Light-Weight Flexible Carbon Nanotube Based Organic Composites with Large Thermoelectric Power Factors

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ABSTRACT Typical organic materials have low thermal conductivities that are best suited to thermoelectrics, but their poor electrical properties with strong adverse correlations have prevented them from being feasible candidates. Our composites, containing single-wall carbon nanotubes, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) and/or polyvinyl acetate, show thermopowers weakly correlated with electrical conductivities, resulting in large thermoelectric power factors in the in-plane direction of the composites, ~160 μW/m·K^2 at room temperature, which are orders of magnitude larger than those of typical polymer composites. Furthermore, their high electrical conductivities, ~10^5 S/m at room temperature, make our composites very promising for various electronic applications. The optimum nanotube concentrations for better power factors were identified to be 60 wt % with 40 wt % polymers. It was noticed that high nanotube concentrations above 60 wt % decreased the electrical conductivity of the composites due to less effective nanotube dispersions. The thermal conductivities of our 60 wt % nanotube composites in the out-of-plane direction were measured to be 0.2–0.4 W/m·K at room temperature. The in-plane thermal conductivity and thermal contact conductance between nanotubes were also theoretically estimated.

KEYWORDS: thermoelectric · carbon nanotube · organic composite · power factor · polymer

Thermoelectric energy conversion is very effective in harvesting electricity from heat sources with low temperature gradients relative to the environmental temperature.[1−3] Electricity can also be supplied to a thermoelectric system for refrigeration. Their high energy densities without moving parts are ideal for compact mobile power sources and distribution systems for the applications that necessitate robustness and silence. Recent large improvement in the thermoelectric efficiency of inorganic alloy materials based on Bi−Te−Sb−Pb[4−6] makes thermoelectrics more attractive for a variety of applications including on-chip electronics cooling and energy harvesting from automobiles. Current state-of-the-art thermoelectric materials, however, often contain heavy, expensive, brittle, and toxic elements such as lead and tellurium.[7]

This paper reports carbon nanotube based organic composites that provide great opportunities for achieving easy-to-manufacture, light-weight, flexible, inexpensive, and nontoxic energy recovery and solid-state cooling. This brings great advantages over the recently reported hybrid materials[8,9] containing a considerable amount of heavy and/or toxic inorganic materials. Carbon-based materials have low density (~1 g/cm^3) in comparison to that of the state-of-the-art thermoelectric material, Bi_2Te_3 (~7.86 g/cm^3), which is particularly important in mobile energy conversion technology. Furthermore, manufacturing processes are simple without using high temperatures and special environment (*e.g.*, vacuum or inert environment chambers to prevent oxidation) that are typically necessary for preparing inorganic semiconductor materials. In comparison to the previous work with polymer-based composites,[10−13] this study demonstrates that carbon nanotube concentrations in the composites can be increased up to 75 wt % without using high-concentration binders such as polyvinyl acetate (PVAc). More importantly, the thermoelectric power factor of our composites with only carbon-based materials has been increased by orders of magnitude compared to those of typical nanotube-filled polymer composites, providing very promising opportunities for efficient polymer thermoelectrics.

The thermoelectric efficiency can be described by the thermoelectric figure of merit (ZT),

$$ZT \equiv S^2\sigma T/k \qquad (1)$$

where S, σ, T, and k are thermopower (or the Seebeck coefficient), electrical conductivity, temperature, and thermal conductivity,

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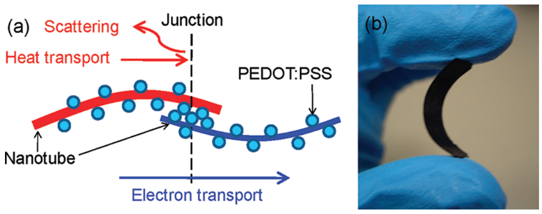

Figure 1. (a) Nanotubes are coated by PEDOT:PSS particles, making nanotube-PEDOT:PSS-nanotube junctions in the composites. The presence of the junction is believed to give rise to exceptional thermoelectric transport properties (*i.e.*, deterring heat transport as opposed to favorable pathways for electrons). (b) Fully dried composite held between two fingers indicates that it is a free-standing flexible black material.

TABLE 1. Concentrations of Carbon Nanotube (CNT), PEDOT:PSS, and PVAc in the Composites[a]

		PEDOT:PSS wt %		PVAc wt %		
sample	CNT wt %	PH500	PH1000	Vinac	Vinnapas	
1	35	35		30		
2	40	40		20		
3	45	22.5		32.5		
4	60	30		10		
5	70	17.5		12.5		
6	75	18.75		6.25		DMSO
7	60	30			10	
8	60		30	10		
9	60		30		10	
10	60	40				
11	60		40			

[a] The nanotube concentrations were varied from 35 to 75 wt %, and the ratios of nanotubes to PEDOT:PSS were 1:1, 1:0.67, 1:0.5, and 1:0.25. Two different grades of PEDOT:PSS (PH500 and PH1000) and PVAc (Vinac xx210 and Vinnapas 410) were tested.

respectively. Typical organic materials have highly desirable thermal conductivities (*e.g.*, polymers made of PVAc: ~0.2 W/m·K at 300 K) compared to inorganic semiconductors (*e.g.*, crystalline silicon: ~140 W/m·K at 300 K). However, their poor electrical conductivities and/or thermopowers generally result in small ZT values. The recent progress in developing electrically conducting polymeric materials considerably enhanced electrical conductivity,[14,15] but ZT improvement has been very challenging due to strong correlations between thermoelectric transport properties. For instance, highly electrically conductive materials often have low thermopower values.[16]

Our approach demonstrates that it is feasible to make thermoelectric properties deviated from such traditional behaviors so as to achieve a large improvement in ZT. In essence, this study employs an organic material that has relatively high electrical conductivity but low thermal conductivity. The organic material modifies the junctions between nanotubes, suppressing phonon transport but maintaining electronic properties. In order to increase electrical conductivity, carbon nanotubes were added to the organic materials because their "intrinsic" electrical conductivities were reported to be very high up to ~2 × 10^7 S/m at room temperature.[17] Nevertheless, nanotubes have been considered to be irrelevant for thermoelectric applications due to high intrinsic thermal conductivity, ~10^3 W/m·K at room temperature.[18,19] The thermal conductivity, however, can be considerably reduced when nanotubes are bundled in bulk-scale materials. For instance, the thermal conductivities of nanotube mats[20] and beds[21] were measured to be ~210 and 0.1–0.2 W/m·K at 300 K, respectively. In our composites, thermal conduction through nanotubes was substantially impeded by sandwiching organic particles between the nanotubes whose vibrational spectra are different from those of the particles. Such mismatches often effectively block phonon transport and thereby suppress thermal conductivity. The particles are made of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), and a schematic showing electron and phonon transport across a junction is illustrated in Figure 1a. Despite the large barrier for phonons, electrons can be transported across the junction since PEDOT:PSS has relatively high electrical conductivity up to ~10^4 S/m.[15,22]

The junction is also believed to play an important role in filtering low energy electrons, keeping relatively constant thermopowers (27–41 μV/K for the samples containing 35–60 wt % nanotubes) even with the case where the electrical conductivity of the composite was significantly raised to 1.35 × 10^5 S/m by using 60 wt % nanotubes in the composites. This electrical conductivity is orders of magnitude higher than those of other typical organic composites with conductive fillers (10^{-2}–10^{-1} S/m).[23−25] The high electrical conductivity with the relatively constant thermopower resulted in large thermoelectric power factors ($S^2\sigma$) up to ~160 μW/m·K^2. On the other hand, the thermal conductivity of the composites was maintained within the range of typical organic materials, 0.2–0.4 W/m·K. Note that the electrical properties were measured in the in-plane direction of our composite films and thermal conductivity in the out-of-plane direction. The loosely related thermoelectric transport properties may lead to a ZT close to those of inorganic semiconductors such as bulk PbTe (ZT = 0.2–0.3 at 300 K[1,2]) and bulk Bi_2Te_3 (ZT = 0.7–0.8 at 300 K[1,2]) as well as higher than that of bulk silicon (ZT ~ 0.01 at 300 K[26]).

RESULTS AND DISCUSSION

Samples were made of single-wall carbon nanotubes mixed with different grade PEDOT:PSS or/and PVAc polymers. They are black, flexible, and free-standing materials, as shown in Figure 1b. The concentrations of nanotubes, PVAc, and PEDOT:PSS are listed in Table 1. The composites were cold-fractured,

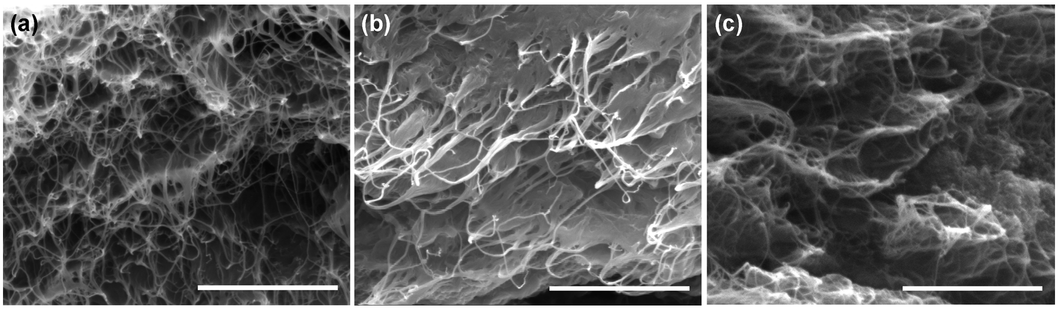

Figure 2. Scanning electron micrographs of cold-fractured cross sections along the out-of-plane direction for (a) sample 2, (b) sample 5, and (c) sample 11. The less amount of the stabilizer (PEDOT:PSS) resulted in thicker and less dispersed nanotubes. All scale bars represent 2 μm.

and their cross sections were inspected under a scanning electron microscope, as shown in Figure 2. Nanotubes shown like spaghetti are randomly distributed. Their microstructures are very different from those of segregated-network polymer composites.[10−12] This is attributed to the high nanotube concentrations with relatively small concentrations of the polymers and an annealing process at an elevated temperature (80 °C). The fractured surfaces were highly irregular due to the randomly distributed nanotubes that reinforce the mechanical strength of the composites. The nanotubes were pulled out from the composite rather than fractured or embedded in the matrix, due to their high mechanical strengths. The nanotubes were better dispersed in sample 2 (Figure 2a), showing smaller diameter nanotube bundles, in comparison to sample 5 (Figure 2b) containing a less amount of PEDOT:PSS. The dispersion condition is also denoted by the radius of curvature for the curved nanotubes because it is easier to bend smaller and less clumped bundles. From the composites synthesized without the polymer binder (*e.g.*, PVAc) (sample 11), aggregated PEDOT:PSS particles were identified as shown in Figure 2c.

The electrical conductivities of samples 1−6 are shown as red filled circles in Figure 3 when the nanotube concentrations was varied from 35 to 75 wt %. The ratio of nanotubes and PH500 was 1:1 for 35 and 40 wt % samples, 1:0.5 for 45 and 60 wt % samples, and 1:0.25 for 70 and 75 wt % samples. PH500 was used without additional doping except for the 75 wt % sample whose PEDOT:PSS was doped with dimethyl sulfoxide (DMSO) at 80 °C for 2 h. The electrical conductivity was gradually increased by raising the nanotube concentration up to 60 wt %. However, additional nanotubes used in 70 and 75 wt % composites (samples 5 and 6) suppressed the electrical conductivity. With 35 and 60 wt % of nanotubes, electrical conductivities were measured to be 4.71 × 10^4 and 1.35 × 10^5 S/m, respectively, which are orders of magnitude higher than those of typical nanotube-filled polymer composites.[23−25] The electrical conductivities of nanotube-only networks may be calculated as ∼10^5 S/m by considering the nanotube network and the polymer as parallel resistors. This conductivity is close to recent measurement results for the films made of only nanotubes,[27] which provides an indirect evidence of good electrical pathways across nanotube junctions.

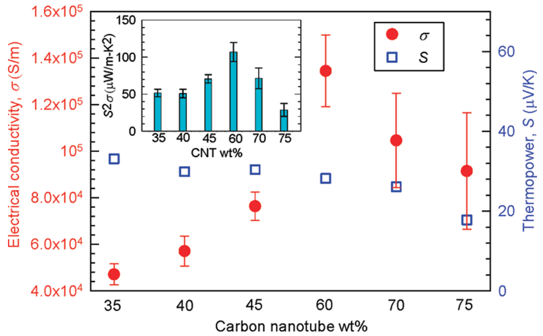

Figure 3. Electrical conductivities (red circles) and thermopowers (blue squares) of the composites with different nanotube concentrations (samples 1−6 from the left to the right plot). The inset shows the thermoelectric power factors ($S^2\sigma$).

It is worth pointing out that the intrinsic electrical conductivity of an "individual" nanotube considerably varies between 10^1 and 10^7 S/m at room temperature depending on the chirality.[17] Bulk-scale composites contain various chirality nanotubes whose intrinsic electrical characteristics are either metallic or semiconducting. Nevertheless, when nanotubes are exposed to air (particularly for nanotubes made in an oxygen-rich environment like our sample preparation processes with aqueous solutions), semiconducting nanotubes become degenerate p-type conductors,[27−30] making less electrically resistive paths across the junctions. The work functions of both metallic and semiconducting nanotubes become ∼5.0 eV after doping,[28] which matches that of PEDOT:PSS.[31−33] In our doping experiments, we also observed that the electrical conductivity of nanotube-only films was significantly decreased when nanotubes were annealed in vacuum, but the conductivity was recovered when they were exposed to air. The reduction in the electrical conductivity from the samples containing more than 60 wt % nanotubes could be attributed to less effective nanotube dispersion due to the lack of the stabilizer (PEDOT:PSS), as indicated by the thicker bundles in Figure 2b. PEDOT:PSS coats the surface of nanotubes, playing an important role in separating bundled/clumped nanotubes into smaller bundles or individual tubes in water as well as binding them to form composites upon drying. Bundled and aggregated nanotubes due to the lack of dispersants lessen the number of nanotube connections responsible for electron transport. The image of sample 5 in Figure 2b (the ratio of nanotube to PEDOT:PSS = 1:0.25) shows bigger diameter bundles than sample 2 (the ratio of nanotube to PEDOT:PSS = 1:1). The electrical conductivity of the doped samples (sample 6; 75 wt % nanotube) was also decreased, although the electrical conductivity of PEDOT:PSS was improved by DMSO doping.[15] In addition to the inferior dispersion, insufficient polymeric binding materials in sample 6 are likely to be partly responsible for the suppression. This influence is also reflected in the thermopower lower than 20 μV/K. Note that typical PEDOT:PSS films show ~10 μV/K,[14,22,34] and a composite made of DMSO-doped PEDOT:PSS (30 wt %) and electrically insulating PVAc has only 17 μV/K at room temperature.[12] It is striking that thermopowers of samples 1–4 were high and consistent (28–33 μV/K) even with the very high and 3-fold increase in the electrical conductivity (from 4.71×10^4 to 1.35×10^5 S/m). The power factor was calculated to be up to ~100 μW/m·K^2, as plotted in the inset of Figure 3.

The influence of PEDOT:PSS and PVAc on the thermoelectric properties of the composites was studied by using PH500 and PH1000 (different grades of PEDOT:PSS) as well as Vinac XX210 and Vinnapas 401, as shown in Figure 4a. The concentration of nanotubes was fixed to 60 wt % from which the highest power factor was obtained (see Figure 3). In our study, the composites with PH500 showed higher electrical conductivity while thermopowers from the composites with PH1000 were better regardless of PVAc type and concentration. The electrical conductivity of PH1000 is generally higher than that of PH500 upon doping with DMSO, and undoped PEDOT:PSS has poor conductivities.[15] The deviation from the typical behaviors might originate from their different interactions with nanotubes as well as the thermal annealing process in our experiments. Note that DMSO is not replacing anything in PEDOT:PSS (not like inorganic materials such as Si) but is rearranging it to have better electrical conduction. In fact, when DMSO remains in PEDOT, electrical conductivity decreases. Our experiments did not utilize DMSO except sample 6 in order not to sacrifice thermopower since the power factor is proportional to a square of thermopower (*i.e.*, $S^2\sigma$). The thermopowers (~40 μV/K) of the composites with PH1000 are larger than those of other composites containing PH500. In particular, it is remarkable that the high electrical conductivity (~10^5 S/m) did not diminish thermopower. On the other hand, the small difference of the electrical properties with Vinac and Vinnapas may be attributed to their small concentrations in the composites. When Vinac or Vinnapas was replaced by PH1000 (Figure 4a(iii)), the thermopower was slightly decreased, possibly due to the low thermopower of PEDOT:PSS. The inset of Figure 4a suggests that the larger thermopowers of the samples with PH1000 give rise to superior power factors. The power factors of our samples in this study are very high, ~10 times higher than those of segregated polymer composites[10–12] and nanotube–polyaniline composite,[35] and 10–100 times higher than "organic" conducting polymer materials.[14,22]

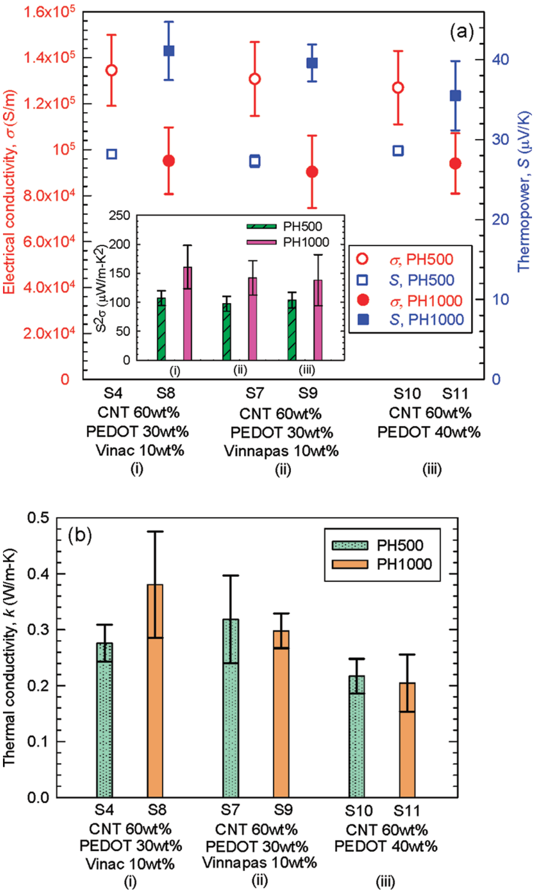

Figure 4. Thermoelectric properties of the composites when the types and concentrations of PEDOT:PSS and PVAc were varied (samples 4, 8, 7, 9, 10, and 11 in the order from the left to the right in the plot). (a) Electrical conductivities (red circles) and thermopowers (blue squares) of the composites made of 60 wt % carbon nanotubes. Hollow and filled plots indicate PH500 and PH1000, respectively, and two different PVAc, Vinac and Vinnapas, were used. The inset shows the thermoelectric power factors ($S^2\sigma$). (b) Thermal conductivities of the composites containing 60 wt % carbon nanotubes.

A steady-state method (ASTM D5470)[36] was employed for measuring thermal conductivity in the out-of-plane direction. The thermal conductivity measurements were performed in the out-of-plane direction, whereas electrical transport was measured along the in-plane direction. It should be noted that thermal conductivity measurements along the in-plane direction

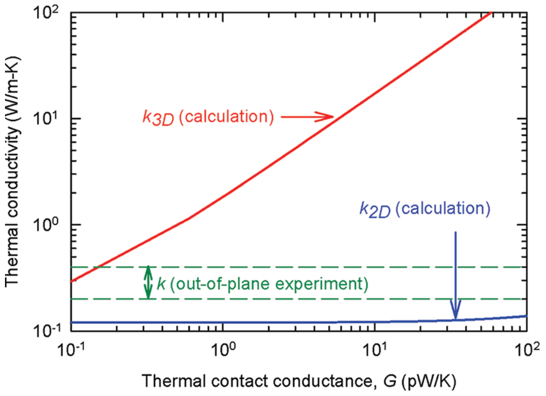

Figure 5. Theoretical thermal conductivity (k_{3D}) of a composite containing a 3D nanotube network and the theoretical out-of-plane thermal conductivity (k_{2D}) of a composite containing a 2D nanotube network when thermal contact conductance varies from 0.1 to 100 pW/K. The out-of-plane experimental thermal conductivity ranges from 0.2 to 0.4 W/m·K. For the calculations, nanotube vol % and the polymer thermal conductivity were set to be 60 and 0.3 W/m·K, respectively, and the parallel resistor model (eq 2) was used.

are not trivial because thermal radiation from the sample surface compared to thermal conduction along the in-plane direction is comparable due to the low thermal conductivity and the small sample thicknesses. The electrical property measurements in the out-of-plane direction is also very challenging because the samples are thin and highly electrically conductive. Nevertheless, it is very surprising that the thermal conductivities of the composites were measured to be 0.2−0.4 W/m·K for samples 4 and 8 (Figure 4b(i)), 7 and 9 (Figure 4b(ii)), and 10 and 11 (Figure 4b(iii)), considering the high nanotube concentration (60 wt %) and electrical conductivity. Similar thermal conductivities from the composites containing PVAc and PEDOT:PSS were reported to be 0.2−0.4 W/m·K,[10−12] but their electrical conductivities were orders of magnitude lower than 10^5 S/m. Moreover, nanotube concentrations were much lower than 60 wt %, and thermal conductivities were increased by adding more nanotubes to the composites.[10,12]

The thermal conductivity (k) of a composite may be calculated by using a parallel resistor model

$$k = k_n'V_n + k_pV_p \qquad (2)$$

This indicates that the thermal conductivity (k_n') of the nanotube networks is only 0.3−0.7 W/m·K when the thermal conductivity of the polymer (k_p) is assumed to be 0.2−0.3 W/m·K[10,12,22,37] and the volume fractions of the nanotubes and polymers are, respectively, ∼0.6 and ∼0.4; k_n' is much lower than the intrinsic nanotube property, ∼10^3 W/m·K.[18,19] This discrepancy is likely to come from thermal contact resistance between the nanotubes as well as between the nanotubes and PEDOT:PSS. According to the micrographs in Figure 2, the nanotubes are randomly distributed and oriented, although it is likely that some of nanotubes are deposited in the in-plane direction due to their high aspect ratios.

When we assume the nanotubes formed random three-dimensional (3D) networks, the thermal conductivity ($k_{3D,NT}$) may be calculated using eq 3.[38]

$$k_{3D,NT} = \frac{G}{R}\frac{\pi(nL^2R)^2}{36}\left(1+16\left(\frac{R}{L}\right)+80\left(\frac{R}{L}\right)^2 + 192\left(\frac{R}{L}\right)^3+153.6\left(\frac{R}{L}\right)^4\right) \qquad (3)$$

where G, R, n, and L indicate thermal contact conductance between nanotubes, the radius of nanotubes, the volume number density of intertube contacts, and the length of nanotubes, respectively. The volume number density, n, is equal to $\rho/(2\pi RLn_\sigma m)$, where ρ, n_σ, and m indicate density (∼1.1 g/cm^3),[39] the number density of carbon atoms on the surface of a nanotube, and the mass of a carbon atom, respectively. In our experiments, the average nanotube length and diameter are ∼550 nm and ∼1 nm, respectively, according to the specification from the manufacturer.[40] The nanotube dispersion process by ultrasonication may make the nanotubes shorter, but the micrographs in Figure 2 indicate the length has not been significantly shortened. We also separately confirmed it by using a transmission electron microscope. Furthermore, we used long time sonication processes up to 3 h, but we did not observe any noticeable changes in the transport properties of our polymer composites. The thermal contact conductance, G, is unknown since PEDOT:PSS particles are present between nanotubes, as shown in Figure 1a. Figure 5 shows the calculated thermal conductivity (k_{3D}) of a composite made of a 3D nanotube network ($k_{3D,NT}$) and polymers (k_p) with eq 2 and 3 when G varies from 0.1 to 100 pW/K. The plotted values also match the results that we calculated by using the model provided by Chalopin *et al.*[41] The thermal contact conductance for the nanotubes directly in contact without having other molecules in between has been theoretically and experimentally estimated to be on the order of 10 pW/K.[38,41−44] This conductance results in the composite thermal conductivity of ∼10 W/m·K, which may be considered as an upper bound since polymer particles (whose concentrations are more than 40 vol % in our experiments) are present between the nanotubes. On the contrary, our experimental results, 0.2−0.4 W/m·K, indicate that the corresponding G is ∼0.1 pW/K, which is 2 orders smaller than that of the case that nanotubes are directly in contact. The thermal contact conductance may diminish orders of magnitude depending on the spacing between nanotubes.[42] However, we do not exclude the possibility of preferentially oriented nanotubes in the in-plane direction.

The out-of-plane thermal conductivity (k_{2D}) of a composite made of 2D nanotube networks ($k_{2D,NT}$) and polymers (k_p) may be considered as a lower bound since it is unlikely that we have a composite structure made of stacked 2D layers. This structure has a very low out-of-plane thermal conductivity due to small thermal contact conductance between each layer. The $k_{2D,NT}$ may be calculated by using eq 4.[38]

$$k_{2D,NT} = \frac{2G}{\pi}\left(\frac{\rho(2R+h)}{2\pi(R/L)n_\sigma m}\right)(2R+h) \qquad \textbf{(4)}$$

where h indicates the equilibrium distance between the surfaces of parallel nanotubes; k_{2D} is more or less invariant $\sim$0.1 W/m·K due to very small $k_{2D,NT} \sim 10^{-2}$ W/m·K. Our experimental results are closer to k_{2D} than k_{3D}, which may suggest that some nanotubes were embedded into the composites in the in-plane direction. When the samples were dried from aqueous nanotube mixtures, nanotubes are likely to be pushed to the bottom by the water surface. In comparison to other work, polyaniline composites containing nanotubes up to 50 wt % exhibited $\sim$1.7 W/m·K,[35] but the orientation of the nanotubes and the direction of the measurements were not identified. The electronic contribution to the in-plane thermal conductivity is also estimated to be $\sim$0.7 W/m·K by using the Wiedemann–Franz law with a Lorenz number of 2.44×10^{-8} W/Ω·K^2, which may indicate that the in-plane thermal conductivity may be 1–10 W/m·K. However, it should be noted that the Lorenz number is dependent on materials and may not be applicable to our samples.[45]

CONCLUSIONS

Our composites containing polymers and carbon nanotubes without containing heavy and/or toxic inorganic materials exhibited very high electrical conductivities and relatively constant thermopowers. The thermopowers were weakly correlated with the electrical conductivities, resulting in large thermoelectric power factors ($S^2\sigma$), $\sim$160 μW/m·K^2, which are orders of magnitude better than those of typical polymer composites. The optimum nanotube concentrations for better power factors were identified to be 60 wt %. The highest electrical conductivity and thermopower along the in-plane direction of our samples were recorded to be 1.35×10^5 S/m and 41 μV/K at room temperature, respectively. Without additional DMSO doping, PH1000 shows higher thermopowers while PH500 has better electrical conductivities. The thermal conductivity in the out-of-plane direction was measured to be 0.2–0.4 W/m·K at room temperature. The in-plane thermal conductivity and thermal contact conductance between nanotubes in our composites were also theoretically estimated. We believe further research utilizing the loosely related transport properties may enable us to obtain easy-to-manufacture, low-cost, light-weight, and less toxic organic composites for efficient thermoelectric energy conversion in the future.

METHODS

All samples were made of carbon nanotubes mixed with PEDOT:PSS (Clevios PH500 and PH1000 grades from H.C. Starck) and/or PVAc. The PVAc emulsion is either Vinac XX210 from Ashland Inc. or Vinnapass 401 from Wacker Chemical Co. These two emulsions are 55 solid wt % suspensions in water. The glass transition temperatures of Vinac XX210 and Vinnapass 401 are approximately 35 and −15 °C, respectively. Polymer particles in the emulsions have variable sizes ranging from 0.14 to 3.5 μm in diameter with an average diameter of $\sim$650 nm. Purified-grade HiPco single-wall carbon nanotubes were used as conductive fillers in the polymer matrix. The nanotubes were mixed with PEDOT:PSS by sonication with an ultrasonic homogenizer (Misonix Microson XL2000) for 20 min at 50 W. PEDOT:PSS stabilizes nanotubes in water as well as becomes a part of the matrix. The weight ratios of nanotubes to stabilizers were varied from 1:0.25 to 1:1 in order to study the influence of their relative concentrations on transport properties. The viscosity of the aqueous solution was reduced by adding deionized water to the mixture with additional 15 min sonication. Total solids were 2.5 wt % in water for the samples whose nanotube concentrations in fully dried samples are 35, 40, and 45 wt %. For the other samples, 0.4 wt % in water was used due to high viscosity. Then, the emulsion was added to the solution followed by 10 min sonication except for samples 10 and 11. The solution was then poured into a 26 cm^2 container and dried for $\sim$48 h under an ambient condition in a fume hood. Subsequently, the solid composite was baked in an oven at 80 °C for 6 h. Finally, fully dried composites were stored in a vacuum desiccator for 24 h in order to completely remove residual water from the composites. The thickness of the samples ranges from 0.02 to 0.053 mm. The concentrations of nanotubes, PVAc, and PEDOT:PSS in Table 1 are based on the total dry weight of the composites.

Electrical conductivity and thermopower were measured at room temperature along the in-plane direction. A four-probe current–voltage (I–V) measurement method was employed to obtain the resistance of the samples so as to extract electrical conductivity by multiplying geometrical factors. Current from 0 to ±1 mA was passed to the sample to acquire a slope from a linear I–V curve. For thermopower measurements, voltages across the sample were measured at 10 different temperature gradients between −8 and +8 K. Thermopower was obtained from the slope of a linear temperature–voltage curve. Note that the coefficient of determination (R^2) for finding the slope in the measurement is greater than 0.99.

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