Polymer/Alumina Nanofiber Composite Sheets with Anisotropic High Thermal Conductivity

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Abstract

The performance of an electronic product depends on how efficiently it can dissipate the heat of its parts. As a result, intensive ongoing research seeks to improve the thermal conductivity of polymeric materials. In this study we investigated alumina nanofibers as thermal conductive filler in resin and compare them to conventional spherical filler. Aligned $\alpha$-alumina nanofiber mats were fabricated by electrospinning PVA and boehmite dispersion; they were then impregnated with resins to obtain a composite sheet. We assessed the thermal conductivities of the sheet. Resin sheets with alumina nanofiber content (33 vol.\%) had high thermal conductivity (19.7 W/mK) in the direction parallel to the aligned alumina nanofibers. Conductivity increased in proportion to alumina nanofiber content. In addition, the alumina nanofiber composite sheet showed anisotropic thermal conductivity derived from the fiber direction, and had electrical insulating property ($2.7 \times 10^{13} \Omega/\square$) and flexibility. This electrically insulating sheet with anisotropy in thermal conductivity would be useful in designing effective heat-removal paths in electronic devices.

Key Words: Alumina nanofibers, Electrospinning, Thermal conductive filler, Linear heat-pathway, Anisotropic thermal conductivity, Electrical insulation

1. Introduction

The rapid spread of digital consumer electronics requires constant reductions in size and weight. Meanwhile, heat generation increases in electronic devices that must handle high-speed, large-capacity information. How efficiently a product can dissipate the heat of its electronic components has a major impact on its performance. Thus, the importance of measures against heat generation is increasing. Carbon and metal materials have good thermal conductivities, and are used as heat-dissipation materials for electronics, even though they are also good electric conductors. In the development of electric devices, much attention has been paid to the heat-dissipation performance of electrically insulating materials. Polymeric materials have good moldability and electric insulation, but also thermal insulating properties. Thus, research efforts are underway to improve the thermal conductivity of polymeric materials for use in next-generation electronic devices.

The compounding of thermally conductive and electrically insulating inorganic particles, such as silica, alumina, aluminum nitride (AIN), and boron nitride (BN) in polymer matrices has been investigated to improve the thermal conductivity of polymeric materials [1-4]. There have been recent reports on the thermal conductivity of polymers compounded with BN particles [5-7]. Muratov et al. investigated the thermal conductivity of polypropylene/BN particle composites [6]. They used two types of particle: high-purity hexagonal BN nano-sized powder (average particle size, 140 nm); and hexagonal BN micron-sized powder (5 μm). They found that the amount, quality, and small particle size of BN were the factors that appeared to improve thermal conductive properties (0.629 W/mK at 4 wt.% of BN nanopowder). Kim et al. modified the surfaces of BN particles (12 μm) with surface curing agents to form epoxy/BN composites. They reported that the surface modification of BN increased the thermal conductivity of the composites (4.11 W/mK at 70 wt.% of modified BN particle) [7]. Meanwhile, Choi and Kim investigated the thermal conductivity of epoxy composites with a binary blend of alumina and AIN particles [8]. They found the thermal conductivity of a composite with large AIN (10 μm) and small alumina (0.5 μm) particles was 3.402 W/mK at 58.4 vol.% total filler content.

In general, particle content above 50 vol.% is needed to form a heat conduction pass in composites. Here we investigate use of inorganic nanofibers, several hundred nanometers in diameter, as...
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composite filler. In doing so, we considered that a heat conduction pass could be introduced very easily into composites with low filler content because the ratio of length/diameter in nanofibers is, in theory, infinite.

Alumina (Al$_2$O$_3$) is the third-most prevalent element in the earth’s crust next to silica, and thus is cheaper than inorganic materials such as AlN and BN. In addition, alumina nanofibers can be easily prepared with the electrospinning (ES) technique [9-11]. Electrosprining was introduced in the 1930s. It is used to manufacture nanofibers for various applications, including filtration, heat insulation, sensors, and medical materials [12, 13]. Figure 1 contains a simple illustration of the electrospinning process. Our lab has also formed alumina nanofibers by heating composite nanofibers of poly(vinyl alcohol) (PVA)/boehmite (AlO(OH)•H$_2$O) obtained by ES [14].

In our previous study we investigated the thermal conductivity of alumina nanofibers and urethane resin composite sheets [15]. However, the alumina content in the composite was limited to less than 7 vol.%, because there were large spaces between nanofibers in the mats, and the urethane monomers had no solvent. In this study, we used polymer solutions instead of resin monomers to impregnate alumina nanofiber mats, and the solvent was then evaporated. Results confirmed an increase in the alumina nanofiber content of the composites. The composites showed much higher thermal conductivity than those in previous research. We also investigated the effects of the alignment of the alumina nanofibers in the resin sheets on the thermal conductivity of the sheets.

2. Experimental

2.1 Preparation of alumina nanofibers

Boehmite nanoparticles (Disperal P-2) with an average dispersed particle diameter of 20 nm were a kind gift from Sasol Japan KK. PVA (degree of polymerization=1,500; molecular weight=67,000; saponification=98.0 mol%) was purchased from Wako Pure Chemicals Ind., Ltd. (Japan), and a 10 wt.% aqueous PVA solution was prepared. boehmite nanoparticles (Disper P-2) were added to the PVA solution to form the spinning solution. The calculated ratio of PVA/alumina was 70/30 wt.%. PVA and boehmite content in the spinning solution were 9.4 and 5.6 wt.%, respectively.

The spinning solution was loaded into a plastic syringe (2 ml) equipped with a metal needle, and extruded at a rate of 0.015 ml/min. The fiber collector, a rotating drum collector (aluminum; diameter: 160 mm; rotating speed: 4000 rpm), was grounded. The distance between the tip of the needle and the collector was 150 mm. A 20.0 kV voltage was applied to the needle. PVA/boehmite composite nanofibers were prepared on the collector as a nonwoven fabric (the fibers were aligned). These were used as precursors to the alumina nanofibers. The precursor nanofiber mats were sintered in air up to 1200 °C at a heating rate of 10 °C/min, kept at 1200 °C for 5 h in an electric furnace, and they transformed into α-alumina nanofiber mats.

2.2 Formation of polyurethane sheets containing α-alumina nanofibers

Polyurethane water emulsion containing 30 wt.% solid (Superflex #300), a kind gift from DKS Co., Ltd. (Japan), was dissolved in water; the polyurethane content was varied from 1.5-10 wt.%. Using a polymeric solution with lower solid content yielded higher alumina content in the composite sheets. The polymeric solutions were dropped onto the alumina nanofiber mats, placed under vacuum, and cured at 120 °C.

2.3 Formation of PVA sheets containing α-alumina nanofibers

PVA was dissolved in water at concentrations ranging from 1.5-10 wt.%. It was composited with alumina nanofibers in the same way as the polyurethane emulsion described above.

2.4 Characterization

The morphology of the nanofibers was observed with a scanning electron microscope (SEM, Keyence VE-9800). Thermo gravimetric (TG) analysis was carried out in air to estimate the alumina content (wt.%) in the composite sheet with a heating speed of 10 °C/min (Bruker TG-DTA 2000SA, Japan). The alumina content (vol.%) in the sheet was calculated using the density of alumina, 3.890 g/cm$^3$. Thermal diffusivity (m$^2$/s) was measured in the plane and thickness directions with a Thermowave Analyzer TA35 (Bethel Co., Ltd., Japan) at room temperature. This system uses temperature wave analysis to measure thermal diffusivity. Average and relative standard deviation (RSD) of 4 different measurements were calculated. The sample size was about 100 mm$^2$. Thermal conductivity (W/mK) of the composite was

![Electrospinning Process](image-url)
calculated using the density and heat capacity of alumina (3,890 kg/m$^3$ and 750 J/kg·°C, respectively), polyurethane (1,200 kg/m$^3$ and 900 J/kg·°C, respectively), and PVA (1,250 kg/m$^3$ and 1,680 J/kg·°C, respectively). Surface resistance of the composite sheet was measured with Hiresta-UP (Mitsubishi Chemical Analytech, Japan) following ASTM D257. Bending endurance of the sheet was measured using a cylindrical mandrel tester (TP Giken, Japan) following ISO 1519; the composite sheet was folded over the $\Phi 5$mm cylinder such that bending occurred parallel to the direction of the alumina nanofibers. Two cylinders were used with a diameter of 3 and 5 mm. Mechanical properties of the as-prepared nanofiber mats could not be measured due to brittleness.

3. Results and discussion

3.1 Properties of alumina nanofibers

In our previous study [13], TEM images of the PVA/boehmite precursor nanofibers showed that the boehmite nanoparticles were aligned along the fiber axis. This indicated that boehmite nanoparticles were dispersed uniformly in the PVA matrix. The specific surface area and average pore diameter of the obtained alumina nanofibers were 5.4 m$^2$/g and 2.4 nm, respectively. Thus, non-porous alumina nanofibers were formed by heating PVA/boehmite precursor nanofibers.

Figure 2 shows SEM images and fiber diameter distributions of the nanofibers before and after the PVA/boehmite precursors were heated at 1200 °C. The average diameter of the precursor nanofibers and alumina nanofibers were 302 nm (RSD=17.8%) and 176 nm (RSD=26.1%), respectively. The fiber diameter decreased due to sintering, but the aligned structure of the fiber remained after the heat treatment.

3.2 Impregnation of alumina nanofiber mats with polyurethane emulsion

Figure 3 shows SEM images of the polyurethane sheet containing the aligned alumina nanofiber (nanofiber content 54 vol.%). According to the cross-sectional view, the polyurethane successfully filled the space between the nanofibers, and the nanofibers were distributed homogeneously in the polyurethane matrix. Nanofibers were also observed on the surface of the sheet, and it was likely that once impregnated with polyurethane emulsion, the fibers were not broken or disconnected.

3.3 Thermal conductivity of polyurethane sheets containing alumina nanofiber mats

We could not measure the thermal conductivity of the as-prepared alumina nanofiber mats due to their brittleness. The thermal conductivities of the polyurethane sheet containing aligned $\alpha$-alumina nanofibers were measured, however. The composite sheets were measured in three directions; parallel to the aligned nanofibers; perpendicular to the aligned nanofibers; and in the thickness direction of the composite sheet.

Figure 4 shows the thermal conductivities of the different directions in the polyurethane sheet with aligned $\alpha$-alumina nanofibers. Thermal conductivity in the direction parallel to the
aligned α-alumina nanofibers (▲) was greatly enhanced to about 19.7 W/mK (RSD=14.7%) with alumina nanofiber content of about 33 vol.%. This was much higher than that in the direction perpendicular to the aligned nanofibers (●). Meanwhile, thermal conductivity in the thickness direction of the sheet (●) was the lowest.

Equation 1 shows the Bruggeman Model [16]. This expression predicts the thermal conductivity of a spherical particle/continuous matrix composite using the thermal conductivity of the particle and matrix, and the volume fractions of the matrix. \( \Phi_{\text{filler}} \) represents the volume fractions of the filler, \( \lambda_{\text{resin}} \) represents the thermal conductivity of the resin, \( \lambda_{\text{filler}} \) represents the thermal conductivity of the filler, and \( \lambda_{\text{composite}} \) represents the thermal conductivity of the composite. In Figure 4, the curved line represents the Bruggeman model using the thermal conductivity of the resin \( \lambda_{\text{resin}} \) (0.1 W/mK) and that of the filler \( \lambda_{\text{filler}} \) (30 W/mK).

\[
1 - \Phi_{\text{filler}} = \left( \frac{\lambda_{\text{composite}} - \lambda_{\text{filler}}}{\lambda_{\text{resin}} - \lambda_{\text{filler}}} \right) \times \sqrt{\frac{\lambda_{\text{resin}}}{\lambda_{\text{composite}}}}
\]  

(1)

The thermal conductivity of the thickness direction (●) in the sheet was similar to the Bruggeman model. There are few heat-transfer pathways in the alumina nanofibers in the thickness direction, and it would be equivalent to using spherical particles as filler. On the other hand, the thermal conductivity parallel to the aligned alumina nanofibers (▲) increased proportionately to the nanofiber content. This improvement was due to the linear heat-transfer pathway of the aligned alumina nanofibers in the sheet, and demonstrates that the aligned nanofibers provide effective heat-transfer pathways and anisotropy.

### 3.4 Thermal conductivity of PVA sheets containing alumina nanofiber mats

Figure 5 shows the thermal conductivities of the three directions in the PVA sheet containing aligned α-alumina nanofibers. Thermal conductivity was greatly enhanced in the direction parallel to the aligned α-alumina nanofibers (▲), to 16.3 W/mK (RSD=25.0%), with alumina nanofiber content of 24 vol.%; the anisotropy of thermal conductivity was the same as that of the polyurethane/
alumina nanofiber composite.

3.5 Electrical insulation of polyurethane sheets containing alumina nanofiber mats (ASTM D257)

The surface resistance of the alumina nanofiber/polyurethane composite sheet showed good insulating property, 2.7×10^{13} \Omega/\square. The alumina nanofiber content and thickness of the sheet were 28 vol.% and 166 µm, respectively.

3.6 Bending endurance test of polyurethane sheets containing alumina nanofiber mats (ISO1519)

Figure 6 shows the thermal conductivity of the composite sheets containing 46 vol.% alumina nanofibers before and after a bending endurance test using a φ5-mm cylinder. Thermal conductivity did not deteriorate in any direction after bending 10 times in the direction parallel to the alumina nanofibers; in bending over a thinner cylinder (φ3 mm), however, the composite sheet broke after only one trial.

4. Conclusions

In this study, aligned α-alumina nanofiber mats were prepared by electrospinning using boehmite particles dispersed in PVA aqueous solution as a spinning solution, followed by heat treatment. Nanofiber mats were then impregnated with polyurethane or PVA aqueous solution. The obtained composite sheets containing 33 vol.% of the aligned α-alumina nanofibers had high thermal conductivity (19.7 W/mK) in the direction parallel to the aligned alumina nanofibers. Thermal conductivity of the sheets increased proportionately to the alumina nanofiber content. Our findings indicate that the elongated shape of alumina nanofibers serves as an effective filler, creating linear heat-pathways in the resin. In addition, the alumina nanofiber composite sheet showed anisotropic thermal conductivity derived from the fiber direction, as well as electrical insulating property (2.7×10^{13} \Omega/\square) and bendability. This electrically insulating sheet with anisotropy in thermal conductivity would be useful in designing an effective heat-removal path to avoid or protect heat-sensitive parts in electronics design.

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