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Factors affecting the magnitudes and anisotropies of the thermal and electrical conductivities of poly(L-lactic) acid composites with carbon fibers of various sizes

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Abstract Investigation of the thermal and electrical conductivities of poly(L-lactic acid) composites containing carbon fibers (CFs) of various sizes has revealed that the thermal conductivity depends largely on the length of the CFs in the composites and that the electrical conductivity depends largely on the aspect ratio of the CFs. These different dependencies are due to the effect of the number of interfaces between the CFs in a percolation network formed in the composites, where electron transport is enhanced but phonon thermal conduction is limited by phonon scattering at the interfaces between the CFs. The anisotropy of each conductivity is also influenced by the length of the CFs, which could determine the alignment of the CFs in the molded composites.

Introduction

Electrically and/or thermally conductive composites consisting of polymers hybridized with conductive fillers such as carbon fibers (CFs) and carbon nanotubes (CNTs) deserve much attention in various applications [1–5]. Such composites with low filler content have excellent viscoelastic properties and can be used in sensors, actuators, and electrodes and as electromagnetic-shielding and heat-dissipating materials.

There have been many efforts to increase the electrical and thermal conductivities of polymer composites [6–9], and it has been found that adding a small amount of high-aspect-ratio fillers such as graphite flakes or CNTs increases the electrical conductivity dramatically [10–12] but increases the thermal conductivity only a little [13, 14]. The reason that the increase in thermal conductivity is relatively small is that phonon scattering at the interfaces between high-aspect-ratio fillers makes the interfacial thermal resistance too high for thermal percolation to occur [15–17]. Others have shown that composites containing CFs aligned by using a magnetic field have a very high thermal conductivity in directions parallel to the fibers [18–20], and we have shown that thermal diffusivity of poly(L-lactic acid) (PLLA) composites containing randomly aligned CFs strongly depends on the size of the CFs [21].

Although the factors affecting the electrical and thermal conductivities of CF/polymer composites have been discussed in terms of percolation [22–24], the mechanisms of the conductivity increases due to CFs and the relationship between these conductivities remain unclear. There are several reasons which make the conductivity behaviors difficult to understand. First, electrical and thermal conductivities of the composites would be based on different mechanism: electron and phonon conduction. Second, the percolation behaviors are always involved with the dispersion of CFs, which is influenced by physicochemical interactions between the CFs and a polymer matrix as well as those between the CFs. Third, molding conditions also affect the morphology of the composites and often causes an anisotropy, which is closely related to the alignment of CFs in molded composites. Accordingly, the problem seems to lie in the complication of some physicochemical and rheological factors for the conductivities. Therefore, it is important to investigate the influence of the factors on these conductivities of the composites with a more elemental approach.

Developing methods that can increase the electrical and thermal conductivities of polymer composites, we have

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recently made thermally conductive CF/PLLA composites by using fatty acid amides as binders to form a net-like structure of CFs in them. A previous study using infrared thermography has shown that the length of CFs is one of the important factors for the increase of thermal diffusivity of the composites, which is related to the interfacial thermal resistance between the CFs in a percolation network formed in the composites [21]. However, this result essentially involves the anisotropic effect of the CFs aligned in the composites during molding, so that the dominant factors affecting the thermal diffusivity still remain controversial.

The aim of the work reported here was to describe the anomalous behaviors of the electrical and thermal conductivities of CF/PLLA composites and to identify the dominant factors affecting these conductivities. To evaluate anisotropy, two different planar directions of the conductivities were investigated by measuring them both parallel and perpendicular to the surface of molded composites with a special technique. Based on the anisotropy, the factors for the electrical and thermal conductivities were analyzed by investigating them in the composites containing CFs of various sizes.

Experimental

The PLLA matrix TE-4000 (weight-average molecular weight $M_w = 120{,}000$, polydispersity index $M_w/M_n = 1.3$) was supplied by Unitika Ltd., and the properties and suppliers of the fillers used in this study—carbon black (CB), CNT, carbon nanofiber (CNF), and CFs of various lengths—are listed in Table 1. The fatty acid amide *N*,*N*′-ethylene bis-olearamide was used as a CF binder in order to form a net-like structure of CFs in PLLA resin [21]. The composites were prepared by melt-mixing the materials at about 473 K and then hot-pressing them at 453 K under a pressure of 10 MPa for 10 min to form 7 × 7 cm plates of 2 mm thick. After the hot-pressing, the molded plates were quickly quenched between glass plates and annealed at 383 K for 2 h for crystallization (this annealing increased the 37% crystallinity of the PLLA in the composites to 44%). The molecular weight M_w and polydispersity index M_w/M_n of PLLA were determined by gel permeation chromatography (using chloroform as eluent and using polystyrene standards) with a Shimadzu LC-10 system and Tosoh TSK 8025C/80MC gel columns. The crystallinity of PLLA was determined by differential scanning calorimetry with an Exter 6000 system (Seiko Instrument Inc., Tokyo, Japan) and is expressed here as a percentage calculated by dividing the sample heat of fusion by that of 100% crystalline PLLA (93 J/g) [25]. The morphologies of the composites were observed with a digital optical microscope (VHX-500, Keyence Co., Tokyo, Japan).

The thermal conductivity of the composites was measured using a thermal conductivity test meter (HC-110, Eko Instrument Co. Ltd., Japan), which is based on a steady-state heat flux technique, and their electrical conductivity was measured with an ultrahigh-resistance meter (R8340, Advantest Co., Japan). The anisotropy of each conductivity was evaluated by measuring the conductivity perpendicular to the surface of molded composite plates that had been cut into disks 50 mm in diameter and 2 mm thick and by measuring the conductivity parallel to surface of molded composite plates that had been made into layered disks 50 mm in diameter and 10 mm thick (see Fig. 1). For each measurement of thermal conductivity, the sample temperature was adjusted to 293 K.

Results and discussion

Thermal conductivity in CF/PLLA composites

The thermal conductivities of PLLA composites containing 5 wt% CFs and 5 wt% *N*,*N*″-ethylene bis-oleamide binder

Table 1 Properties of the fillers used in this study[a]

	Length (μm)	Diameter (μm)	Aspect ratio (L/D)	Thermal conductivity (W/mK)	Electrical resistivity (Ωm)	Manufacturer
CB	15	15	1	–	–	Showa Denko
CNT (MWNT)	10	0.02	500	–	1×10^{-6}	Sun Nanotech
CNF (VGCF)	20	0.15	130	1200	1×10^{-6}	Showa Denko
Short CF	40	9	4	500	–	Teijin
Medium-length CF	200	9	20	500	–	Teijin
Long CF	6000	10	600	500	5×10^{-6}	Nippon Graphite Fiber

[a] Properties provided by the manufacturers

MWNT multi-walled carbon nanotube, *VGCF* vapor-grown carbon fiber

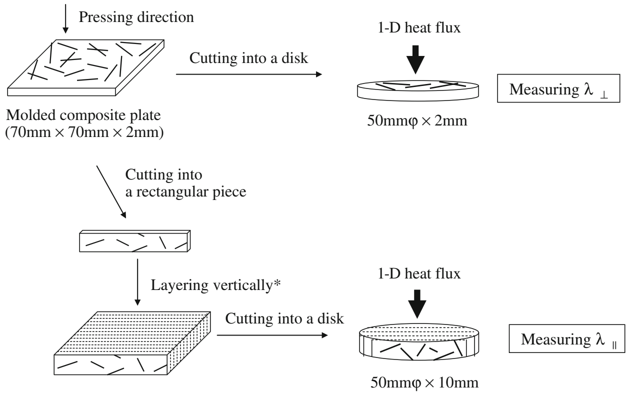

Fig. 1 Preparation of samples for measurement of electrical conductivity and steady-state thermal conductivity. * The space at the interfaces between the neighboring layered pieces was filled with an epoxy resin and each space distance was less than 10 μm. The influence of the contact space on the thermal conductivity ($\lambda_{||}$) was almost negligible because the thermal conductivity of the epoxy resin ($\approx$0.2 W/mK) is close to that of PLLA resin and the surface area of the space in the measuring direction is less than 0.5% that of the layered composite

showed anisotropy that depended on the size of the CFs in them (see Table 2). The conductivity parallel to the surface of the composite plates ($\lambda_{||}$) generally increased with the length of CFs, but the $\lambda_{||}$ of the composite with the short CF was lower than that of the composite with the CNF even though the short CF was longer than the CNF. This is because low aspect ratio of the short CF interfered with the formation of a percolation network, as indicated by the morphology of the composite shown in Fig. 2. This relation between $\lambda_{||}$ and CF length is consistent with our previous study using infrared thermography and showing that the thermal diffusivity of CF/PLLA composites with CFs of various sizes is closely associated with the length of the CFs [21].

The thermal conductivity perpendicular to the flat surfaces of the composites ($\lambda_{\perp}$) showed less improvement than the $\lambda_{||}$ did. The geometric mean thermal conductivity (λ_{mean}) of $\lambda_{||}$ and $\lambda_{\perp}$ is shown in Fig. 3 as a function of the number of CFs per unit volume of the composites (estimated by assuming CFs to be cylinders uniformly dispersed at a density 2.2×10^3 kg/m^3 and PLLA to be a perfect matrix with a density of 1.2×10^3 kg/m^3). One sees there that λ_{mean} is inversely related to the normalized number of CFs. In addition, the thermal anisotropy ($\lambda_{||}/\lambda_{\perp}$) was greater for longer CFs, which could reduce the number of interfaces between the CFs in directions parallel to the flat surfaces of the composites by aligning parallel to those surfaces. We can thus conclude that the dominant factor affecting thermal conductivity of CF composites is the size of the CFs, which can determine the efficiency of thermal transport between the CFs in the percolation network in the composites. Phonon thermal conduction in the network is limited by scattering where CFs contact each other, so longer CFs increase the thermal conductivity of the composites by reducing the number of CF contacts. Paradoxically, this result indicates that the thermal conductivity also depends on the size of the molded composites used in measurements or applied to some products. That is, it suggests that the size (or scale) dependence should be taken into account when evaluating the thermal conductivity (both experimentally and numerically). In this sense, the thermal conductivity of composites with short CFs such as CNTs and CNFs could be considered high when we are dealing with small-scale thermal transport (for instance, heat flow in thin films and microdevices).

Electrical conductivity in CF/PLLA composites

As shown in Table 3, the electrical conductivity σ of the CF/PLLA composites mainly depended on the aspect ratio of CFs. The electrical conductivity perpendicular to the surfaces of the composites ($\sigma_{\perp}$) is shown in Fig. 4 as a function of the CF content. A typical decrease in the percolation threshold, which is the critical filler content at which a composite becomes electrically conductive, was exhibited in CNT/PLLA and CNF/PLLA composites. As is commonly known, CNTs and CNFs with high aspect ratios have an advantage of forming a percolation network in a polymer matrix morphologically, and such a network is the

Table 2 Thermal conductivity (measured at 293 K) of PLLA composites with 5 wt% fillers

	Thermal conductivity (W/mK)			Anisotropy	Filler size	
	$\lambda_{||}$	$\lambda_{\perp}$	λ_{mean}	($\lambda_{||}/\lambda_{\perp}$)	Length (μm)	Aspect ratio
PLLA	0.18	0.18	–	–	–	–
CB/PLLA	0.22	0.19	0.21	1.2	15	1
CNT/PLLA	0.26	0.22	0.24	1.2	10	500
CNF/PLLA	0.71	0.34	0.53	2.1	20	130
Short CF/PLLA	0.38	0.19	0.29	2.0	40	4
Medium-length CF/PLLA	0.95	0.20	0.58	4.8	200	20
Long CF/PLLA	2.08	0.17	1.13	12.2	6000	600

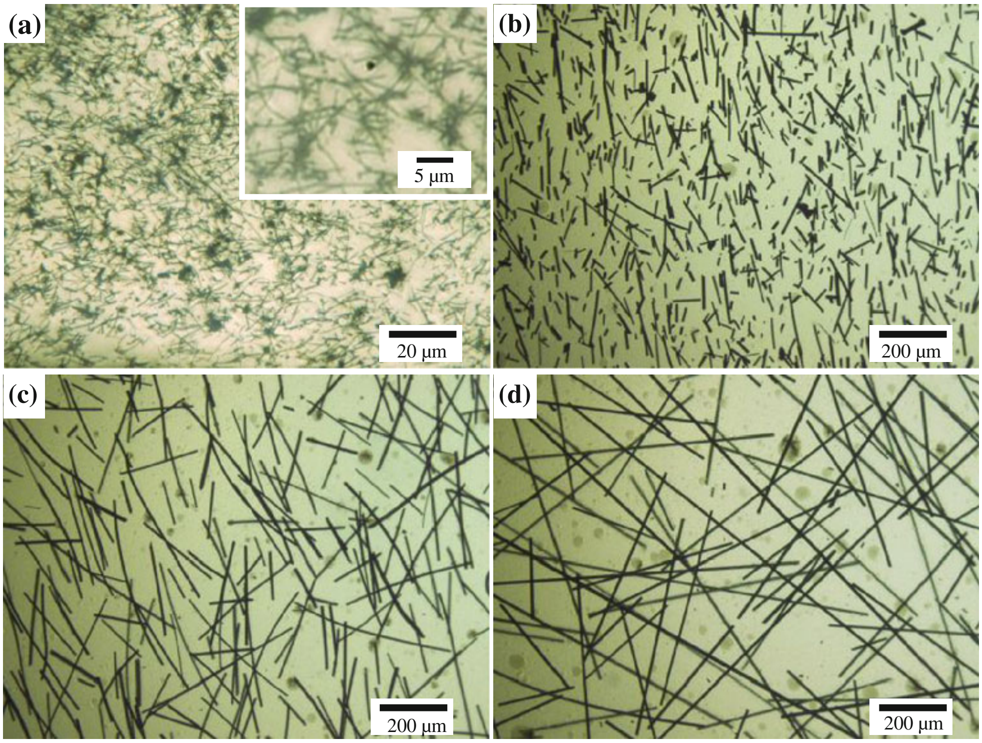

Fig. 2 Micrographs of PLLA composites with 5 wt% CFs and 5 wt% of *N*,*N*″-ethylene bis-oleamide: **a** CNF/PLLA composite, **b** short CF/PLLA composite, **c** medium-length CF/PLLA composite, and **d** long CF/PLLA composite

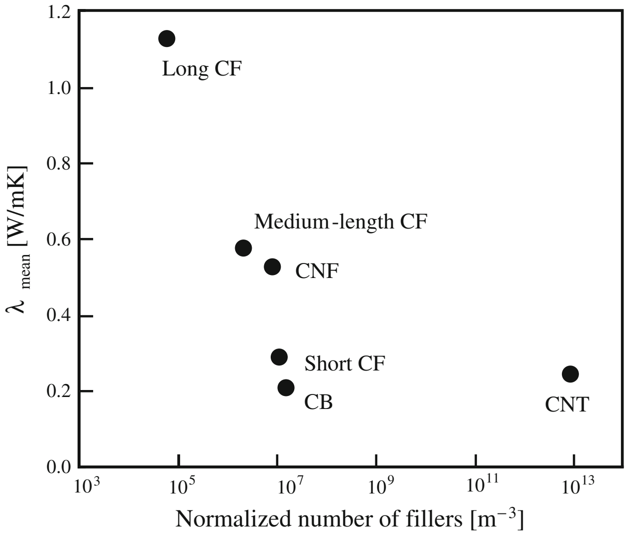

Fig. 3 Mean thermal conductivity of PLLA composites as a function of the normalized number of fillers per unit volume of the composites

only effective path for electron transport in an insulating matrix (the interfacial resistance between CFs affects electron conduction much less than phonon conduction because transport kinetics differ between electrons and phonons). However, due to the large specific surface area, high flexibility and strong hydrophobicity, CNTs and CNFs can easily agglomerate in polar resins such as PLLA to result in poor dispersion in composites. To overcome this problem, we used a specific fatty acid amid binder which has a strong affinity for hydrophobic surface of the CFs and a moderate affinity for polar PLLA resin [21], so that the composites with CNTs and CNFs achieved good dispersion and showed the lowest electrical percolation threshold.

In spite of the long CF having the highest aspect ratio, the composite with the long CF did not exhibit the highest $\sigma_{\perp}$. This is because the long CF dominantly enhances the conductivity parallel rather than perpendicular to the flat surfaces because it aligns parallel to those surfaces (a longer CF is likely to be aligned parallel to the flat surface of composites during their molding). Actually, the electrical conductivity anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) was influenced by the length of the CFs (Table 3). That is why the electrical conductivity principally depends on the aspect ratio of the CFs in the well-dispersed CF/PLLA composites, while the thermal conductivity depends on the length of CFs.

Conclusion

We demonstrated that the thermal conductivity of CF/PLLA composites depended primarily on the length of the CFs, while the electrical conductivity depended primarily on the aspect ratio of the CFs. While the CF aspect ratio was involved with the formation of the percolation network in the composites, the thermal conductivity of the composites depended primarily on CF size because this size was associated with the number of interfaces between the CFs in the

Table 3 Electrical conductivity (measured at 293 K) of PLLA composites with 5 wt% fillers

	Electrical conductivity (S/m)		Anisotropy	Filler size	
	$\sigma_{\parallel}$	$\sigma_{\perp}$	$(\sigma_{\parallel}/\sigma_{\perp})$	Length (μm)	Aspect ratio
PLLA	$<1 \times 10^{-13}$	$<1 \times 10^{-13}$	–	–	–
CB/PLLA	$<1 \times 10^{-13}$	$<1 \times 10^{-13}$	–	15	1
CNT/PLLA	5×10^{-6}	1×10^{-4}	0.05	10	500
CNF/PLLA	1×10^{-4}	1×10^{-4}	1	20	130
Short CF/PLLA	1×10^{-11}	3×10^{-13}	30	40	4
Medium-length CF/PLLA	5×10^{-10}	2×10^{-11}	30	200	20
Long CF/PLLA	2×10^{-4}	1×10^{-7}	2000	6000	600

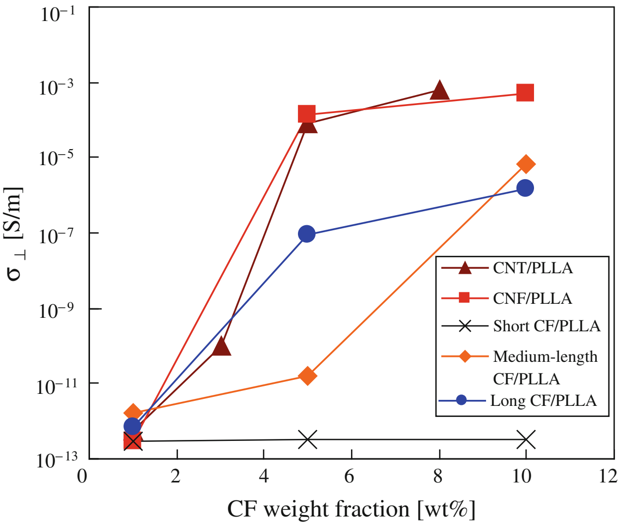

Fig. 4 Electrical conductivity of CF/PLLA composites versus CF weight fraction

network. The anisotropies of both conductivities were also influenced by the length of the CFs, which could determine the alignment of the CFs in the composites.

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