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COPPER/CARBON CORE SHELL NANOPARTICLES AS ADDITIVE FOR NATURAL FIBER/WOOD PLASTIC BLENDS

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Copper/carbon core/shell nanoparticles (CCCSNs) recently have been introduced as an industrial material. In this paper, composites based on high density polyethylene (HDPE), bamboo fiber, CCCSNs, and coupling agent (MAPE) were prepared by melt compounding. The influence of CCCSN content on the resulting composites' mechanical, biological resistance, and thermal properties was investigated. It was found that CCCSNs within the carbon black matrix were processed well with bamboo fiber-plastic blends through mixing and injection molding. The materials enhanced composite strength and modulus-related properties. Composites with CCCSNs and natural fibers reduced heat capacity and thermal diffusivity. Composites with CCCSN materials also enhanced termite and mold performance. Thus, the material can be used as additive for plastics and other polymers to modify strength properties, biological resistance (*e.g.,* mold and stain), and thermal conductivity properties.

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INTRODUCTION

New generation wood-based composites offer enhanced long-term durability for structures that typically have been constructed with natural wood products. Among the composite products, wood-plastic composites (WPCs) are being developed for both structural and non-structural uses. These composites offer some inherent technical advantages over conventional composites, such as lower costs, lower weight, and less energy used in their production, which together would qualify them to be called "environmentally friendly" or "green" (Lu *et al.* 2000; Clemons 2002; Clemons and Caulfield 2005). WPCs can be manufactured in a variety of colors, shapes, and sizes, as well as with different surface textures. The emerging WPC products include fencing materials, roof shingles, siding, facia, beadboards, and molding components (Clemons and Caulfield 2005).

WPCs do not require painting or other finishes, and they normally will not warp or rot like wood does. However, WPCs are not maintenance-free, and they can be degraded in outdoor environments. The wood in the WPCs can still be attacked by termites, rot, and mold fungi, and sunlight can discolor and break down the plastic component (Laks *et al.* 2000; Verhey *et al.* 2001). Various preservatives such as zinc

borate have been used in WPC formulations to enhance their biological performances (Simonsen *et al.* 2004)

Copper/carbon core/shell nanoparticles (CCCSNs) are a newly available type of industrial material that is prepared using a proprietary manufacturing technology (Lian and Wu 2012). Past work with this material has shown strong biological efficacy for protecting solid wood and tree health (*e.g.*, Qi *et al*. 2009; Lian and Wu 2012). The application of CCCSNs in wood/natural fiber plastic composites has not been reported. CCCSNs within the carbon black matrix have potential to modify thermal performance of the composites for applications such as roof shingles and sidings. The objective of this study was to use CCCSNs and carbon black mixture as an additive in natural fiber/wood plastic blends and to test their effect on mechanical, termite, and mold resistance, as well as thermal properties of the composites.

EXPERIMENTAL

CCCSN Preparation

CCCSNs were prepared by using cellulosic fibers (*e.g.*, cotton, wood, and straw) as the template and $CuSO_4$ as the metal source (Lian and Wu 2012). The manufacturing process involved soaking the chosen fibers in the metal salt solution and then carbonizing the processed fibers under N_2 flow. The metal nanoparticles and their carbon shell formed simultaneously during carbonization within the carbon black matrix (Fig. 1). After being gradually cooled to room temperature inside the furnace, the carbonized fibers were ground with a grinding mill to reduce their size and to help separate the particles from the carbon black matrix. In this process, the actual metal loading (*e.g.*, copper) can be varied by controlling the soaking process.

Transmission Electron Microscopy (TEM) clearly indicated that CCCSNs were generally spherical, with a core-shell structure, and the growth of the carbon shell followed a heteroepitaxial pattern (Fig. 1).
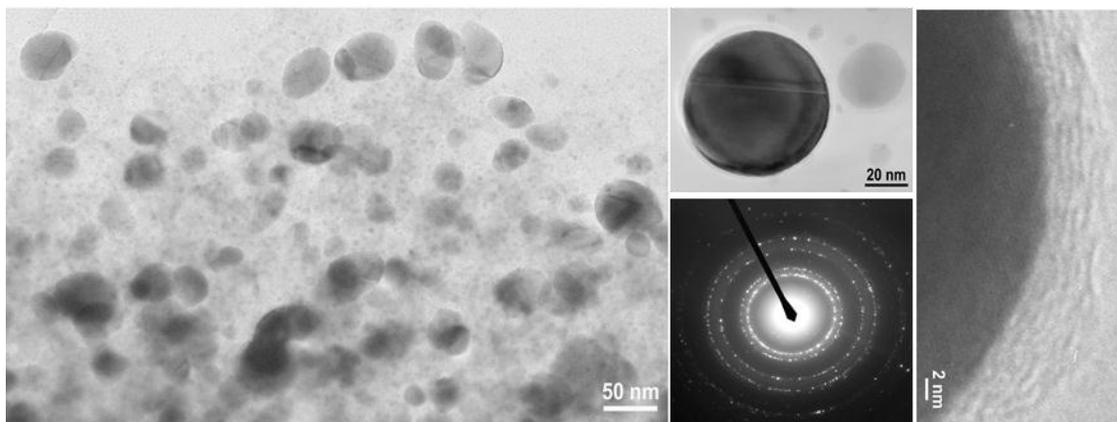
Fig. 1. TEM observation of CCCSNs within carbon black matrix, magnified image of a CCCSN; electron diffraction pattern of the copper core; and high resolution image of copper core and carbon coating surface

Bamboo Fiber Plastics Blend Preparation

The composite blends were prepared using a CW Brabender Intelli-torque rheometer with a screw speed of 60 rpm at 170ºC. Both torque and temperature were measured during compounding. Table 1 shows the design for various blends. High density polyethylene (HDPE 6761 from ExxonMobil Chemical Co., Houston, TX, USA), bamboo fiber (40-mesh size), CCCSN/carbon black mixture, and maleic anhydride-grafted polyethylene (MAPE, Epolene[TM] G2608 from Eastman Chemical Co. Madison, TN, USA) were added separately to the mixer and thoroughly mixed for 15 minutes. The composite plates for property testing were made by compression molding the compounded blends at 175ºC, using a three-piece stainless steel mold in a Wabash V200 hot press (Wabash, ID) for 5 min and then cooling to room temperature under pressure. Samples with two nominal thicknesses (1 mm and 4 mm) were made for various tests described below.

Table 1. Bamboo Fiber HDPE Blend Design for the Study

| Blend Number | Base Blends | | Additives | | |
| | HDPE Plastic 6761 -H- (%) | Bamboo Fiber 40 mesh -B- (%) | CCCSN Material -N- | | Coupling Agent MAPE2608[c] -M- (%) |
			Total[a] (%)	Cu[b] (%)	
1	100	0	0	0.000	0
2	100	0	2	0.235	0
3	100	0	4	0.470	0
4	100	0	6	0.705	0
5	60	40	0	0.000	0
6	60	40	2	0.235	0
7	60	40	4	0.470	0
8	60	40	6	0.705	0
9	60	40	0	0.000	3
10	60	40	2	0.235	3
11	60	40	4	0.470	3
12	60	40	6	0.705	3

[a] Based on the total base-blend weight; [b] The material contained an average of 11.5% copper metal based on chemical analysis with an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES); and [c] Based on the bamboo fiber weight.

Composite Property Testing

Mechanical and morphological properties

The storage modulus and loss modulus of the composites were measured with a TA Q800 DMA system (TA Instruments Inc., New Castle, DW). For each group, five replications with a sample size of $60 \times 12 \times 1$ mm were tested. Prior to testing, all DMA specimens were conditioned for 72 h at a temperature of 23°C and a relative humidity of 50%. The storage modulus of each DMA specimen was measured in a dual cantilever mode at a 1 Hz frequency and 25°C temperature. After the DMA test, tensile strength was measured according to the ASTM D638 method using an INSTRON machine (Model 5582, Instron Co. Boston, MA). For each treatment level, five replications were tested. A

TINIUS 92T impact tester (Testing Machine Co., Horsham, PA) was used for the Izod impact test. All the samples were notched on the center of one longitudinal side according to the ASTM D256 standard. For each treatment level, five replications were tested. Statistical analysis (Duncan's multiple range test) was done to test the difference of various properties at different treatment levels. The surface morphology of the selected composite samples was analyzed using a Hitachi S-3600N VP Scanning Electron Microscope in combination with an energy dispersive X-ray spectroscope (SEM/EDX - Hitachi Ltd., Tokyo, Japan). The samples were coated with Pt to improve the surface conductivity before observation and observed at an acceleration voltage of 15 kV.

Termite and mold resistance properties

Five matched samples (30 x 12.5 x 4 mm) from each treatment condition and five untreated southern pine controls (25.4 x 25.4 x 6 mm) were taken for no-choice laboratory termite tests according to the AWPA E1 standard (AWPA 2011). Prior to each termite test, the blocks were oven-dried at 105℃ for 24 hours, and sample weight (W_1) and dimensions were measured. Each test bottle (80 mm diameter x 100 mm height) was autoclaved for 30 minutes at 105 kPa and dried. Autoclaved sand (150 g) and distilled water (30 mL) were added to each bottle. Finally, 400 termites (360 workers and 40 soldiers) were added to the opposite sides of the test block in the container. All containers were maintained at room conditions for 4 weeks. The bottle cap was placed loosely. After testing, each bottle was dismantled. Live termites were counted, and test blocks were removed and cleaned. Each block was oven-dried again at 105℃ for 24 hours to determine the dry sample weight (W_2). From the measurements, sample weight loss [$(W_1-W_2)/W_1$] and termite mortalities were determined. The tested samples were ranked visually by five people on a scale of 1 to 10 with 10 as no damage and 1 with the most damage.

Mold test for various composite samples (101.6 x 63.5 x 1 mm) was conducted according to the AWPA E24 standard (AWPA 2007). Molds and their spores were obtained from the USDA Forest Products laboratory, Madison, Wisconsin. They consisted of *Aureobasidium pullulans* (d. By.) Arnaud ATCC 9348, *Aspergillus niger* v. Tiegh. ATCC 6275, *Penicillium citrinum* Thom ATCC 9849, and *Alternaria tenuissima* group (Kunze) Wiltshire Ftk 691B. The inoculums collected were dispersed in distilled water and distributed on potting soil in the mold chambers. The mold chambers were left in warm humid conditions ($28^{o}C$ and 75% relative humidity) for more than two weeks prior to placing them in the samples. Samples were rated every 2 weeks for a total of 4 rating periods. The ratings range from 0 to 5 based on the description provided in the standard. It consists of two estimations, a rating of mold coverage, and a rating of mold intensity. The more severe value of the two ratings (coverage or intensity) was given to each side of the sample.

Thermal properties

Composite thermal diffusivity (TD) and heat capacity (Cp) were measured with a LFA 447^{TM} Nanoflash (ETZSCH Instruments, Inc., Burlington, MA, USA). Tests were made at four temperatures (25°C, 45°C, 65°C, and 85°C) and 270 V flash lamp power. Four round samples with a diameter of 12.6 mm for each group were made using a pair of

scissors and fine sand paper (Fig. 2). The samples were sputter-coated with graphite before use. For the specific heat test, a round AXM-5Q graphite sample with a diameter of 12.6 mm, a thickness of 0.976 mm, and a density of 1.73 g/cm^3 was used as a reference. Five shots were taken from each sample, and the data were corrected for actual sample density.

Fig. 2. Typical composite samples for thermal property analysis (Blend 5)

RESULTS AND DISCUSSION

Blend Torque and Temperature

Figure 3 shows typical mixing torque and temperature data for the composite blends. For all blends, adding HDPE to the mixing chamber led to a sharp increase of the mixing torque and a reduction of the temperature. Both torque and temperature stabilized as mixing time increased. Blend 4 contained 6% CCCSN and carbon black material, and its use did not cause noticeable changes in both equilibrium temperature and torque. Blends 9 and 12 contained about 40% bamboo fibers. Adding bamboo fibers and the additives (CCCSN and carbon black) to melt HDPE led to an initial increase in the blend torque and a decrease in blend temperature (Fig. 3 right).
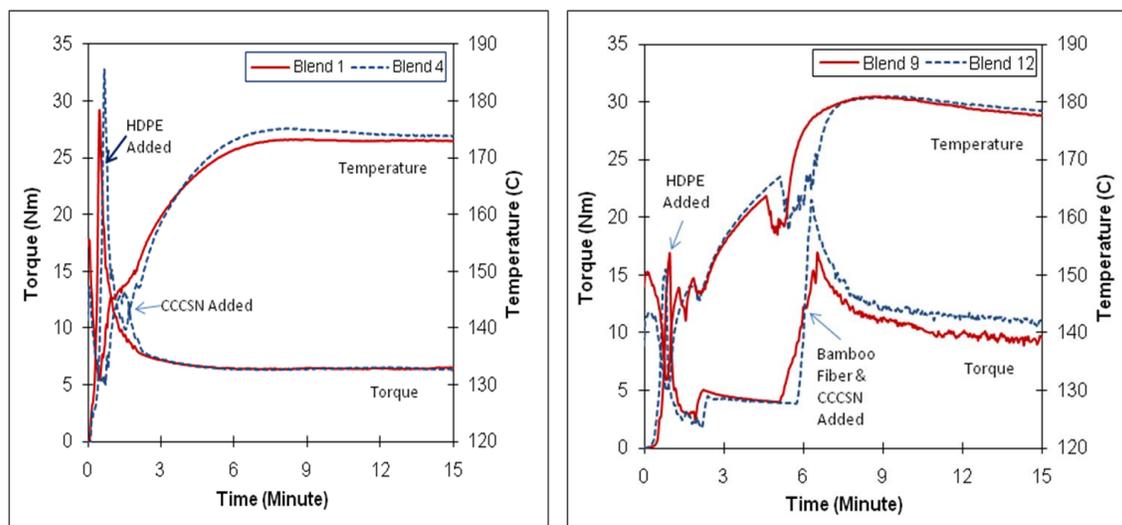

Fig. 3. Typical blend torque and temperature history for HDPE plastic filled with CCCSN, carbon black, and bamboo fibers. Information for Blends 1, 4, 9, and 12 is shown in Table 1

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Both torque and temperature stabilized as mixing continued. The final equilibrium torque significantly increased for blends with bamboo fibers compared with HDPE blends without bamboo fibers (Fig. 3, left), indicating increased friction within the blends. There was a slight increase in the equilibrium torques for the blends containing HDPE/bamboo fiber/CCCSN materials (Blend 12 in Fig. 3, right). This result could indicate improved compatilization with less slippage at the interface within the blends containing CCCSN material. In general, the CCCSN material could be processed well with the mixture of natural fiber and plastic.

Composite Property
Mechanical and morphological properties

Table 2 lists measured impact strength, tensile strength, and dynamic properties for various composite systems with different CCCSN/carbon black loading levels. For HDPE blends without bamboo fibers (Blends 1 through 4), the use of CCCSN/carbon black mixture led to somewhat reduced impact strength and slightly increased tensile strength. There seemed to be little effect of the material on the composite dynamic properties (*i.e.*, storage and loss modulus and Tan delta). For HDPE blends with bamboo fibers (Blends 5 to 12), impact and tensile strength decreased and modulus increased with the addition of bamboo fibers. The use of coupling agent MAPE led to enhanced mechanical properties for these systems (Blends 5 to 8 versus Blends 9 to 12), indicating enhanced coupling at the plastic and fiber interface. Both tensile strength and dynamic modulus increased, while impact strength decreased slightly as the CCCSN/carbon black loading level increased (Blends 5 to 8 without MAPE and Blends 9 to 12 with 3% MAPE based on bamboo fiber weight). Thus, the CCCSN additive showed a positive effect in modifying the mechanical properties of the composite systems with natural (bamboo) fibers.

Table 2. Summary of Mechanical Properties of Various Composites

Blend	Impact strength KJ/m^2	Tensile strength MPa	Dynamic Mechanical Property		
			Dynamic modulus MPa	Loss modulus MPa	Tan (delta)
1	3.88 (0.26)	24.60 (1.13)	1401.93 (45.33)	141.52(10.49)	0.101(0.009)
2	3.33 (0.43)	23.88 (0.77)	1419.11 (78.25)	133.56(9.34)	0.094(0.006)
3	3.64(0.36)	25.09 (1.96)	1355.10 (91.10)	134.96(5.27)	0.099(0.007)
4	3.18(0.21)	26.25 (0.42)	1389.15 (93.95)	139.37(9.51)	0.100(0.005)
5	2.69 (0.22)	13.61 (1.68)	2588.30 (68.54)	187.23(11.54)	0.073(0.005)
6	2.58 (0.23)	15.05 (0.57)	2823.29 (142.33)	204.62(19.96)	0.072(0.001)
7	2.39 (0.13)	15.50 (0.98)	2546.90 (71.14)	202.76(14.73)	0.078(0.001)
8	2.56 (0.15)	14.40 (1.10)	2830.91 (81.11)	203.36(26.66)	0.072(0.004)
9	3.02 (0.35)	16.98 (2.07)	2648.35 (123.01)	198.68(22.49)	0.075(0.002)
10	2.86(0.18)	20.27 (2.17)	3004.99 (57.05)	222.67(15.19)	0.073(0.004)
11	2.80 (0.24)	17.77 (1.46)	2945.71 (45.62)	215.21(7.95)	0.069(0.004)
12	2.77 (0.20)	19.57 (3.68)	2906.14 (67.15)	201.34(34.49)	0.102(0.005)

Figure 4 shows a typical SEM surface micrograph of CCCSN/carbon black filled HDPE sample (Blend 4) and an EDX profile showing the presence of Cu element on the composite surface. The particles seemed to be well-dispersed in the composites.
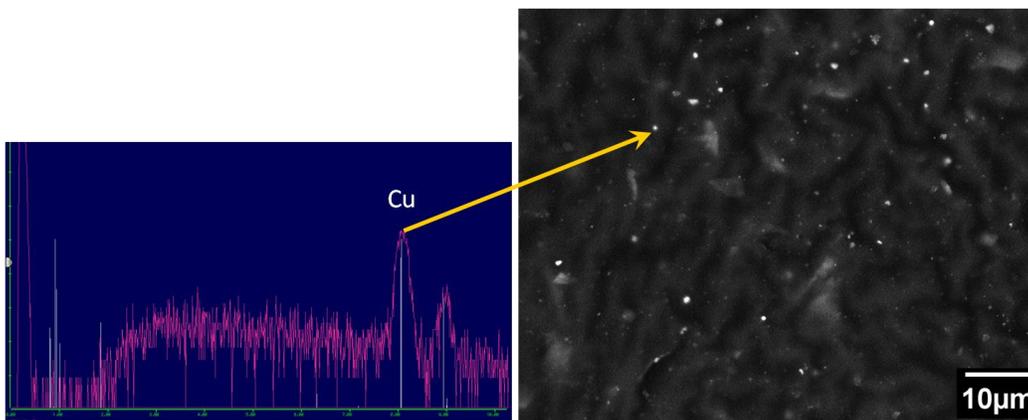
Fig. 4. Typical SEM surface micrograph of CCCSN/carbon black filled HDPE sample and EDX profile showing presence of Cu element

Termite and mold resistance properties

Table 3 lists termite test data including mortality, sample weight loss, and sample damage rating. Pure HDPE plastic had no damage, with a perfect 10 rating, while untreated southern yellow pine wood had significant damage, with an average weight loss of 39.6% and a damage rating of 1.2. The default HDPE/bamboo composite (Blend 5) showed certain damage due to the termite attack, with a 4.53% weight loss and a damage rating of 7.9. Thus, chemical additives are generally needed for the composite material to be termite resistant. The use of CCCSN and carbon black additive in the composite system led to a significant improvement in termite resistance. At the 6 weight percent loading level (Blend 8), sample weight loss was reduced to 0.28% and sample damage rating increased to 9.5 (only minor surface nibbling).

Table 3. Summary of Termite Mortality, Sample Weight Loss, and Sample Damage Data

Blend	Material	Mortality (%)*	Weight Loss (%)*	Ratings (0-10)*
1	HPDE6761 (H)	28.80 D	0.10 A	10.0 F
5	HDPE/Bamboo (H/B)	21.00 B	4.53 A	7.9 D
6	HDPE/Bamboo/CCCSN1 (H/B/C1)	23.50 BC	3.18 A	8.1 CD
7	HDPE/Bamboo/CCCSN2 (H/B/C2)	28.95 D	0.99 A	8.8 E
8	HDPE/Bamboo/CCCSN3 (H/B/C3)	28.45 D	0.28 A	9.5 E
NA	Solid Wood (Wood)	12.35 A	39.60 B	1.2 A

* Groups with the same letter show no significant difference.

Figure 5 shows a comparison of the mold performance of various composite systems. Untreated southern yellow pine (SYP) wood had the most severe mold development (4.75 mold rating after 8 weeks of exposure). The commercially treated ACQ lumber showed a slight mold growth (mold rating = 0.3 after 8 weeks). Pure HDPE

(H) samples did not have any noticeable mold (0 mold rating). HDPE/bamboo composite (H/B) showed certain mold development under the test conditions (1.0 mold rating after 8 weeks). Composite systems containing the CCCSN and carbon black mixture (H/B/C1 to C3) had enhanced mold performance. At the 6 weight percent loading level (Blend 8), the sample was almost free of mold development at the end of eight weeks of testing (mold rating = 0.10).
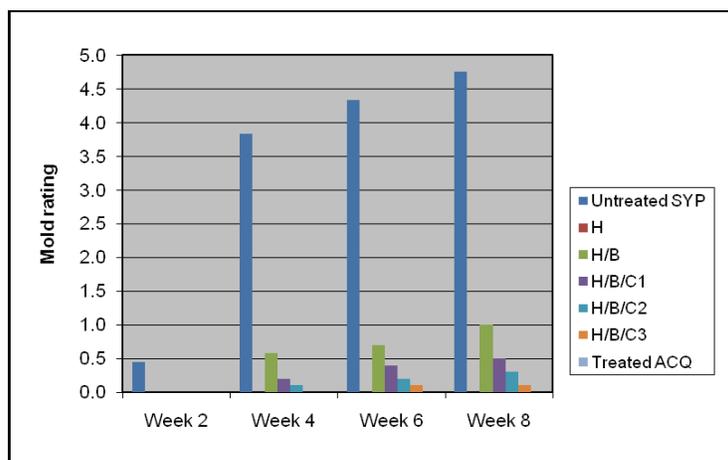

**Fig. 5.** Mold rating for various composite systems in comparison with wood

Thermal properties

Table 4 and Fig. 6 show a comparison of thermal diffusivity and heat capacity data for various composite systems. The measured thermal diffusivity decreased and heat capacity increased with temperature increases.

Table 4. Summary of Thermal Diffusivity (TD) and Heat Capacity (Cp) of Various Composites [a]

Temp, C	HDPE TD mm²/s	HDPE Cp J/g/K	HDPE+2%CCCSN TD mm²/s	HDPE+2%CCCSN Cp J/g/K	HDPE+4%CCCSN TD mm²/s	HDPE+4%CCCSN Cp J/g/K	HDPE+6%CCCSN TD mm²/s	HDPE+6%CCCSN Cp J/g/K
25	0.28	2.412	0.26	2.188	0.26	2.021	0.264	2.192
45	0.245	2.479	0.228	2.343	0.226	2.338	0.239	2.281
65	0.215	2.798	0.198	2.672	0.196	2.506	0.208	2.481
85	0.182	3.172	0.168	2.927	0.167	2.776	0.176	2.753

Temp, C	HDPE+BF TD mm²/s	HDPE+BF Cp J/g/K	HDPE+BF +2%CCCSN TD mm²/s	HDPE+BF +2%CCCSN Cp J/g/K	HDPE+BF +4%CCCSN TD mm²/s	HDPE+BF +4%CCCSN Cp J/g/K	HDPE+BF +6%CCCSN TD mm²/s	HDPE+BF +6%CCCSN Cp J/g/K
25	0.220	1.975	0.221	1.911	0.222	2.026	0.215	1.904
45	0.197	2.158	0.198	2.047	0.199	2.221	0.195	2.095
65	0.176	2.363	0.178	2.265	0.180	2.43	0.175	2.264
85	0.156	2.552	0.156	2.440	0.158	2.640	0.154	2.473

[a] BF – Bamboo fiber
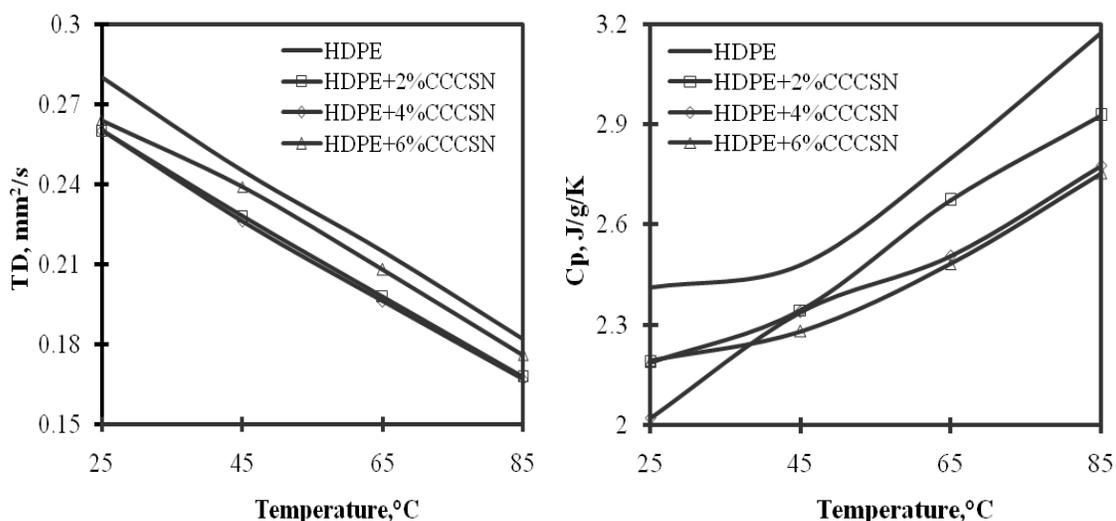
Fig. 6. Effect of CCCSN/carbon black on HPDE's TD and Cp as a function of temperature

The use of CCCSN and carbon black led to somewhat reduced heat capacity and thermal diffusivity for pure HDPE composites at a given temperature level. For systems containing bamboo fiber, both heat capacity and thermal diffusivity were significantly reduced. The use of CCCSN and carbon black mixture further decreased values of these two properties, indicating less heat conduction through the material.

CONCLUSIONS

1. CCCSNs with carbon black can be processed well with natural fiber/wood plastic composite blends through mixing and molding.

2. The material slightly enhanced strength and modulus properties for composites containing bamboo fibers.

3. Composites with CCCSN/carbon black material had much enhanced termite and mold performance properties.

4. Composites with CCCSN and carbon black mixture had somewhat reduced heat capacity and thermal diffusivity, which means less heat conduction through the composite material.

5. The material can be used as an additive for plastics, asphalt, and other polymer to modify strength properties, biological resistance (*e.g.*, mold and stain), and thermal conductivity.

ACKNOWLEDGMENTS

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