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How hybridization with zinc oxide whiskers and carbon fibers affects the thermal diffusivity and mechanical properties of poly(L-lactic acid) nanocomposites

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Abstract The enhanced thermal diffusivity and mechanical properties of poly(L-lactic acid) (PLLA) nanocomposites reported here are based on the percolation network formed when PLLA is hybridized with short carbon fibers (CFs) and functionalized zinc oxide whiskers. The PLLA nanocomposite containing 30 wt% ($\approx$9.5 vol%) ZnO whiskers and 10 wt% ($\approx$8.1 vol%) CFs had a thermal diffusivity almost as high as that of stainless steel and an insulator-level electrical resistivity ($>10^{10}$ Ωm). Modifying the surface of the ZnO whiskers by esterifying them using specific alcohols with long linear alkyl chains improved the elastic strength and toughness of the nanocomposites significantly. These results suggest that hybridizing PLLA with short CFs and functionalized ZnO whiskers yields nanocomposites with high thermal diffusivity as well as high electrical resistivity and excellent mechanical properties.

Introduction

Polymer composites conducting heat but not electricity conduct heat away from the electrical components of electronic products and would therefore be useful for encapsulating components and die attachments, printed circuit boards, thermal interface materials, and the casings of various electronic products. Composites consisting of polymers hybridized with thermo-conductive ceramic fillers potentially have low dielectric constant and high thermal conductivity, electrical resistivity, and electromagnetic wave transmittance but still might be easy to process because they retain the viscoelasticity of the polymer matrix.

Studies of the hybridization of polymers and thermo-conductive ceramic fillers such as aluminum oxides, aluminum nitrides, and boron nitrides have found that adding enough of these fillers to increase thermal conductivity decreases the strength and toughness of their composites and makes them hard to mold [1–8]. Adding a relatively small amount of graphitic carbon fibers (CFs) to a polymer can increase its thermal conductivity, but can also greatly increase its electrical conductivity if the CFs form a percolation network [9–11]. It has been suggested that the formation of the percolation network is closely associated with the aspect ratio of CFs in polymer composites [12–15].

Developing methods that can increase the thermal conductivity of polymer composites, we have recently made thermally conductive poly(L-lactic acid) (PLLA) composites by using fatty acid amide binders to form a net-like structure of CFs in them. A previous study using infrared thermography has shown that the thermal diffusivity of CF/PLLA composites is influenced more by the lengths of the CFs than their aspect ratios [16]. This indicates that the thermal diffusivity and thermal conductivity of the composites should depend on the number of interfaces between the CFs in the percolation network, where electron transport is assisted but phonon conduction is limited by phonon scattering. We think that composites with high thermal diffusivity as well as high electrical resistivity can be made by increasing the phonon thermal conduction between the CFs instead of the electron transport in the percolation network. In the work reported here, we have investigated the hybridization of PLLA resin with thermo-conductive

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zinc oxide (ZnO) whiskers and CFs to form a percolation network that gives PLLA nanocomposites both high thermal diffusivity and high electrical resistivity. We have also investigated the feasibility of improving the mechanical properties of the nanocomposites by the modification of the ZnO whiskers by using specific alcohols with long linear alkyl chains to esterify hydroxides of the surface of the ZnO whiskers.

Experimental

Materials and composites preparation

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. The properties and suppliers of the CFs used in this study are listed in Table 1. The long single-crystal ZnO whiskers obtained from Amtec Co., Ltd (Osaka, Japan) was used because longer fibers are easy to form a percolation network in composites [16]. The properties of the whisker provided by the manufacturer are listed in Table 2. The fatty acid amide *N,N′*-ethylene bisoleamide was used as a binder for CFs in PLLA resin [16]. A series of higher alcohols (ROH, R = n-$C_mH_{2m+1}OH$; $m = 6, 8, 9$, and 12), carbon tetrachloride, and phosphorus pentoxide were purchased from Wako Pure Chemical Industries, Inc. and used as received.

Alkoxy groups were attached to the surface of ZnO whiskers by adding 20 g of the whiskers and 50 mL of one of the alcohols to a solution of 20 g of P_2O_5 in 150 mL of CCl_4 and stirring the mixture for 5 h at room temperature. The precipitate was filtered, washed thoroughly with fresh CCl_4 and acetone, and then dried overnight under reduced pressure. The whiskers esterified with each of four different linear alkyl chains (*n*-hexyl, *n*-octyl, *n*-nonyl, and *n*-dodecyl) were obtained this way.

The PLLA nanocomposites 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 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 nanocomposites to 44%).

Table 2 Properties of single-crystal ZnO whiskers

Shape	Tetrapod
Length (μm)	~50
Diameter (μm)	~3
Specific surface area (m^2/g)[a]	1.21
Thermal conductivity (W/mK)	25.3
Electrical resistivity (Ωm)	10
Specific density (kg/m^3)	5.78×10^3

[a] Measured by the BET method

Characterization

The morphologies of the nanocomposites were characterized by using a Keyence VHX-500 digital microscope. X-ray diffraction (XRD, Rigaku RU-200 with Cu K_α radiation and a normal θ–2θ scan) was used to study the crystal structure of the ZnO whisker. The thermal diffusivity was analyzed by using infrared thermography when heat was applied to the bottoms of specimens observed with an infrared thermal imaging camera (TH9100, NEC Avio Infrared Technologies Co., Ltd., Japan). The specimens for thermography measurement were first coated with a black paint with a known emissivity. An ultrahigh-resistance meter (R8340, Advantest Co., Japan) was used to measure the electrical resistivity in the thickness direction of the specimen. The FTIR spectra in the range of 3000–2800 cm^{-1} were recorded using the KBr disk method and a Perkin Elmer Model 1000 infrared spectrophotometer. The amount of the alkoxy groups on the whiskers was evaluated by pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) using a PY-2020iD pyrolyzer (Frontier Laboratories Ltd., Japan) coupled to an Agilent 5975 inert GC/MS system and a HP-5ms capillary column. The pyrolysis was carried out at 873 K with a helium carrier gas (1 mL/min) and the 70-eV mass in the range of 20–600 *m*/*z* were recorded. The mechanical properties of the 2-mm-thick hot-pressed specimens were measured, using an Instron™ 5567 testing machine, by the

Table 1 Properties of CFs used in this study

	Length (μm)	Diameter (μm)	Aspect ratio (*L*/*D*)	Thermal conductivity (W/mK)	Electrical resistivity (Ωm)	Manufacturer
Short CF	40	9	4	500	–	Teijin
Medium-length CF	200	9	20	500	–	Teijin
Long CF	6,000	10	600	500	5×10^{-6}	Nippon Graphite Fiber

Properties provided by the manufacturers three-point flexure test. 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 the heat of fusion of 100% crystalline PLLA (93 J/g) [17].

Results and discussion

Formation of percolation network due to PLLA hybridization with ZnO whiskers and CFs

Longer CFs easily form a percolation network in PLLA resin but decrease the resin's electrical resistivity because of their high aspect ratios. As shown in Fig. 3, the electrical resistivity of PLLA composites with long CFs decreased with increasing CF content, whereas that of composites with short CFs stayed high (>10^{12} Ωm). This result is consistent with the morphologies of the composites in that the long CFs formed a percolation network in the composite while most of the short CFs were not in contact with another (see Fig. 4). Although the thermal diffusivity of PLLA composites with short CFs is not a great deal higher than that of PLLA resin [16], using thermo-conductive and electro-insulating fillers to enhance phonon thermal conduction between the short CFs would result in a composite with high thermal diffusivity and high electrical resistivity. We therefore made composites in which PLLA resin hybridized with thermo-conductive ZnO whiskers and short CFs to form a percolation network as illustrated schematically in Fig. 5. In this study, we used a long single-crystal ZnO whisker which has a relatively high thermal conductivity (Fig. 1), because longer fiber fillers are easy to form a percolation network in composites [16]. A XRD pattern of the whiskers is shown in Fig. 2. All the diffraction peaks can be indexed to the hexagonal

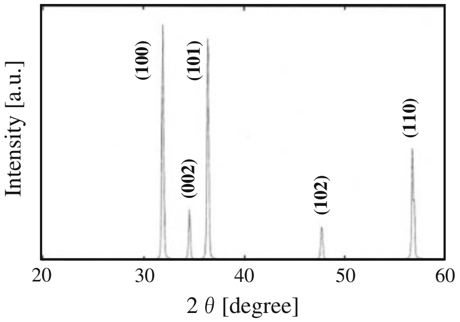

Fig. 2 XRD pattern of the ZnO whisker

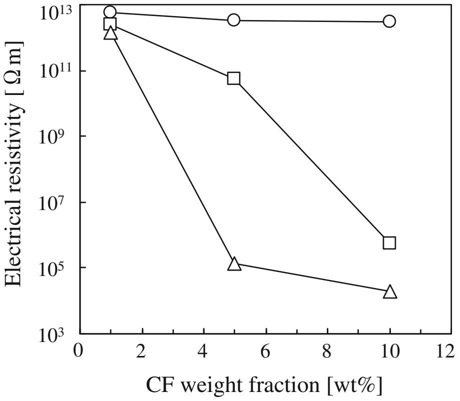

Fig. 3 Relation between the CF weight fraction and electrical resistivity of CF/PLLA composites with (*circle*) short, (*square*) medium-length, and (*triangle*) long CFs

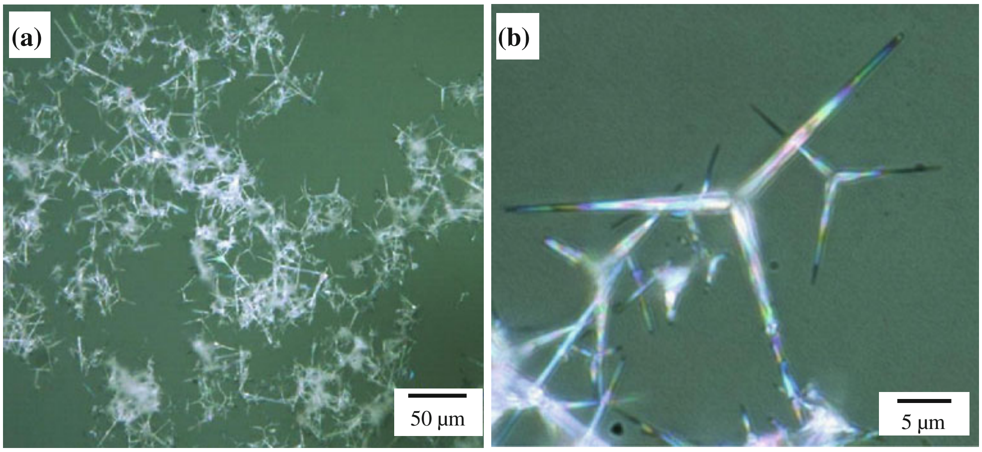

Fig. 1 Micrographs of ZnO single-crystal whisker: **a** low magnification and **b** high magnification

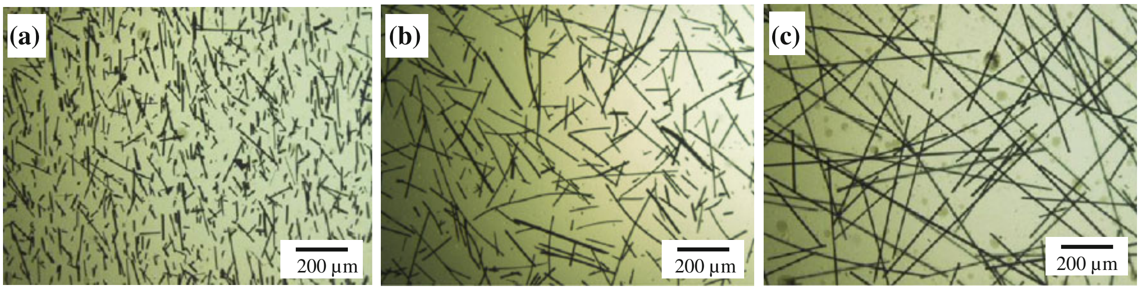

Fig. 4 Micrographs of PLLA composites containing 5 wt% *N*,*N*′-ethylene bis-oleamide and 5 wt% of **a** short, **b** medium-length, and **c** long CFs

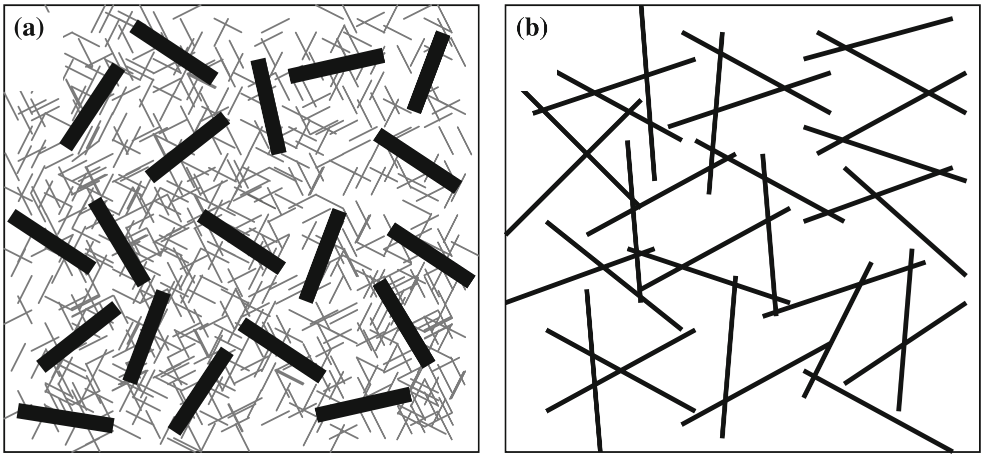

Fig. 5 Schematic diagrams of percolation networks in PLLA nanocomposites **a** with short (or medium-length) CFs and ZnO whiskers, and **b** only with long CFs

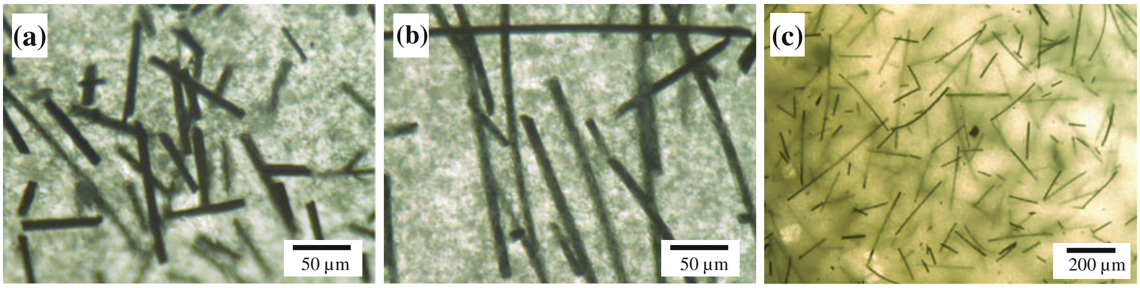

Fig. 6 Micrographs of PLLA composites containing **a** 10 wt% short CFs and 30 wt% whiskers, **b** 10 wt% medium-length CFs and 30 wt% whiskers. **c** Low magnification view of PLLA composite containing 10 wt% medium-length CFs and 30 wt% whiskers

wurtzite ZnO. The crystalline direction of the whiskers growth should be along the [001] *c*-axis [18, 19]. No other compositions were detected and the clear and sharp peaks also confirmed that the whiskers were well-crystallized.

Observation of the morphologies of PLLA nanocomposites in which PLLA hybridized with ZnO whiskers and either short or medium-length CFs showed that the composites contained percolation networks (Fig. 6). The infrared thermograms in Fig. 7 indicate that the percolation networks substantially affected the thermal diffusivity of the nanocomposites. The thermal diffusivity of the nanocomposite containing 30 wt% ($\approx$9.5 vol%) ZnO whiskers and 10 wt% ($\approx$8.1 vol%) short CFs was higher than that of the composite with the ZnO whiskers only as well as that of the composite with the short CFs only and was close to that of SUS304 stainless steel. The thermal diffusivity of the composite with the medium-length CFs and ZnO whiskers was higher than that of the composites with the short CFs and ZnO whiskers, because medium-length CFs form a percolation network in PLLA resin more easily than short CFs do. These results indicate that the formation of a percolation network incorporating the CFs and ZnO whiskers can increase phonon thermal conduction in the composites.

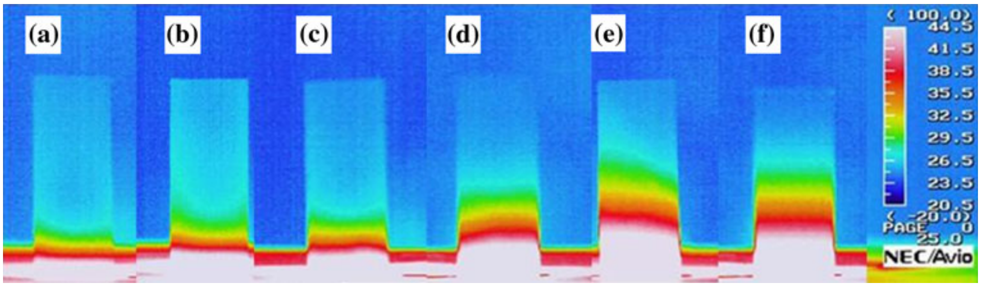

Fig. 7 Infrared thermograms of **a** PLLA and of PLLA hybridized with **b** 10 wt% short CFs, **c** 30 wt% ZnO whiskers, **d** 10 wt% short CFs and 30 wt% ZnO whiskers, **e** 10 wt% of medium-length CFs and 30 wt% ZnO whiskers, and **f** comparison thermograms of stainless steel (SUS 304)

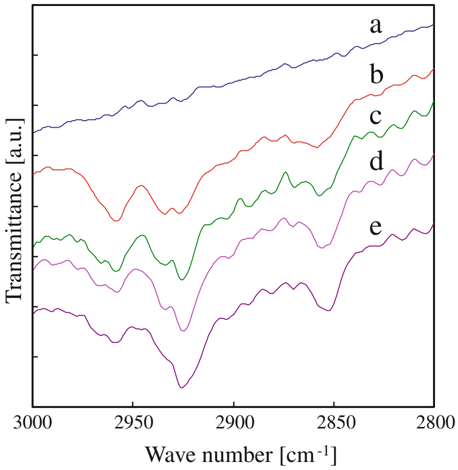

Fig. 8 FTIR spectra of *a* unmodified ZnO whisker and of ZnO whiskers modified with *b* *n*-hexyl alcohol, *c* *n*-octyl alcohol, *d* *n*-nonyl alcohol, and *e* *n*-dodecyl alcohol

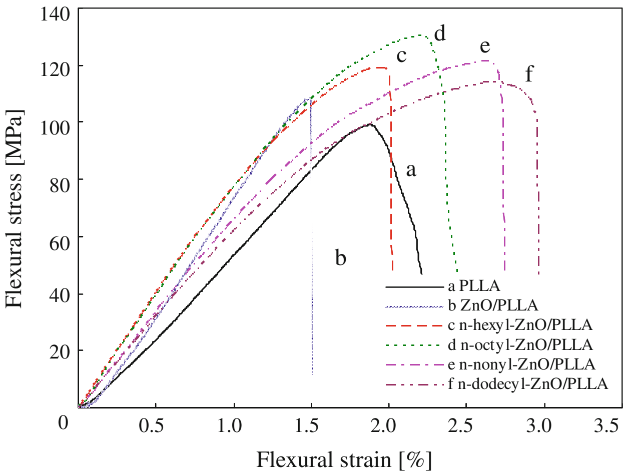

Fig. 9 Stress–strain curves of PLLA and of PLLA composites containing 30 wt% modified and unmodified ZnO whiskers: *a* PLLA, *b* PLLA composite with unmodified whiskers, **c** PLLA composite with *n*-hexyl-esterified whiskers, *d* PLLA composite with *n*-octyl-esterified whiskers, *e* PLLA composite with *n*-nonyl-esterified whiskers, and **f** PLLA composite with *n*-dodecyl-esterified whiskers

Modification of ZnO whisker surface: effects on mechanical properties of PLLA composites

Figure 8 shows the FTIR spectra of control ZnO whiskers and ZnO whiskers whose surfaces were modified with different higher alcohols. The IR spectra of all the modified whiskers exhibited a C–H stretching band around 2870–2960 cm^{-1} that was attributed to the alkoxy groups introduced to the surface of the whiskers by esterification [20]. The amount of surface alkoxy groups on the whiskers was estimated by calculating the area of the peak of the specific alcohols and alkenes detected by the Py–GC/MS (Table 3). The amount of alkoxy groups on the whiskers was decreased with increasing the length of their alkyl chains. This could be because larger alcohols were more difficult to react with the whisker surface due to the steric hindrance in the molecules.

The effect of the ZnO whisker surface modification on the mechanical properties of the composites was confirmed by flexural testing. Figure 9 shows that both the flexural strength and strain in the composites with the functionalized whiskers (curves c–f) were significantly greater than those of the PLLA resin (curve a) and those of the composite with unmodified whiskers (curves b). As the hydrophobic surfaces of the functionalized whiskers with

Table 3 Surface properties of unmodified ZnO whiskers and ZnO whiskers modified with different alcohols

Sample	Treated alcohol	Amount of surface alkoxy group on ZnO whisker		MFR of PLLA composite (g/10 min)
		(mol/g)	(molecules/nm^2)	
ZnO (pristine)	None	0	0	515
n-hexyl-ZnO	*n*-hexyl alcohol	9.4×10^{-5}	46.8	28
n-octyl-ZnO	*n*-octyl alcohol	1.8×10^{-5}	8.9	28
n-nonyl-ZnO	*n*-nonyl alcohol	2.8×10^{-6}	1.4	28
n-nonyl-ZnO	*n*-dodecyl alcohol	1.1×10^{-6}	0.6	30

Data of PLLA composite with 30 wt% whiskers measured at 200 °C under a load of 5 kg

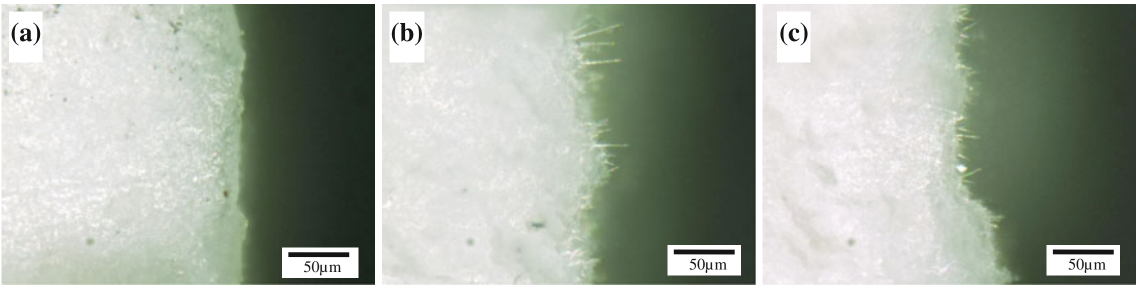

Fig. 10 Micrographs of the cross-sectional fracture of PLLA composites with 30 wt% of **a** unmodified whiskers, or **b** *n*-octyl-esterified whiskers, **c** *n*-dodecyl-esterified whiskers

alkoxy groups give those whiskers an affinity for PLLA resin, the whiskers reinforce the PLLA matrix resin. These interactions between the whiskers and the PLLA matrix are deduced from investigation of the fracture surfaces of the composites. As seen in Fig. 10, the fracture of the composites with *n*-octyl-esterified whiskers and *n*-dodecyl-esterified whiskers had several whiskers sticking out compared with that of the composites with unmodified whiskers. This result indicates that the esterified whiskers provide better wettability, thereby increasing the flexural strength of the PLLA composites. Note that the breaking strain of the nanocomposites increased with the length of the introduced alkoxy chains (*n*-hexyl < *n*-octyl < *n*-nonyl < *n*-dodecyl). This could be because the whiskers with longer alkoxy chains dissipate energy better by dispersing into entangled PLLA molecules and facilitating the molecular-chain slip between the PLLA molecules.

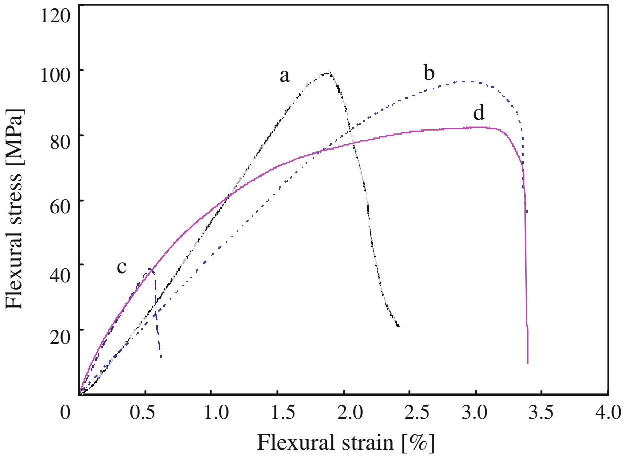

Fig. 11 Stress–strain curves of *a* PLLA, *b* PLLA composite with 10 wt% short CFs, *c* PLLA composite with 10 wt% short CFs and 30 wt% unmodified ZnO whiskers, *d* PLLA composite with 10 wt% short CFs and 30 wt% *n*-octyl-esterified whiskers

The modification of ZnO whiskers surfaces significantly improved the mechanical properties of the nanocomposites with the whiskers and short CFs. Figure 11 shows typical stress–strain curves of the PLLA nanocomposites containing 10 wt% short CFs and 30 wt% *n*-octyl-esterified whiskers. The elastic modulus and strength, the breaking strain, and the electrical resistivity of PLLA and PLLA hybridized with short and medium-length CFs and modified and unmodified ZnO whiskers are summarized in Table 4. Both flexural strength and strain showed a significant increase in the composite with *n*-octyl-esterified whiskers and the short CFs (curve d in Fig. 11), compared to those of the composite with unmodified whiskers and the short CFs (curve c in Fig. 11). These results indicate that the alkoxy groups on the functionalized whiskers could give the nanocomposites better whisker–PLLA interactions that are essential to the mechanical enhancement. Consequently, hybridizing PLLA with functionalized ZnO whiskers and the short CFs seems to be a way to make

Table 4 Flexural properties of PLLA and PLLA composites with different fillers

	Flexural strength (MPa)	Flexural modulus (MPa)	Strain at break (%)	Electrical resistivity (Ωm)
PLLA	99	4,100	1.9	$>10^{13}$
PLLA + short CF 10%	89	4,300	3.3	3×10^{12}
PLLA + short CF 10% + unmodified ZnO 30 wt%	40	8,100	0.6	5×10^{10}
PLLA + short CF 10% + *n*-octyl-ZnO 30 wt%	80	8,900	3.2	5×10^{10}
PLLA + medium-length CF 10%	101	6,400	3.1	6×10^{5}
PLLA + medium-length CF 10% + unmodified ZnO 30 wt%	46	8,300	0.7	5×10^{4}
PLLA + medium-length CF 10% + *n*-octyl-ZnO 30 wt%	80	7,200	3.6	5×10^{4}

PLLA composites with high thermal diffusivity and low electrical conductivity without sacrificing the advantageous mechanical properties of PLLA.

Conclusion

We demonstrated that hybridizing PLLA with functionalized ZnO whiskers and short CFs resulted in the production of composites having a high thermal diffusivity and retaining the high electrical resistivity of PLLA matrix. This high thermal diffusivity is due to the formation of a percolation network incorporating these two fillers, and composites with 30 wt% ZnO whiskers and 10 wt% short CFs showed a thermal diffusivity almost as high as that of stainless steel and an insulator-level electrical resistivity ($>10^{10}$ Ωm). Using certain alcohols with long linear alkyl chains to modify the surface of the whiskers improved the mechanical properties of the composites significantly. These results could lead to the production of thermally conductive and electrically insulating polymer composites for widespread use in various applications.

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