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Notes

Excellent Thermal Conductivity of Transparent Cellulose Nanofiber/Epoxy Resin Nanocomposites

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Introduction

High thermoconductive materials have been of great interest because the amount of heat generated in electronic devices is getting larger and larger, leading manufacturers to seek new sealants that can release the heat efficiently from the devices. Polymeric materials are frequently used as sealant because of their high adaptability to the industrial processes. However, considering their future application to the highly heat-generating parts in devices such as integrated circuits, their thermal conductivity is not enough and should be improved; low thermal conductivity of the sealant would lead to an increase in device temperature, resulting in destruction of the device as well as deterioration of the sealant itself. A general way to increase the thermal conductivity is to introduce thermoconductive fillers in the resin.[1] The existence of the fillers helps phonons transport through the sealant, leading to a higher thermal conductivity of the filler−resin composite. However, the introduction of the micron-sized fillers makes the composite opaque because of the scattering of light, which narrows the range of its application as sealant on high-output light-emitting diodes. Therefore, a novel technique must be developed to obtain transparent materials with a high thermal conductivity.

This paper reports on a transparent organic nanocomposite with a high thermal conductivity over 1 W m^{-1} K^{-1}, which is 3−5 times higher than that of conventional transparent resin. The nanocomposite consists of fibrillated pulp nanofibers embedded in an epoxy resin matrix. There are several reports on cellulose nanofiber/polymer nanocomposites in literature,[2−5] although the thermal conductivity of the nanocomposites has not been reported. Since the nanofibers are a bundle of microfibrils that consist of crystallized cellulose chains, phonon scattering in the nanofibers is very small compared with that in the amorphous resin. Therefore, the nanofibers would function as efficient pathways of phonons in the composite, making higher the thermal conductivity of the nanocomposite. Furthermore, since (a) the diameter of fibrillated pulp is less than 50 nm and (b) the difference in refractive index between nanofibers ($n_{\|} = 1.618$ and $n_{\perp} = 1.544$)[6] and resin ($n = 1.53$ for resin used in this study) is small, photon scattering from the nanocomposite is suppressed, resulting in high transparency of the nanocomposite. These factors lead to the formation of a transparent organic nanocomposite with a high thermal conductivity over 1 W m^{-1} K^{-1}. We believe this is the first report of an organic−organic nanocomposite that has both good transparency and high thermal conductivity over 1 W m^{-1} K^{-1}, which is as high as that of inorganic glass (amorphous SiO_2) that can be processed only at a higher temperature (above 600 °C). It should be also noted that the cellulose nanofiber, a gift from nature, realized these conflicting properties (e.g., good transparency and high thermal conductivity) at the same time, being a good example of natural resources that enhance the properties of polymeric materials.

Experimental Section

Materials. CELISH (Daicel Chemical Industries, Ltd.; average diameter: 30 nm; length: more than 2 μm) was used as cellulose nanofibers. A bis-phenol A-type epoxy resin (D.E.R.332) was purchased from Dow Chemical Co. HN5500 (Hitachi Chemical Company, Ltd.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (Aldrich) were used as a curing agent and catalyst, respectively. All of the chemicals were used as received. The structures of these chemicals are shown in Figure 1.

Sample Preparation. The nanofiber/epoxy resin nanocomposite was fabricated according to the following procedure: First, the cellulose was vacuum-filtered from the aqueous dispersion (0.2 wt %) by using a membrane filter with a pore diameter of 0.1 μm. After the filtration, the sheet obtained was dried at 55 °C for 48 h, followed by the immersion in the epoxy resin (10.0 g) containing the curing agent (10.1 g) and catalyst (116 mg). The impregnated sheet was then sandwiched by glass slides and cured at 120 °C for 3 h and 140 °C for 2 h to obtain the nanofiber/epoxy resin nanocomposite. The thickness and nanofiber content of the nanocomposite were 70 μm and 58 wt %, respectively.

Characterization and Measurements. Transmission spectra of the samples were measured by a Hitachi U-4000 spectrophotometer. The cross-section of the nanocomposite was observed by a Hitachi S-4800 FE-SEM operated at 0.8 kV. Coefficients of thermal expansion (CTE) of the samples were evaluated by measuring strains along the surface direction by a thermomechanical analyzer (ULVAC, TM-9000). The glass transition temperature (T_g) was determined by differential scanning calorimetry. The T_g was taken as the midpoint of the endothermic transition. The values reported were almost constant (within 10% of deviation) and were not influenced by repeated thermal cycles.

The λ_{xy} values were evaluated at room temperature by the ac calorimetric method,[7−9] while the λ_z values were measured by thermal wave analysis, using an ai-Phase mobile 1 (ai-Phase Co., Ltd.).[10,11] These measurements yielded the thermal diffusibility (α) of the sample. The thermal conductivity (λ) was calculated by using the equation $\lambda = \alpha\rho C_p$, where ρ and C_p are the density and specific heat capacity of the sample at constant pressure, respectively. The ρ and C_p values of the sample were calculated by using the ρ and C_p values of the

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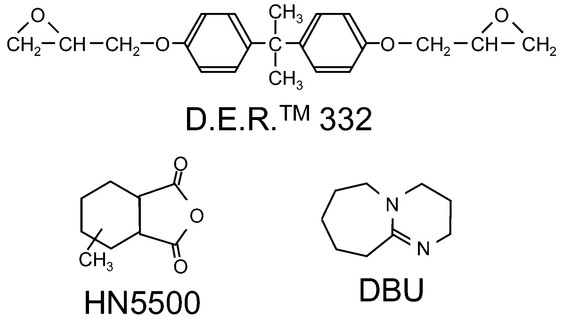

Figure 1. Chemical structures of the reagents used in this study.

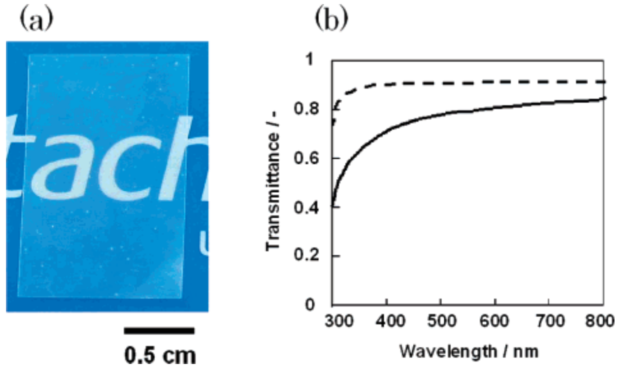

Figure 2. (a) Photograph of cellulose nanofiber/epoxy resin nanocomposite. (b) Transmission spectra of nanofiber/epoxy resin nanocomposite (solid line) and epoxy resin without nanofibers (dashed line).

components, which are written in ref 6. For the thermographic observation, the heat was provided from the right side of the samples by using a heat plate (100 °C), and the equilibrium state was captured by a thermoviewer (LAIRD-S270A, Nikon).

Results and Discussion

Figure 2a shows a photograph of the nanofiber/epoxy resin nanocomposite. Letters in the background (“a” and “c”) can be seen through the film, indicating that the nanocomposite was highly transparent. The transmission spectrum also proved high transparency of the nanocomposite (Figure 2b). The average transmittance of the nanocomposite was 80% (400−800 nm). This value almost reached the value for the 65-micron epoxy resin sheet (91%), which was prepared through the same procedure for the nanocomposite but without the nanofibers. This high transparency of the nanocomposite probably resulted from the small diameter of nanofibers and the small difference in refractive index between the nanofibers and the matrix, which suppressed scattering of the photons at the nanofiber/epoxy resin interface.

Figure 3 shows a cross-section scanning electron microscopy (SEM) image of the nanofiber/epoxy resin nanocomposite. The contrast of the image was homogeneous, and agglomeration of the cellulose nanofibers, which would be seen as a bright area, was not observed. This implies that the nanofibers were distributed homogeneously in the epoxy matrix, forming few scattering centers by their aggregation. The small cracks and voids observed in the cross-section are probably due to less compatibility of nanofibers against epoxy matrix. Improvement of the compatibility would reduce the number of cracks and voids in the matrix, leading to better transparency of the nanocomposite.

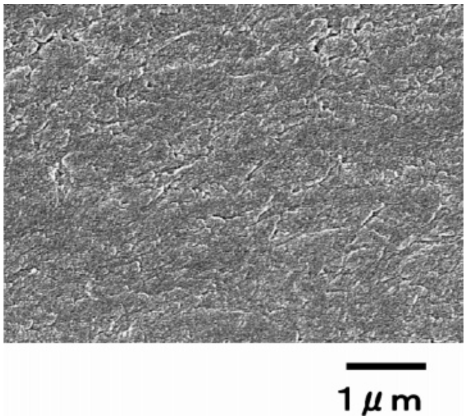

Figure 3. Cross-section SEM image of the nanofiber / epoxy resin nanocomposite.

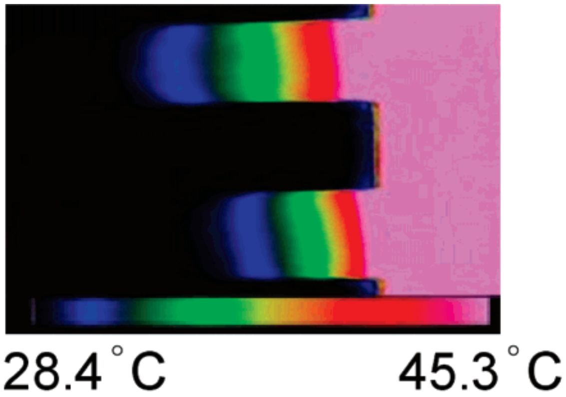

Figure 4. Thermographic image of the nanocomposite with a nanofiber content of 58 wt % (above), and the epoxy resin without nanofibers (below). The heat was provided from the right side of the samples by using a heat plate (100 °C).

Figure 4 shows a thermographic image of the cellulose nanofiber/epoxy resin nanocomposite (cellulose content: 58 wt %) and epoxy resin without nanofibers. The length of the samples was adjusted to 2 cm. From Figure 4, it is noticed that the temperature of the nanocomposite was higher than that of the epoxy resin at the same distance from the heat plate (right side in Figure 4). Therefore, the heat provided to the nanocomposite was transferred farther than that provided to the epoxy resin without nanofibers, indicating that the in-plane thermal conductivity of the nanocomposite was higher than that of epoxy resin without nanofibers.

Table 1 shows characteristic values of the cellulose nanofiber/epoxy resin composite. The values of the epoxy resin without nanofibers are also shown as a reference. In Table 1, λ_{xy} shows an in-plane thermal conductivity, whereas λ_z shows a thermal conductivity along the surface normal. The λ_{xy} value of the nanocomposite was about 5 times larger than that of epoxy resin without nanofibers. This result demonstrated that the incorporation of cellulose nanofibers enhances the thermal conductivity of the nanocomposite, owing to the better phonon-transporting

Table 1. Characteristic Values of the Nanofiber (58 wt %)/Epoxy Resin Nanocomposite and Epoxy Resin Sheet without Nanofibers[a]

	ρ/g cm^{-3}	C_p/J g^{-1} K^{-1}	α_{xy}/mm^2 s^{-1}	α_z/mm^{2}s^{-1}	λ_{xy}/W m^{-1} K^{-1}	λ_z/W m^{-1} K^{-1}
nanofiber/epoxy resin nanocomposite	1.39	1.31	0.59	0.13	1.1	0.23
epoxy resin without nanofibers	1.19	1.28	0.10	0.10	0.15	0.15

[a] ρ: density; C_p: specific heat capacity at constant pressure; α: thermal diffusibility; λ: thermal conductivity.

efficiency of cellulose nanofibers in the resin. The λ_{xy} value was larger than that of the nanocomposite with less nanofiber content ($\lambda_{xy} = 0.7$ W m^{-1} K^{-1}, nanofiber content: 39 wt %).[12] This result indicates that a larger amount of nanofibers can transport more phonons through the nanocomposite, demonstrating that the nanofibers are responsible for the improvement of the thermal conductivity of the nanocomposite.

However, the λ_z value was almost the same as that of epoxy resin without nanofibers. This result can be explained by the in-plane orientation of nanofibers that occurred during the preparation of a nanofiber sheet from the aqueous dispersion. This orientation would make the phonon pathway more in the *xy* direction than the *z* direction, leading to the anisotropic behavior of the thermal conductivity of the nanocomposite.

Significantly low thermal expansion is another interesting property of the nanofiber/epoxy resin nanocomposite. The CTE value for the nanocomposite was 23 ppm K^{-1} (below the glass transition temperature ($T_g = 88$ °C)), which was much smaller than that of the epoxy resin without nanofibers (84 ppm K^{-1}). This result indicates that the thermal expansion was significantly suppressed by the introduction of nanofibers, which have a small CTE value of less than 0.1 ppm K^{-1} (in the axial direction).[5,13] Furthermore, the CTE value became smaller above the T_g (8 ppm K^{-1}), while the epoxy resin without nanofibers showed a larger CTE value above the T_g (192 ppm K^{-1}). Segal et al. reported that the efficient transfer of thermal stress from the matrix to the fibers reduced the CTE above the T_g when high aspect-ratio glass fibers were incorporated in the nylon-6 resin.[14] Since cellulose nanofibers with a large aspect ratio were used in our system, it seems that the efficient thermal stress transfer greatly reduced the CTE of the nanofiber/epoxy resin nanocomposite to a value smaller than that below the T_g. The detailed study on the effect of cellulose nanofibers on the thermal expansion is currently going on, and will be reported elsewhere.

We also observed that the storage modulus of elasticity of the nanocomposite (5.0 GPa at 80 °C) was larger than that of the epoxy resin (3.7 GPa at 80 °C), showing that the cellulose nanofiber has a reinforcing effect on the epoxy resin.

In summary, a transparent cellulose nanofiber/epoxy resin nanocomposite with high thermal conductivity and low thermal expansion was reported. The in-plane thermal conductivity of the nanocomposite was over 1.0 W m^{-1} K^{-1}, which was 3−5 times higher than that of conventional transparent resins. The crystalline nature of the cellulose nanofibers provided excellent phonon pathways through the nanocomposite, realizing the high thermal conductivity. The introduction of cellulose nanofibers also resulted in the low thermal expansion of the nanocomposite. Furthermore, the thinness in diameter of the nanofiber and the little difference in refractive index between the nanofiber and epoxy resin made the nanocomposite transparent. Further studies are currently going on to improve these properties for future applications.

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