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Enhancement of thermal diffusivity of poly(L-lactic acid) composites with a net-like structure of carbon fibers

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Abstract Thermally conductive carbon fiber/poly(L-lactic acid) (PLLA) composites were made by using fatty acid amides as binders to form a net-like structure of carbon fibers in them, aiming at achieving high thermal diffusivity of the composites with a small amount of the fibers and facilitating their processing without much cost. Infrared thermography analysis of composites with varying the size of carbon fibers and controlling the solubility parameters of fatty acid amides in them revealed that the composite with 10 wt% of 6 mm-long carbon fiber and 5 wt% of *N*,*N*′-ethylene bis-olearamide had a thermal diffusivity comparable to that of stainless steel (SUS304). This high thermal diffusivity was due to percolation networks of long carbon fibers bound by the specific low-polarity amide in the composite.

Introduction

Thermally conductive polymer composites, consisting of conductive fillers in an insulating polymer matrix, have become increasingly important for many applications such as heat exchangers and heat dissipation materials, especially in electronic products. The rapid reduction of the size of electronic products is increasing the difficulty of dissipating the heat they produce. Because small and slim products such as the latest mobile phones and personal computers cannot easily be equipped with conventional cooling devices like fans and coolers, many of the plastic parts used in these products need to be able to conduct heat away from the electric parts.

Thermally conductive fillers such as metals, oxides, and carbon fibers increase the thermal diffusivity and thermal conductivity of polymers [1–5], but sufficiently large amounts of these fillers also increase the density of the polymers, reduce their mechanical strength, and make them hard to mold. Although recent studies have shown that adding a small amount of nano-sized fillers with high-aspect ratios, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs), can make polymers electrically conductive through a percolation mechanism [6–10], it does not substantially improve their thermal diffusivity and thermal conductivity [11–14]. This is because the electric current in those polymers is carried by electrons traveling along the fibers in the percolation networks whereas the heat there is carried by phonon conduction through the polymer matrix as well as the fibers, and this conduction is much reduced by phonon scattering at the interfaces between the fibers [15–18]. From this point of view, it doesn’t seem that polymer nanocomposites based on nano-sized fillers would be best candidates to achieve high thermal diffusivity and thermal conductivity for the bulk-sized electronic components and assemblies. Furthermore, nanocomposites still remain technical problems to achieve good dispersion of nano-sized fillers in a polymer matrix, and their use are limited by their prohibitively high cost.

In this article, we have explored two approaches to increasing the thermal diffusivity of poly(L-lactic acid) (PLLA) composites by using long-sized carbon fibers and specific polarity-controlled amides, aiming at achieving high thermal diffusivity of the composites and facilitating their processing without much cost. The first is based on forming a net-like structure of carbon fibers in PLLA resin by using fatty acid amides as binders to form a percolation

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network with a small amount of the fibers. The second approach focuses on the dependence of the thermal diffusivity of composites on the size of carbon fibers in them to realize the effect of reducing interfaces between the long fibers in the percolation networks. The advantages of using PLLA, a promising biomass-derived polymer, as the matrix are that PLLA have good fluidity, compared to other ordinal thermoplastic resins, for processing and dispersion with carbon fibers and the resulting composites will be environmentally friendly materials expected to be used in various industrial products [19, 20]. In the article reported here we investigated the relation between the thermal diffusivity of PLLA composites and the size of the carbon fibers in those composites and used fatty acid amide binders with different solubility parameters so that we could investigate the relation between the thermal diffusivity of those composites and the structures of their binders.

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. Carbon black and carbon fibers, including CNTs, were of six size classes denoted here by the letters A through F (Table 1). Fatty acid amides were used as binders for carbon fibers because their polarities could be easily adjusted by adding functional groups. The composites were prepared by melt-mixing the materials at about 200 °C and then hot-pressing them at 180 °C under a pressure of 10 MPa for 10 min to form 7 × 7-cm plates 2 mm thick. After the hot-pressing, the molded plates were quickly quenched between glass plates and annealed at 110 °C for 2 h for crystallization. The samples were cut into rectangular pieces subjected to all measurements. The molecular weight (M_w) and polymer dispersion (M_w/M_n) of PLLA were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform as eluent with a Shimadzu LC-10 system and Tosoh TSK 8025C/80MC gel columns. The crystallinity of PLLA was determined by differential scanning calorimetry (DSC) based on the difference between the heat of fusion and crystallization of the samples divided by 93 J/g for the 100% crystalline PLLA [21] with an Exter 6000 system (Seiko Instrument Inc., Tokyo, Japan). The morphologies of the composites were observed with a Nikon BIOPHOT microscope. The thermal diffusivity was analyzed by infrared thermography when heat was applied to bottoms of specimens observed with an infrared thermal imaging camera (TH9100, NEC Avio Infrared Technologies Co. Ltd., Japan). An ultrahigh-resistance meter (R8340, Advantest Co., Japan) was used to evaluate the specific volumetric resistance (VR) in the thickness direction of the specimen.

Results and discussion

Formation of a net-like structure of carbon fibers in PLLA resin

As a first approach to realizing percolation with a small amount of carbon fibers in PLLA resin, we tried using as binders fatty acid amides having a specific affinity to the fibers as well as PLLA resin to form a net-like structure of carbon fibers in it. The specific volumetric resistances of composites (VRs) to which the fatty acid amides with different solubility parameters (SPs) are added, which are associated with electrical percolation, are listed in Table 2. The results show that the electrical resistance of a composite to which an amide has been added is inversely related to the SP of that amide. We can thus conclude that these amides with low polarity including *N*,*N*′-ethylene bis-olearamide and *N*,*N*′-ethylene bis-stearamide can induce electrical percolation in the composites.

Observation of the morphologies of the composites revealed the formation of a net-like structure of carbon fibers and amides, as shown in Fig. 1. The PLLA resin with 5 wt% *N*,*N*′-ethylene bis-stearamide had a sea-island

Table 1 Properties of the fillers used in this study

	Length (μm)	Diameter (μm)	Aspect ratio (L/D)	Thermal conductivity (W/mk)	Electrical resistivity (Ωm)	Manufacturer
Carbon balck (CB)	≈15	≈15	≈1	–	–	Show Denko
CNT (MWNT)	≈10	≈0.02	≈500	–	1×10^{-6}	Sun Nanotech
CNF (VGCF)	≈10	≈0.1	≈100	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

Properties provided by the manufacturers

Table 2 Specific volumetric resistances (VRs) of a composites containing 5 wt% CNF and 5 wt% fatty acid amide

	Chemical formula of amide	Solubility parameter* of amide $(J/cm^3)^{0.5}$	VR of composite (Ωm)
PLLA	–	–	10^{13}
CF/PLLA	–	–	2×10^4
N,*N*′-ethylene bis-stearamide	$(C_{17}H_{35}CONH)_2(CH_2)_2$	19.7	3×10^2
N,*N*′-ethylene bis-oleamide	$(C_{17}H_{33}CONH)_2(CH_2)_2$	19.7	2×10^2
N,*N*′-ethylene bis-hydroxyl stearamide	$(C_{17}H_{34}(OH)CONH)(CH_2)_2$	21.4	2×10^3
N,*N*′-hexamethylene-bis-hydroxyl-stearamide	$(C_{17}H_{34}(OH)CONH)(CH_2)_6$	21.0	1×10^4
N,*N*′-ethylene bis-dihydroxyl stearamide	$(C_{17}H_{33}(OH)_2CONH)(CH_2)_2$	23.0	5×10^3
N,*N*′-*p*-xylylene-bis-dihydroxyl stearamide	$(C_{17}H_{33}(OH)_2CONH)C_6H_4(CH_2)_2$	24.2	3 × 103
N,*N*′-*m*-xylylene-bis-dihydroxyl stearamide	$(C_{17}H_{33}(OH)_2CONH)C_6H_4(CH_2)_2$	24.2	3 × 103

* Estimated by Fedors' method [25]

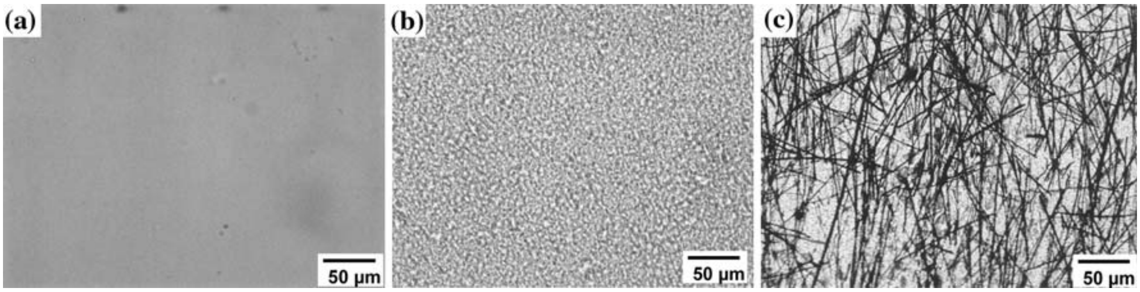

Fig. 1 Micrographs of PLLA composites: **a** PLLA, **b** PLLA with 5 wt% of *N*,*N*′-ethylene bis-stearamide, **c** PLLA with 10 wt% of long CF and 5 wt% of *N*,*N*′-ethylene bis-stearamide

structure in which the amide was finely dispersed as particles of micron-order size. When the carbon fibers were added to it, they were adsorptively cross-linked by the amide. Because the specific low-polarity amide has a strong affinity for the hydrophobic surface of carbon fibers and a moderate affinity for the more polar PLLA resin (SP = $22(J/cm^3)^{0.5}$) [22], the fibers could disperse in the PLLA resin and form a net-like structure held together by the amide adsorbing to the fibers.

Thermal diffusivity of carbon fiber/PLLA composites

To confirm the higher thermal diffusivity of the carbon fiber/PLLA composites, we examined them by heating them to 70 °C and using infrared thermography. The infrared thermograms in Fig. 2 show that the thermal diffusion of a composite containing 10 wt% of carbon fiber in PLLA resin was higher than that of neat PLLA and that the composite with 10 wt% of carbon fiber and 5 wt% of

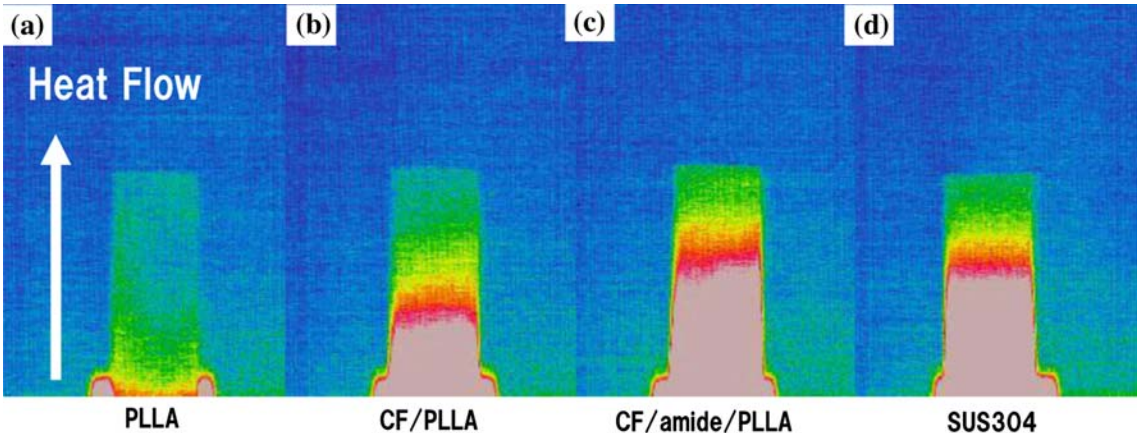

Fig. 2 Infrared thermography of composite plates of: **a** PLLA, **b** PLLA with 10 wt% of long CF, **c** PLLA with 10 wt% of long CF and 5 wt% of *N*,*N*′-ethylene bis-olearamide, and **d** stainless steel

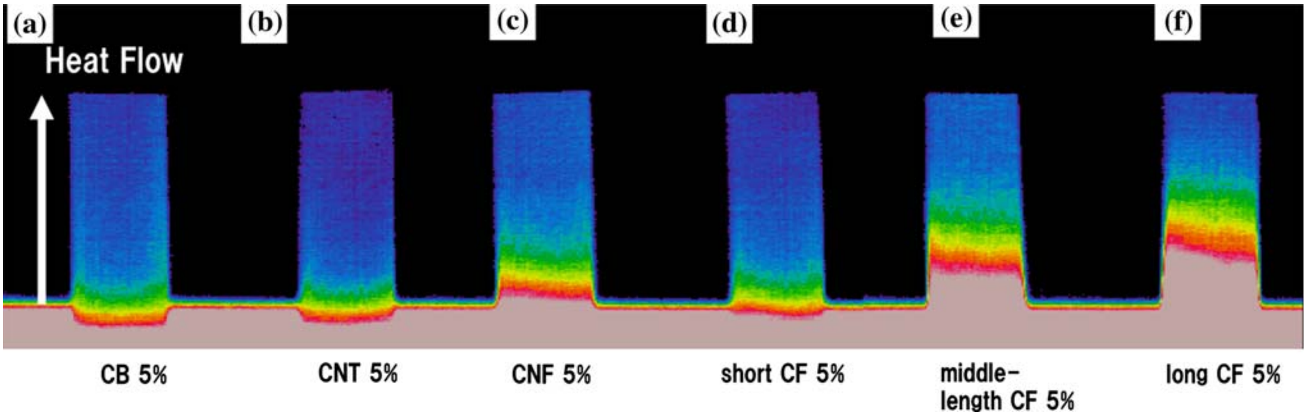

Fig. 3 Infrared thermography of PLLA composite plates containing 5 wt% various sizes of carbon filler and 5 wt% *N*,*N*′-ethylene bis-oleamide. The filler was: **a** CB, **b** CNT, **c** CNF, **d** short CF, **e** medium-length CF, and **f** long CF

N,*N*′-ethylene bis-olearamide had a thermal diffusion comparable to that of SUS304 stainless steel. That is, the specific low-polarity amide had a remarkable effect on improving thermal diffusivity of the carbon fiber/PLLA composite, promoting formation of a net-like structure of the fibers in PLLA resin.

It is well-known that the molecular weight and crystallinity of polymers affect their thermal properties. In particular, the thermal transport property including thermal diffusivity, which is based on phonon conduction, is strongly influenced by their crystal structures [23, 24]. In the experiments, the crystallinity of PLLA in the composites increased from 37 to 44% by annealing, while the molecular weight (M_w) of PLLA remained nearly unchanged through the processing even after thermal molding: the decrease of M_w after the molding was less than 10% of that of the PLLA before the molding. In spite of the increased crystallinity, the composites showed thermal diffusivity almost equal to that before annealing. Because such semicrystalline polymers as PLLA usually include topological defects such as chain ends and chain entanglements that can induce phonon scattering, their thermal diffusivity is hardly improved unless the molecular chains are elongated for crystal alignment.

Our second approach to increasing the thermal diffusivity of the composites was to use longer carbon fibers to reduce the effect of the interfacial phonon scattering between the fibers in them. Figure 3 shows that the thermal diffusion of composites with various sizes of carbon fibers and *N*,*N*′-ethylene bis-oleamide. The result indicates that thermal diffusion was highest for the composite with the longest carbon fibers (6 mm) in this experiment. This could be because longer fibers reduced the number of fiber contacts in the percolation networks more, thus more greatly reducing the effect of phonon scattering between the fibers in the percolation networks. In addition, longer fibers are more likely to be aligned in the composite plates during the molding, thereby increasing the thermal diffusivity anisotoropically parallel to the surfaces of the composite plates.

Conclusions

We have successfully fabricated thermally conductive PLLA composites by using a small amount of carbon fibers and the specific low-polarity fatty acid amides. A net-like structure of carbon fibers, which were promoted by these specific amides dispersed particulately in PLLA resin, had a remarkable effect on enhancing thermal diffusivity of the composites. The thermal diffusivity of the composite with 10 wt% of 6 mm-long carbon fiber and 5 wt% of *N*,*N*′-ethylene bis-oleamide was comparable to that of stainless steel. This high thermal diffusivity was due to percolation networks of long carbon fibers bound by the amide in the composite.

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