Surface modification of magnesium oxide/epoxy composites with significantly improved mechanical and thermal properties

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ABSTRACT

This work demonstrated the effect of functionalized magnesium oxide (MgO) nanoparticles with 3-(aminopropyl) triethoxysilane (APTES) as fillers on the mechanical and thermal properties of epoxy composite. The functionalization of MgO (S-MgO) considerably improved the interface between the MgO and epoxy resin. The mechanical properties of the composites revealed that the addition of functionalized MgO improved their tensile strength, modulus of elasticity, and ductility when compared to neat epoxy. In comparison to neat epoxy, the in-plane thermal conductivity of the epoxy composite with S-MgO filler is improved by 10 folds. These observations indicated that the silane functionalization on MgO contributes to the formation of a strong interfacial bond and a compact interconnected network between the filler and the epoxy matrix.

1 Introduction

As the development in electronic industry is progressing, the electronic component is reducing its volume. The problem of heat dissipating in these devices becomes more severe and worst that arises the need for producing a suitable thermal interface materials (TIMs) for modern packaging of such electronic devices [1–3]. The operating temperature influences the durability of electronic components, and the difference in temperature leads to decrement in the performance of electronic devices [4, 5]. To achieve reliable, effective materials for heat dissipation, the thermal conductivity of thermal interface material must be improved. Heat sinks are commonly used to overcome this issues, but it often leads micro-cracking that induced due to thermal fatigue [6].

Most of the researchers recently use the thermal conductive fillers such as alumina, magnesium oxide, or boron nitride which require high proportion (50–70 vol%) of filler in polymers to achieve good thermal conductivity values from 1–5 W m−1 K−1 [7–9]. A variety of fibers and particles have already
been used as a filler to improve the thermal conductivity of polymer composite \([10–12]\). However, a large proportion of thermal conductive filler is usually required for the improvement of thermal properties, but on the downside leading to the deprived mechanical properties of the composite owing to the high stiffness of the filler and low interfacial interaction between the filler and matrix \([13]\). The challenge in that area is the better interfacial bonding, good physical and mechanical properties of the composite \([14–17]\).

Nanocomposites have shown better considerable characteristics and thermal properties due to their high surface area; they have better interfacial interaction with matrix \([18, 19]\). But due to high surface energy these nanoparticles are the cause of the agglomeration and aggregation which depletes the properties of polymer composites. One of the best routes to deal with these problems is chemical functionalization of the nanoparticle that develops a strong interconnecting networks between particles and the polymers \([20, 21]\). Surface-modified titania showed the improved mechanical properties when it incorporated in phthalonitrile resin \([22]\). In our previous work, the functionalization of graphene with O-phenylenediamine (OPD) shows significant improvement in thermal conductivity. By adding just 6 wt% of OPD-f-graphene, ~ 13-fold of rise in thermal conductivity has been noted \([23]\). The thermal conductivity of polyimide-filled boron nitride is improved to 1.2 W m\(^{-1}\) K\(^{-1}\) after surface modification of boron nitride particles \([24]\). The addition of filler also improves mechanical properties of the composite; a 22% improvement in compressive strength has been recorded in carbon fiber/epoxy composites via microwave curing. This is due to improved interfacial bonding between the resin and the fiber \([25]\). In other report, the mechanical and thermal properties were altered by adding functionalized graphene nanoplates in polyurethane matrix and demonstrated that functionalized graphene increased 10 times Young’s modulus of f-GNP/PU as compared to neat PU \([26]\). Moreover, the addition of 1 wt.% functionalized silica nanoparticles attached with graphene oxide enhances the tensile strength and modulus by 29.2% and 22.0% as compared to pure epoxy \([27]\). It is realized that the chemical functionalization in nanoparticles can help in better dispersion of the filler and generates strong interconnecting networks for better thermal and mechanical properties. In this paper, the functionalization of nano-MgO with APTES(S-MgO) has been performed and introduced to epoxy for improving the dispersibility of the filler in epoxy matrix. The mechanical and thermal properties of epoxy nanocomposite are improved as S-MgO particles enhance the interfacial bond.

2 Experimental section

2.1 Materials

Magnesium chloride (MgCl\(_2\).6H\(_2\)O) and sodium hydroxide (NaOH) were purchased from Samchun Chemicals Co. Ltd. Toluene and (3-aminopropyl) triethoxysilane (APTES) were taken from DaeJung Chemicals, South Korea. The epoxy resin (DGEBA, YD-128) and hardener (KH-602) were obtained from Kukdo Chem. Co, South Korea. The specification of resin and hardener is listed in Table 1. These chemicals have been used as obtained without further treatment.

2.2 Synthesis of MgO nanoparticles

MgO nanoparticles were synthesized by magnesium chloride precursor with sodium hydroxide (NaOH). In a typical procedure, 100 mL, 0.1 M solution MgCl\(_2\) was slowly mixed with 100 mL, 0.1 M solution of NaOH under a vigorous string for 30 min, and then the solution was centrifuged at 8000 RPM for 15 min and washed frequently with ethanol to remove the impurities. Finally, the magnesium hydroxide (Mg(OH)\(_2\)) is collected and dried at 80°C for overnight. To convert Mg (OH)\(_2\) to MgO, calcination was done using a step temperature controller in infrared furnace at 300 °C for 1.5 h and finally further heated at 600 °C for 02 h.

2.3 Functionalization of MgO nanoparticles

Functionalization of MgO was simply done with (3-aminopropyl) triethoxysilane [APTES] through refluxing. In brief, 10 mL of 2 M solution of APTES in anhydrous toluene was hydrolyzed at RT. The pH of the solution is maintained in acidic range (3–4) by adding few drops of 01 M acetic acid. Finally, 2.0 gm MgO nanoparticles were first dispersed in 45 mL
anhydrous toluene and then added in the above reactor. The reactor was refluxed in oil bath at 135 °C for 24 h. The functionalized MgO (S-MgO) was centrifuged at 8000 RPM for 15 min and washed several times with water and methanol to remove the unreacted silane and vacuum dried at 80 °C for overnight, as illustrated in Fig. 1.

### 2.4 Fabrication of epoxy nanocomposite

S-MgO powder was mixed in the epoxy matrix (YD-128, Kukdo Epoxy) through shear mixer. The MgO and resin are blended in Thinky Mixer (ARE-310) at 1000 RPM for 15 min, after that, bath sonication at RT for further 30 min. The addition of aliphatic amine-modified curing agent (KH-602, Kukdo Epoxy) was done mechanically and followed by sonication at RT for 05 min. Finally, the composite was vacuum-degassed to remove the entrapped air during synthesis and then poured into prepared Teflon mold. The mold was first cured at 80 °C for 30 min and then at RT for 48 h. Similarly, the non-functionalized MgO sample was prepared to compare the mechanical and thermal properties of the epoxy composite.

### 2.5 Characterization

Thermal conductivity of epoxy composites (sample dimension: 30 × 05 × 0.3 mm) was recorded on thermal diffusivity analyzer (ULVAC LPIT (Laser-PIT-M2, Japan). Thermal stability of the composite was measured by using thermogravimetric analyzer (TGA-Q50, USA). The mechanical properties of composite were measured through Universal Testing Machine (LR5K plus, Lloyd Instruments, UK). The Fourier transform infrared (FT-IR) spectra were measured and analyzed on Fourier transform infrared spectrophotometer (JASCO FT/IR-4100, Japan).

**Table 1 Specifications of epoxy and hardener**

| Specifications of epoxy and hardener | Epoxy Resin “Kukdo YD-128” |
|-------------------------------------|-----------------------------|
| Epoxy equivalent weight (EEW)       | 184–190 g/eq                |
| Specific gravity (25 °C)            | 1.17 g/mL                   |
| Viscosity (25 °C)                   | 11,500–13,500 cps           |
| Color (APHA)                        | 50 max                      |
| Curing Agent (Hardener) *Aliphatic Amine-modified Hardener KH-602* | |
| Total amine value                   | 670–730 mgKOH/g             |
| Viscosity (25 °C)                   | 50–250 cps                  |
| Use level (phr)                     | 25 (YD-128 = 186 g/eq))     |
| Color                               | 5 max                       |

![Fig. 1 Schematic illustration of functionalization MgO](image)
The crystallinity of magnesium oxide was characterized by XRD spectroscopy (X’Pert Pro Powder, PANalytical; Netherland). The surface topography and EDX were characterized on field emission scanning electron microscopy (FE-SEM) (Carl Zeiss Supra 40VP, Germany).

3 Result and discussion

3.1 Functionalization and homogenous dispersion of MgO and MgO epoxy composite

Filler morphology is one of the most important factors that affects composite properties. The amount of filler in composite is based on the filler shape and geometry [28]. The spherical morphology is more favorable for homogenous dispersion of filler in comparison to irregular shape [29]. Figure 2 shows the pristine image of MgO nanoparticles with average particle size of 65 nm. The elemental analysis further confirms the synthesis of MgO without the presence of any impurities. The silane-functionalized magnesium oxide (S-MgO) is presented in Fig. 3; one can see that the nanoparticles are aggregated compared to neat MgO (Fig. 2). We assume that this aggregate is due to formation of coupling agent molecules, which led the attractive forces between the particles. FTIR spectroscopy further confirmed the functionalization of MgO, as shown in Fig. 4a. The FTIR spectra of S-MgO display bands at 1080 cm$^{-1}$ which shows the formation of network system of Si-O-Mg, indicating the crosslinking through salinization on MgO. The band at 1630 cm$^{-1}$ is due to moisture absorbed by the sample. The bands at 2820 cm$^{-1}$ and 2970 cm$^{-1}$ represent the symmetric and asymmetric vibration of CH$_2$ bond, respectively. The observed infrared bands are similar with the FTIR spectrum of silane and elsewhere [30, 31]. The crystalline properties of S-MgO have been checked by XRD (Fig. 4b). There is no considerable change in the XRD peaks of S-MgO, which confirms the crystallinity maintained after functionalization.

Homogenous dispersion of S-MgO in epoxy has been examined through the surface morphology of the nanocomposite, as shown in Fig. 5a–d. The non-functionalized MgO-filled epoxy nanocomposites shows highly agglomerated MgO particles, which might cause the degradation of composite properties, leading to the propagation of cracks (Fig. 5a, b), while the surface of S-MgO–epoxy shows well-oriented and homogeneous dispersion of the filler in the epoxy matrix (Fig. 5c, d). This indicates that the functionalization of MgO improves the interfacial characteristic of filler and epoxy matrix. It is further observed that the fracture surface of MgO–epoxy, i.e., similar to cleavage fracture, whereas the fracture surface of the S-MgO–epoxy composite is similar to fibrous structure (Fig. 5c, d). It clearly suggests that the S-MgO-filled nanocomposite is more ductile as compared to unfunctionalized MgO-filled nanocomposite. Figure 5e shows the electron energy-dispersive X-ray spectroscopy (EDX) analysis of S-MgO-filled epoxy, which exhibits the presence of all prospective elements. Figure 5f–i shows the elemental mapping of S-MgO–epoxy, which reveals the homogenous dispersion of S-MgO all over the epoxy matrix. The morphological and compositional characteristics reveal that the S-MgO-filled epoxy displays the highly homogeneous and well-dispersed surface.

3.2 Mechanical properties of MgO epoxy composite

Table 2 shows the mechanical properties of MgO–epoxy and S-MgO–epoxy nanocomposites. The tensile strength of S-MgO–epoxy with 15 wt%, S-MgO (i.e., ~77 Mpa) is higher than that of 15 wt% untreated MgO-filled epoxy (~69Mpa) and neat epoxy (~52 Mpa), as illustrated in Table 2. It is eminent from the results that the tensile strength escalates by increasing the filler content up to 15 wt.%. However, further incorporation of the filler exhibited in considerable reduction in tensile strength of nanocomposites. At high filler contents (30 wt%), ~40% reduction in the tensile strength in nanocomposite is recorded, which can be attributed to high proportion of filler that increases the brittleness and decreases strain [32]. The incorporation of S-MgO in epoxy elevates the modulus of elasticity because of high modulus of elasticity of MgO (i.e., 295GPa) [33]. The modulus of elasticity is enhanced ~28% with addition of just 15 wt% of S-MgO in comparison to neat epoxy. The interfacial adhesion force is increased due to polar–polar interaction S-MgO and epoxy matrix, as a result the composite becomes stiffened. This result is quite comparable with previously reported work [27]. Furthermore, silane functionalization of MgO...
Fig. 2  a, b FESEM image of pristine magnesium oxide (MgO); c particle size of b; d EDX spectra of b

Fig. 3  a, b FESEM image of functionalized magnesium oxide (S-MgO)
considerably improves the ductility of the composite. 33% improvement in strain to break (ductility) has been recorded in nanocomposite with 15 wt% of S-MgO in the epoxy as compared to neat epoxy. The enhancement in the mechanical properties after functionalization is attributed with high surface area of nanoparticles and interaction of the silane functional group on the S-MgO with epoxy matrix.

### 3.3 Thermal properties of MgO–epoxy composite

The thermal stability of the epoxy nanocomposite with 15 wt% of MgO filler is studied through thermogravimetric analysis (TGA), in Fig. 6. A significant loss in nanocomposite has been recorded at around 300–500 °C due to the degradation of epoxy [34]. The thermal stability parameters are shown in Table 3, which are estimated from peak degradation temperature of TGA curve using Universal Analysis 2000 software. Thermal stability parameters have been determined by integral procedure temperature (IPDT), activation energy (Eₐ) and residue left at 750 °C, as reported elsewhere [35, 36]. The IPDT of nanocomposite is significantly increased by the addition of MgO filler. The IPDT of S-MgO–epoxy (15 wt%) expresses a significant improvement by a factor of ~1.7 (70% increased) in comparison with neat epoxy. Activation energy (Eₐ) is calculated by plot of plots of ln [ln (1 – α) – 1] vs. Θ as shown in Fig. 6b. Activation energy (Eₐ) of the MgO–epoxy (15 wt%) and S-MgO–epoxy (15 wt%) is recorded 88 and 90 kJ/mol, respectively, which is notably improved in comparison to neat epoxy (Eₐ = 80 kJ/mol). Furthermore, the higher proportion of residue at 750 °C also suggests the higher thermal stability of the nanocomposite. Figure 7 displays the in-plane thermal conductivity of composites. The thermal conductivity is increasing linearly with addition of the filler as presented in Fig. 7a. The resistance of the interface (Kapitza resistance (R_K)) is important factor in heat flow and the thermal resistance increase due to weak contact at the interface [37], which leads to back scattering of thermal energy wave (phonons). In this case, functionalization improves interfacial bonds between the MgO filler and the epoxy matrix, which results in the formation of interconnective networks that eventually results in increasing in—plane thermal conductivity by adding just 5 wt% of the S-MgO to 0.96 W·m⁻¹·K⁻¹. Thermal conductivity enhancement (TCE) of ~377% (Fig. 7b) is seen in comparison with neat epoxy. At high loading, the thermal conductivity is constantly improved reaching to 30 wt% of the S-MgO, which results in high thermal conductivity of 2.14 W·m⁻¹·K⁻¹. This value is comparatively higher by 20% than of MgO (non-functionalized) with 30 wt% loading. This improvement is thermal conductivity is attributed to the strong interfacial interaction between S-MgO and epoxy.
Fig. 5 FESEM micrographs of fracture surface of epoxy composite with 15 wt% of filler (a, b) MgO–epoxy; c, d S-MgO–epoxy; e corresponding EDX spectra of c; f–i elemental mapping of c; f(Carbon); g(Oxygen); h(Magnesium); i(COMgK)
4 Conclusion

In conclusion, we functionalize magnesium oxide with APTES through nucleophilic addition reaction. Functionalization improves the dispersibility of the filler and generates strong interconnective networks, which reduce thermal interface resistance. The mechanical and thermal properties are significantly improved. The tensile strength is increased up to 50%, and the overall ductility and modulus of elasticity of the composite are increased. Better thermal stability is recorded after functionalization, and the IPDT and $E_t$ are increased to ~ 70% and ~ 12%, respectively. The in-plane thermal conductivity is also enhanced to ~ 10 fold by addition of 30 wt% of the S-MgO, compared to the neat epoxy. Improved mechanical and thermal upgradation of the developed composite is recommended for thermal management applications.
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Fig. 7  a Thermal conductivity of MgO–epoxy and S-MgO–epoxy; b enhancement in thermal conductivity as a function of MgO content
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