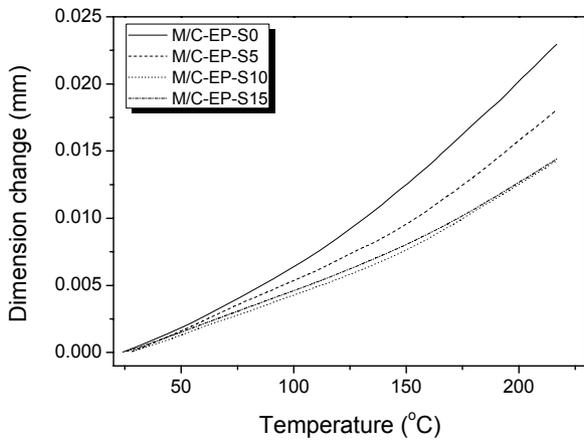
**Figure 3.** TGA thermogram of M/C-EP-S0 and M/C-EP-S15.

**Table 2.** Thermal Stabilities of Pure Epoxy and Nanocomposites

SA	IDT (°C)	$T_{\max}$ (°C)
M/C-EP-S0	349.2	486
M/C-EP-S15	373.8	498



**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.<sup>16</sup>

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.<sup>17</sup>

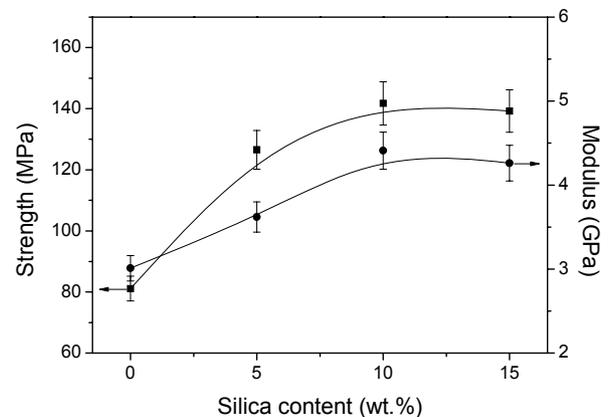
**Table 3.** CTE of the Nanocomposites as a Function of Silica Content

SA	C.T.E (ppm)
M/C-EP-S0	4.94
M/C-EP-S5	3.80
M/C-EP-S10	3.00
M/C-EP-S15	2.98

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.<sup>18</sup>

### 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.<sup>19</sup>



**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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