

# Highly Thermoconductive Polymer Nanocomposite with a Nanoporous $\alpha$ -Alumina Sheet

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**ABSTRACT** A highly thermoconductive insulative polymer nanocomposite with a nanoporous  $\alpha$ -alumina sheet was reported. The thermal conductivity of the nanocomposite along the surface normal was  $12 \text{ W m}^{-1} \text{ K}^{-1}$  (41 vol % alumina), a value as high as that predicted theoretically for a nanocomposite with thermoconductive fillers that form a perfectly connected thermoconductive network. The high thermal conductivity is probably due to the continuous  $\alpha$ -alumina phase that functions as an efficient phonon path in the nanocomposite. The results suggest that the structure of the filler is important for the design of highly thermoconductive materials.

**KEYWORDS:** polymer nanocomposite • thermal conductivity • anodized alumina

A polymer nanocomposite with inorganic fillers is an interesting material because it has excellent characteristics that come from both the polymer and the filler. A highly thermoconductive polymer nanocomposite is an example of these fascinating materials. The material possesses high thermal conductivity as well as high processing ability by forming thermoconducting paths in the polymer matrix through contact between inorganic fillers, which assists the flow of phonons through the nanocomposite. We reported that the branched  $\alpha$ -alumina nanofiber was effective as the filler of highly thermoconductive materials because the interconnected nanofibers increase the number of junctions between nanofibers and yield more thermoconductive paths with low thermal resistivity (1). However, the thermal conductivity of the nanocomposite ( $1.3 \text{ W m}^{-1} \text{ K}^{-1}$  for a 10 vol % filler) was about 40% of the theoretical value ( $3.2 \text{ W m}^{-1} \text{ K}^{-1}$ ), which was based on the assumption that the thermal conductivity is proportional to the volume fraction of the filler. One of the reasons for the smaller thermal conductivity is the discontinuity of the phonon path, which results in an increase in the number of polymer/filler interfaces with high thermal resistivity (2).

In this letter, a crystallized anodized alumina (AA) sheet was shown to be an efficient filler for the highly thermoconductive materials. The AA sheet has a structure in which cylindrical voids with diameters of 10–100 nm run through the alumina along the surface normal. The nanocomposite with the AA sheet showed a thermal conductivity of  $12 \text{ W m}^{-1} \text{ K}^{-1}$ , which was nearly as high as the value predicted for the nanocomposite with fillers that form a perfectly connected thermoconductive network. Better continuity of

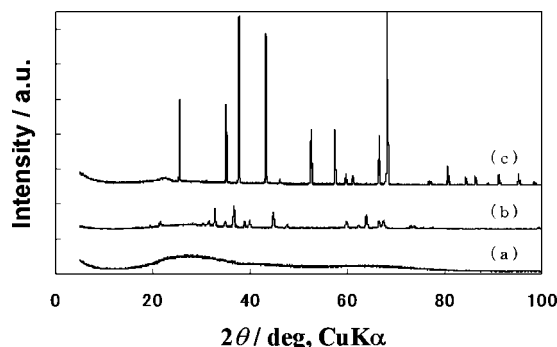


FIGURE 1. XRD charts of (a) an unannealed AA sheet, (b) an AA sheet annealed at 1200 °C, and (c) an AA sheet annealed at 1400 °C.

the phonon path in the nanocomposite would be responsible for the high thermal conductivity.

The crystallized AA sheet was prepared as follows. First, a commercial AA sheet (Anodisc 25 from Whatman) was sandwiched between alumina plates and placed in a furnace. The temperature was increased at a rate of  $4 \text{ °C min}^{-1}$  to a target temperature (1200 or 1400 °C) and kept at the target temperature for 4 h. Then, the temperature was decreased at a rate of  $4 \text{ °C min}^{-1}$  to room temperature. Figure 1 shows an X-ray diffraction (XRD) chart of (a) an unannealed AA sheet, (b) an AA sheet annealed at 1200 °C, and (c) an AA sheet annealed at 1400 °C. The diffraction intensity increased with an increase in the annealing temperature, implying that the crystallization proceeds more with a higher temperature. The chart for the unannealed AA sheet (Figure 1a) showed only a broad peak, which is probably due to the amorphous structure of the AA sheet. The chart of the AA sheet annealed at 1200 °C (Figure 1b) showed peaks from the  $\theta$ -alumina structure with a Sherrer diameter of 31 nm (calculated from the peak at  $36.6^\circ$ ). The chart of the AA sheet annealed at 1400 °C (Figure 1c) showed strong peaks that originated from the  $\alpha$ -alumina structure, which has the highest thermal conductivity of all alumina crystals. The peaks were so sharp that the Sherrer diameter could not

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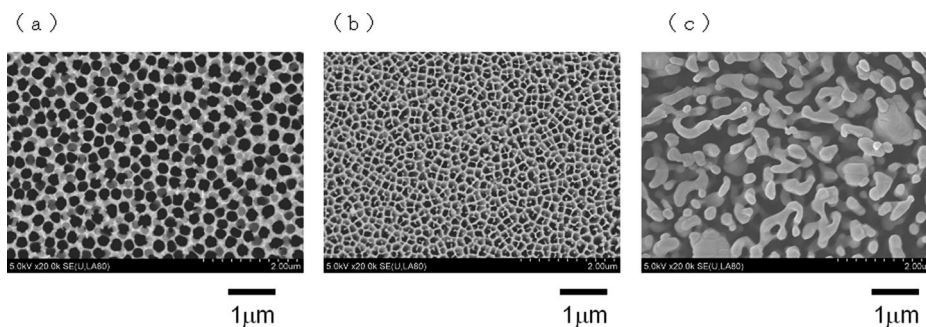


FIGURE 2. Surface images of (a) an unannealed AA sheet, (b) an AA sheet annealed at 1200 °C, and (c) an AA sheet annealed at 1400 °C.

**Table 1. Thermal Diffusibility of Nanocomposites with Various AA Sheets<sup>a</sup>**

	$f$ [vol %]	$\alpha_{xy}$ [mm <sup>2</sup> s <sup>-1</sup> ]	$\alpha_z$ [mm <sup>2</sup> s <sup>-1</sup> ]
neat epoxy resin	0	0.10	0.10
composite with an unannealed AA sheet	32	0.5	0.3
composite with an annealed AA sheet (1200 °C)	40	1.7	4.3
composite with an annealed AA sheet (1400 °C)	41	2.0	5.5

<sup>a</sup>  $f$  = volume fraction of filler.  $\alpha$  = thermal diffusibility.

be determined ( $d > 200$  nm), implying that the structure of the AA sheet was partially fractured.

Figure 2 shows the surface images of (a) an unannealed AA sheet, (b) an AA sheet annealed at 1200 °C, and (c) an AA sheet annealed at 1400 °C. The images were taken with a Hitachi S-4800 field emission scanning electron microscope. The image of the unannealed AA sheet surface was that typically observed for surfaces of AA sheets, with periodic alignment of holes (dark area in the image) in the alumina domain (bright area in the image) (3). The thickness of the wall between the holes decreased after the annealing at 1200 °C (Figure 2b). This implies that the shrinkage of the wall, which is probably associated with the phase transition of alumina, occurred during the annealing at 1200 °C. The occurrence of the phase transition is supported by the XRD results shown in Figure 1.

In the surface image of the AA sheet annealed at 1400 °C (Figure 2c), large aggregates with diameters of around 200–1000 nm were observed, which is probably due to the sintering of alumina during the annealing at 1400 °C. However, a nanocomposite with this AA sheet showed a high thermal diffusibility (thermal conductivity) along the surface normal (Table 1). This result is explained by the fact that the continuity of the alumina along the surface normal was maintained after the annealing at 1400 °C, which was observed with a cross-sectional scanning electron microscopy image of the nanocomposite with the AA sheet (Figure 3c).

Nanocomposites with the AA sheets were prepared as follows (1). The annealed AA sheet was immersed (under reduced pressure) in a Bisphenol A type epoxy resin (Epicote 828 from Japan Epoxy Resin Co., Ltd., 7.5 g) containing a curing agent (MHAC-P from Hitachi Chemical Co., Ltd., 7.0 g)

and a catalyst (2E4MZ-CN from Sikoku Chemicals Corp., 72 mg). The impregnated sheet was sandwiched between glass slides and cured at 180 °C for 3 h to obtain the nanocomposite.

Figure 3 shows cross-sectional images of nanocomposites with (a) an unannealed AA sheet, (b) an AA sheet annealed at 1200 °C, and (c) an AA sheet annealed at 1400 °C. All of the nanocomposites had a structure in which the alumina phase (shown as bright areas in the figures) ran vertically in the epoxy resin (shown as dark areas) along the surface normal. The penetration of the alumina phase through the nanocomposite resulted in a high thermal diffusibility of the nanocomposite along the surface normal (Table 1). Because few voids were observed in the nanocomposite, the epoxy resin was successfully introduced into the voids in the AA sheet.

The thermal diffusibility of the nanocomposites with the various AA sheets is shown in Table 1. The in-plane thermal diffusibility ( $\alpha_{xy}$ ) was measured at room temperature using the alternating current calorimetric method (4–7). The thermal diffusibility of the nanocomposites along the surface normal ( $\alpha_z$ ) was measured using thermal wave analysis, with an ai-Phase mobile 1 (ai-Phase Co. Ltd.) (8, 9).

The thermal diffusibility was increased as the annealing temperature of the AA sheets increased. In the case of the nanocomposite with the unannealed AA sheet, the phonon conduction efficiency was low because of the amorphous nature of the AA sheet, resulting in low thermal diffusibility of the nanocomposite. On the other hand, the nanocomposites with the annealed AA sheets had a higher thermal diffusibility because of better phonon conduction of crystallized alumina compared with that of the amorphous one.

The thermal conductivity of the nanocomposite in the  $z$  direction was 12 W m<sup>-1</sup> K<sup>-1</sup> when the AA sheet annealed at 1400 °C was used (10). This value was as high as that calculated theoretically for the nanocomposites with  $\alpha$ -alumina fillers that form a perfectly connected thermoconductive network (12.3 W m<sup>-1</sup> K<sup>-1</sup>). This result can be explained by the fact that there is little interface between the alumina and resin, which functions as a large heat resistance, in the  $z$  direction, producing efficient phonon flow in the nanocomposite along the surface normal. This result suggests that the crystallized AA sheet can be a good phonon conductor along the cylinder and thus a candidate as a high-performance filler in a highly thermoconductive resin. Furthermore, a sheet with a larger thermal conductivity along the

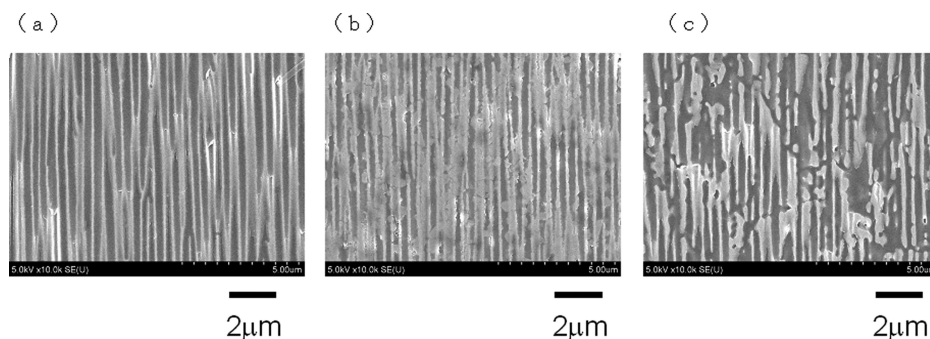


FIGURE 3. Cross-sectional images of nanocomposites with (a) an unannealed AA sheet, (b) an AA sheet annealed at 1200 °C, and (c) an AA sheet annealed at 1400 °C.

surface normal is advantageous for application such as a thermoconductive sheet between a heat generator and a heat sink. Fillers with a large aspect ratio often have a preferential orientation to the surface direction because of the requirement at sample preparation (4), which makes it difficult to prepare a sheet with a large thermal conductivity along the surface normal.

The thermal conductivity of the nanocomposite with the AA sheet annealed at 1400 °C in the surface direction was also large ( $4.6 \text{ W m}^{-1} \text{ K}^{-1}$ ) compared with that of the nanocomposite filled with an equal amount of spherical  $\alpha$ -alumina [ $0.9 \text{ W m}^{-1} \text{ K}^{-1}$  (41 vol %)] (11). The higher thermal conductivity of the nanocomposite in the surface direction was probably due to the network structure of the crystallized AA sheet, although the structure was partly fractured by the annealing. However, phonons moving toward the surface direction should have encountered more alumina/resin interface than those traveling along the surface normal because the interface ran parallel to the surface normal (there was little alumina/resin interface in the phonon path along the surface normal). Therefore, the thermal conductivity in the surface direction was smaller than that along the surface normal.

Concerning the insulative properties of the nanocomposite, the nanocomposite consists of alumina and epoxy resin (insulative materials) and is thought to be insulative. However, there would be some possibility that the insulation breaks at a higher voltage. We would like to investigate the insulative property of the nanocomposite in the near future.

In summary, a crystallized AA sheet was demonstrated to be a good candidate as a filler in highly thermoconductive resins. The nanocomposite with the crystallized AA sheet had a thermal conductivity that was almost equal to the

theoretical value calculated for the nanocomposite with a perfectly connected filler network. The crystallized AA sheet would be more practical for use in industry if a powdered AA sheet could be applied to the thermoconductive resin. A powdered AA sheet could reduce the amount of inorganic fillers in the resin, making it easy to process while maintaining its thermal conductivity.

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- (10) Thermal conductivities of the nanocomposites were evaluated using the equation  $\lambda = \alpha\rho C_p$ , where  $\alpha$ ,  $\rho$ , and  $C_p$  are the thermal diffusibility, density, and specific heat capacity of the nanocomposite at constant pressure, respectively.  $\rho$  and  $C_p$  of the nanocomposite were calculated by using the  $\rho$  and  $C_p$  values of the components.
- (11) The thermal conductivity of the nanocomposite with spherical  $\alpha$ -alumina was calculated by using the Bruggeman equation:

$$1 - \phi_f = \frac{(\lambda_f - \lambda_m)(\lambda_m/\lambda_f)^{1/3}}{\lambda_f - \lambda_m} \quad (1)$$

where  $\lambda$ ,  $\lambda_f$ ,  $\lambda_m$ , and  $\phi_f$  represent thermal conductivities of the composite, filler, and matrix and the volume fraction of the filler in the composite, respectively. For details, see: Bruggeman, D. A. G. *Ann. Phys.* **1936**, *24*, 645.

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