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Multifunctional single-walled carbon nanotube–cellulose composite paper†

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Single-walled carbon nanotubes (SWCNTs) have been used as fillers to produce electrically conductive composite papers. While conductive composite papers have been made using other fillers, they either suffer from instability or low conductivity. Using simple papermaking techniques, we have made SWCNT–cellulose composite paper which possesses a conductivity of 3×10^{-2} S cm^{-1} and is comparable to or exceeds other reports of carbon nanotube–cellulose papers made by layer-by-layer assembly. These composite papers are multifunctional, having both improved electrical conductivity and enhanced flame retardant properties over the control paper.

Introduction

Papermaking may be an ancient art, but it is still very relevant in today's economy. Paper, cardboard, and other wood-based products are used in communication, packaging, construction, and numerous other aspects of modern life. Paper is typically made from cellulose fibres extracted from wood as pulp. This pulp can be mixed with fillers such as calcium carbonate or titanium dioxide to increase its reflectivity and make the paper appear whiter. Paper can be treated with a polymer coating, such as Mylar®, to add a surface gloss. Sizing agents, such as alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), and alum/rosin size, limit water absorption by capillary action and help keep ink on the surface of the paper rather than allowing it to be absorbed into the sheet. These kinds of fillers and additives are important, but do not add functionality to the paper beyond that already mentioned.

Functional papers are an emerging area of research which has the potential to extend the use of paper and revolutionalize the paper and forestry industries. By incorporating specific fillers, paper can take on conductive,[1] magnetic,[2] photoluminescent,[3,4] catalytic,[5] antimicrobial,[6,7] acoustic dampening,[8,9] or flame retardant properties,[10,11] which open the doors to myriad new potential applications. However, while attempting to produce a paper with multiple functionalities, one challenge that arises is that often the enhancement of one property comes at the cost of another. For instance, when adding metal particles to create a magnetic paper, the tensile strength is diminished.[12] Our goal is to produce a multifunctional paper without decreasing other properties.

Conductive papers are of particular interest due to their potential applications in electromagnetic interference shielding, electronic circuits, and active matrix displays. In the recent past, conductive papers have typically been made using conductive polymers or inorganic particles. Layer-by-layer methods of incorporating conductive polymers produce conductive papers but often suffer from the inherent instability of some conductive polymers.[13,14] Conductive papers made using indium tin oxide (ITO) have been reported, but have low conductivities in the 10^{-6} to 10^{-8} S cm^{-1} range.[15] Recently, new conductive paper in the range of 1–20 S cm^{-1} was made by layering polyethyleneimine (PEI), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT–PSS) and an aqueous suspension of carbon nanotubes (CNT–PSS).[16] When compared to these methods, this paper reports a relatively simple method of incorporating carbon nanotubes (CNTs) into paper, facilitating their potential incorporation into packaging, shielding and building materials.

It is important to note here that there will undoubtedly be issues that arise before CNT can be incorporated into in such commonly used materials. CNTs are light-weight fibrous materials which are suspected carcinogens and may have asbestos-like effects on the lungs.[17] However, due to the varying methods of CNT production, purification, dispersion, and functionalization the subject of their toxicity remains one of intense debate. What we present here is the discovery of an exciting new composite material and a toxicological study of this composite is beyond the scope of this paper. We would still like to stress that, as with any new material, it would be suitable for large-scale production only after passing vigorous health and safety assessments.

Setting aside such potential concerns for the moment, single-walled carbon nanotubes (SWCNTs) have excellent electrical conductivities between 100 and 8000 S cm^{-1} (ref. 18–20) and are promising candidates for fillers in electrically conductive composite paper. Jung *et al.* have reported 2.1×10^{-3} S cm^{-1} for paper composites of multi-walled carbon nanotubes (MWCNTs).[21] We have produced SWCNT–cellulose composites that have conductivities of 3×10^{-2} S cm^{-1}, an order of magnitude improvement over that reported for MWCNT–paper composites.

In addition to good electrical conductivity, we report that our SWCNT-paper has flame retardant (FR) properties. Although

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our composite paper has a shorter time to ignition compared to the control paper, it also has a shorter time to flameout. The total burn time is shorter and the total heat release of SWCNT-paper was half that obtained for control paper without SWCNT. Sodium bicarbonate ($NaHCO_3$) has previously been reported as a FR additive for cellulose, but offers no conductive enhancement. The time to ignition for this $NaHCO_3$–paper composite is longer than for cellulose alone, however, the total burn time is longer and hotter.[10] Paper sheets made with cuprites have flame retardant properties and conductivities, but the conductivity is very low (5×10^{-8} S cm^{-1}).[11]

Acoustic dampening is a desirable property in materials used in the construction, automotive, and aerospace industries. The acoustic properties of our electrically conductive and flame retardant paper are not enhanced or reduced relative to native paper. We are aware of no other multifunctional paper composite which maintains its acoustic properties while offering both significant conductivity and flame retardant benefits.

Experimental

Materials

SWCNTs are produced at National Research Council Canada-University de Sherbrooke (NRC-UdS)[22] by the Radio Frequency (RF)-Plasma SWCNT method or by the laser synthesis method.[23] Suspensions of raw (unpurified) SWCNT and purified SWCNT were stabilized by carboxymethyl cellulose (CMC) and used to make the paper handsheets. To obtain purified SWCNTs, raw SWCNTs were purified according to our in-house solvent-based procedure (Wet Chemistry Purification Protocol, WCPP) that does not involve the use of strong acids which would introduce side-wall defects.

Bleached hardwood kraft pulp was made from maple by standard pulping techniques. Carboxymethyl cellulose sodium salt (CMC, Aldrich), dimethylformamide (DMF, EMD Gibbstown, NJ), aluminium sulfate crystals ($Al_2(SO_4)_3 \cdot 18H_2O$; Fisher Scientific), Triton X-100 (BDH), styrene butadiene rubber latex (SBR latex 6692 MNA; Dow), Airvol 203 polyvinyl alcohol (PVOH, Air Products and Chemical Co.), and nano-crystalline cellulose (NCC, FPInnovations) were used as received. For the starch, a 1 in 30 dilution of Sta-Lok 310 Dent Corn Starch (Tate & Lyle) in deionized water was heated to 98.5 °C, and incubated for 25 min with stirring using an overhead stirrer at 800 rpm. The suspension was then cooled on ice and diluted to 2% with deionized water.

SWCNT–CMC dispersions

Metal catalyst particles and amorphous carbons were removed from raw (unpurified) plasma-grown SWCNT (PK-8) *via* the WCPP method to produce purified SWCNT (PK-6). Purity of the SWCNT preparations was tested by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. Dry SWCNT powder (50 g) was ground in a mortar and pestle with a small amount of distilled water. CMC was dissolved in distilled water and added to the SWCNT. The CMC promotes dispersion of the SWCNT in water by sterically stabilizing the hydrophobic SWCNT and preventing their reassembly into rope-like bundles. After multiple sonication and sheer mixing cycles over three days, the precipitate was filtered and collected. The final weight of the mixture was adjusted by adding distilled water. The characteristics and compositions of the SWCNT samples are summarized in Table 1.

Table 1 Composition and characteristics of SWCNT samples used for film and handsheet preparation

Sample	Purification	SWCNT (%)	CMC (%)	CMC : SWCNT ratio	Solids content (%)	pH
PK-6	WCPP	1.12	2.06	1.84	2.89	8.37
PK-8	None	1.67	1.67	1.00	3.24	7.57

SWCNT–cellulose paper composites

PK-6 and PK-8 were used in handsheet preparation. Additions of these dispersions to handsheets or films were based on the weight percentage of SWCNT of each preparation as indicated in Table 1.

To prepare the cellulosic substrates, bleached hardwood kraft pulp was repulped in a Helico pulper at 8% consistency, 50 °C, and 800 rpm for 5 min. For latency removal, the pulp was then diluted to 2% and disintegrated in the British Disintegrator at 80 °C for 3 min. For handsheet preparation, the disintegrated pulp was diluted with deionized water to 0.5% consistency before the addition of the alum retention aid or SWCNT dope.

The British Handsheet Maker fitted with a 150 mesh metal screen was used to make 11 cm wide circular handsheets with a thickness of 110 μm. Prior to formation of the handsheet, PK-6 or PK-8 was added as 0–35% SWCNT to 0.5% consistency pulp and stirred vigorously for 1 min with a magnetic stirrer. Alum was then added in a 1 : 1 dry weight ratio with the SWCNT content of PK-6 or PK-8 and mixed for 1 min. The resulting suspension was poured into the deckle of the handsheet maker containing deionized water and diluted to 1.4 L total volume. After a very gentle stirring to even out the formation, the deckle was drained. At this high alum to SWCNT ratio, no black SWCNT particles were observed in the drained filtrate. The handsheet was couched with two blotters, lifted off the screen, dried at 105 °C and weighed. The proportion of fibre, SWCNT and retention aid was then adjusted to obtain handsheets with a total mass of 1.2 g OD (oven-dried) for standard physical tests, 2 g OD for flame retardancy tests and 4 g OD for acoustic tests. Sheet basis weights were 60, 100 and 200 g m^{-2}. Handsheets with the appropriate mass were prepared as described and pressed and dried according to PAPTAC Standard Method C.5.[24] Pulp consistencies and strength properties were measured according to PAPTAC Standard Method D.16[25] and Standard Method D.3.[26]

Films of SWCNT–CMC

To obtain films that would not crack or fracture upon drying (which was the case for films with SWCNT content >80% without surfactant), various additives were tested: nonionic surfactant (Triton X), starch, latex, PVOH, or NCC. Films were prepared by evaporation or casting. Suspensions of SWCNT were mixed with surfactant, starch, latex, PVOH, or NCC in

Table 2 Composition and conductivity of films made with SWCNT of either PK-6 or PK-8

	Percentage solids (%)						
SWCNT	Triton X-100	Starch	Latex	PVOH	NCC	Conductivity /S cm^{-1}	Thickness /μm
PK-8							
80	0.13	20				2.07×10^{-1}	330
80	0.13		20			2.07×10^{-1}	330
100	0.13					2.77×10^{-1}	330
100	0.09					4.33×10^{-1}	330
91	0.13	9				6.36×10^{-2}	150
90	0.13	10				6.55×10^{-3}	150
PK-6							
50				50		1.14×10^{-5}	330
50					50	1.22×10^{-4}	330

proportions indicated in Table 2. After mixing, the suspensions were poured into Petri dishes or spread onto Mylar sheets and allowed to evaporate at room temperature.

Microscopy

Filter papers containing precipitated PK-8 and alum were observed under light microscope (LM) Zeiss Axio Imager. Light micrographs were taken using the dark-field reflected light mode. For electron micrographs of PK-8 precipitates and handsheets prepared with PK-8, samples were coated with carbon prior to observation using a field emission scanning electron microscope (FESEM; Hitachi SU-70). In addition, prior to carbon coating, handsheet samples were cut with a razor blade in order to reveal both surfaces and cross-sections.

Metals content

Handsheet samples containing 35% SWCNT as PK-6 or PK-8, were ashed at 650 °C to remove carbon black impurities. The ash was then dissolved in hydrochloric acid and the samples analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific, iCAP 6500).

Electrical characterization

Four probe conductivity tests were conducted at room temperature. The sheet resistance (R_s) was measured in the van der Pauw geometry using Keithley 2400 source measure units. Tungsten probe tips (25 μm) pressed into the CNT-paper composites made essentially ohmic contacts. Currents from 10 nA to 10 μA could be sourced at biases in the 1–10 V range, dependent on the composite. Film thicknesses (d) were measured with a micrometer. Sheet resistance and thickness were used to estimate the specific resistivity, $\rho = R_s d$ and conductivity, $\sigma = 1/\rho$. Anisotropies, *i.e.* in (ρ_x, ρ_y, ρ_z) were not studied in detail for these tests. These measurements were best suited for conductive samples (R_s < 10 MΩ).

For measurement of low sheet conductivities, a Dielectric Mapping Device (DMD) was used. The apparatus is an in-house design which relates the two-probe resistance (R) to the effective conductivity: $\sigma = d/AR$, where the contact area (A) is estimated from the probe diameter (1 mm). There was a linear correlation between conductivities extracted from the DMD and the four probe method (see Fig. S4†). The calibration was used for comparison of the results from both techniques.

Cone calorimeter tests

Cone calorimeter tests were conducted to determine the fire retardant properties of 2 g sheets containing 35% SWCNT as PK-8 or PK-6. The test specimens were 100 mm by 100 mm with a thickness of 0.25 mm. Each test specimen was exposed to a radiant heat flux of 25 kW m^{-2} with the glossy or plate side of the paper facing radiant heat exposure.

The radiant heat flux of 25 kW m^{-2} was selected based on the fact that this is the critical heat flux value for non-piloted ignition of many cellulose-based materials. Preliminary tests with the blank paper specimens were also conducted at a heat flux of 15 kW m^{-2}; there was pyrolysis of the specimen by the radiant exposure but there was insufficient gaseous fuel produced for ignition at this lower heat flux level during the 30 min test. It was decided, therefore, to choose an incident flux of 25 kW m^{-2} for use in the tests.

The test procedures were in accordance with the ASTM E1354 and ISO 5660 standard test methods.[27,28] The cone calorimeter was instrumented to measure all the quantities (O_2, CO, CO_2, temperature, and volumetric flow rate) in the exhaust stream that are needed to calculate the heat release rate using the oxygen-depletion technique.[29] Measurements also included mass loss, effective heat of combustion and ignition time.

Acoustic testing of SWCNT–cellulose paper composites

An impedance tube with a 4.5 cm diameter was used for acoustic testing. An acoustic driver is mounted at one end to provide acoustic excitation and the reflected acoustic waves are measured using a microphone probe. Circular samples (6.5 cm diameter) were cut from 200 g m^{-2} handsheets containing no SWCNT (blank) or 35% SWCNT as PK-6 or PK-8. These samples were mounted onto the impedance tube and their reflection coefficients were measured at three different frequencies. Further details of acoustic set up and measurements can be found in the ESI†.

Results and discussion

SWCNT–cellulose paper composite preparation

Adding hydrophobic SWCNT to a hydrophilic cellulose substrate posed the greatest difficulty in preparing a homogeneous suspension of fibre and SWCNT for sheet preparation. CMC not only allowed dispersion of the SWCNT in water but also gave the carbon nanotubes a negative charge. After mixing the CMC-stabilized SWCNT with fibre, addition of a positively charged papermaking additive, alum, acts as a bridge between two anionic surfaces (fibre–fibre, fibre–CMC, CMC–CMC). When compared to layer-by-layer additions reported in the literature, this method is simpler and may convey enough conductivity to be used in many packaging and electrical and magnetic shielding applications. Other types of pulp, softwood Kraft fibres and thermo mechanical pulp were also tested and could serve as a matrix for SWCNT deposition (not shown). In

addition, our experiments also showed that other common papermaking retention aids such as polyethyleneimine, polyacrylamide and polydiallyldimethylammonium chloride, could be used to retain the CMC–SWCNT complexes in the paper (not shown). Polyethyleneimine has been used as a polyelectrolyte in layer-by-layer assemblies of nanocomposites of indium tin oxide and paper and of carbon nanotubes, conductive polymer, and kraft fibre.[1,16]

Electrical conductivity

SWCNT–cellulose paper composites. Electrical properties were insensitive to illumination with white light. The work function of raw SWCNT sheets was approximately the same as gold (5 eV), as measured by a Kelvin Probe. Conductivity of these sheets was practically temperature independent between 20 °C and 100 °C.

Electrical conductivities have been determined on systematically varied concentrations of SWCNT as PK-8 in paper composites of different thicknesses (Fig. 1b). The composites range from paper strips (110 μm), to solid films made by filtration and casting (150 and 330 μm), to thin films made by coating (10–50 μm). Conductive paper composites were made from a raw stock of SWCNT electrostatically and/or sterically stabilized with carboxymethyl cellulose (CMC), hardwood kraft fibre and alum. Incorporation of the black SWCNT preparations was easy to visualize as the sheet brightness dropped from 80% to 5% with increasing SWCNT content as shown in Fig. 1a.

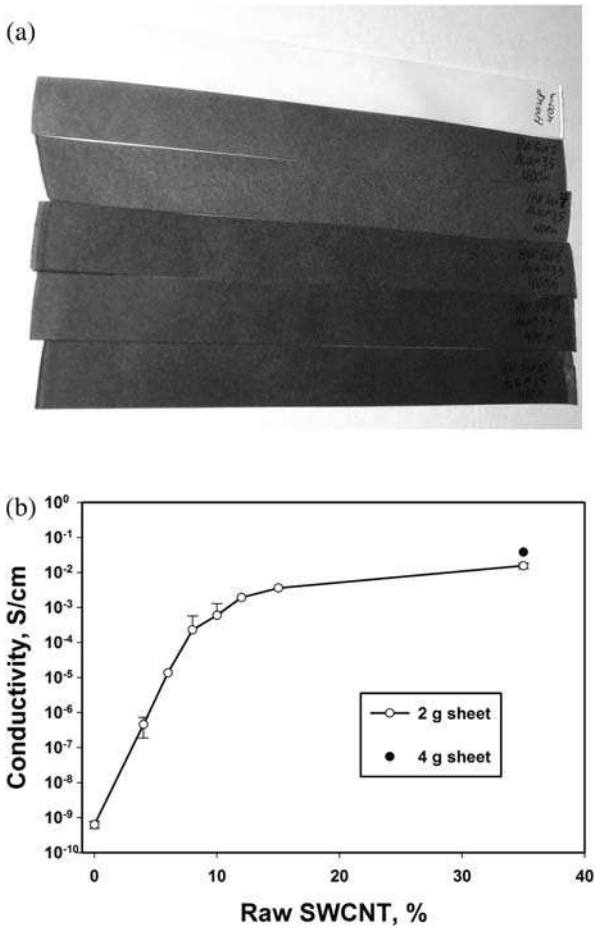

Fig. 1 (a) Photograph of paper strips made from hardwood kraft fibre with increasing content (0–10%) of SWCNT as PK-8. (b) Conductivity of SWCNT-composite papers. Composite paper was made by mixing hardwood kraft fibres with 4–35% PK-8 with an equivalent weight of alum or for the control with no PK-8, 35% CMC and 35% alum. Error bars indicate the standard deviation of average of five measurements per handsheet on 1–3 replicate handsheets.

Table 3 Comparison of the conductivity of paper composite sheets containing 35% SWCNT by weight of either PK-6 or PK-8

	Conductivity/S cm^{-1}	
SWCNT dispersion	2 g sheet	4 g sheet
PK-6	3.52×10^{-5}	4.26×10^{-4}
PK-8	1.34×10^{-2}	3.78×10^{-2}

In Fig. 1b, paper composites prepared from PK-8 exhibit increasing conductivity with increasing SWCNT concentration. Changing the composition from 0% to 35% PK-8 increases the conductivity of the sheet by eight orders of magnitude to ranges typical of low doped semiconductors. At 35%, the conductivity increased from 0.015 S cm^{-1} to 0.038 S cm^{-1} as the mass of the sheet doubled from 2 g to 4 g at a comparable thickness thereby increasing the density. Conductivity decreases rapidly for composites containing less than 4% SWCNT, approaching that of raw insulating paper.

Table 3 compares 2 and 4 g handsheets prepared from unpurified PK-8 and purified PK-6. PK-8 contained approximately 40% SWCNT while PK-6 had about 70% purity as estimated by TEM, SEM, and Raman spectroscopy. We had expected that handsheets prepared with PK-6 would have higher conductivity than those prepared with those made with PK-8, due to their higher SWCNT content. Surprisingly, sheets prepared from the unpurified SWCNT (PK-8) exhibited 2–3 magnitude higher conductivities than the sheets prepared from purified SWCNTs (PK-6). This might be explained by the higher CMC content in PK-6, which may increase the sheet's resistance. Another explanation could be that sheets made using unpurified SWCNTs would have higher contents of metal catalyst particles, such as nickel and cobalt, which could enhance the sheet's conductivity. To evaluate this, we used ICP-OES. Slightly higher nickel content was found in sheets prepared from PK-8, however, both SWCNT samples have significant catalyst impurities (due to the lack of strong acid in our purification procedure). Sheets made from PK-6 and PK-8 all contained approximately the same amount 3.6 ± 1.0 g kg^{-1} of cobalt and 2.6 ± 0.5 g kg^{-1} of nickel (readings are mean concentrations of control, PK-6 and PK-8 containing sheets and standard deviation).

Because the purification of SWCNT is time consuming and costly, it is interesting that the unpurified source of SWCNT (PK-8) gave significantly higher conductivities than those sheets prepared from partially purified source of SWCNT (PK-6). After significant health and safety evaluations on this composite have been conducted, this cheaper source of SWCNT may render it attractive to incorporation into lower value products such as packaging, shielding and building materials. The conductivities obtained with PK-8 are 4–8 orders of magnitude superior to values obtained on indium tin oxide applied on paper substrates with the help of polyethyleneimine using layer-by-layer

applications where values were between 5.2×10^{-6} S cm^{-1} and 1.9×10^{-8} S cm^{-1}.[30] On the other hand, the PK-8 composite sheets have lower conductivities than those reported by Johnston *et al.* who reported from 2×10^{-3} to 6 S cm^{-1} for composites made by coating kraft fibres with polypyrrole and polyaniline, respectively.[31,32] Similarly, conductivities ranging from 1 to 20 S cm^{-1} were reported by Agarwal *et al.* for paper handsheets made by coating fibres with layers of PEI, PEDOT–PSS and an aqueous suspension of CNT–PSS.[16] The conductivity of paper composites made with SWCNT was higher than those obtained with wool and conductive polymers (9.9×10^{-5} to 1×10^{-4} S cm^{-1} with polyaniline and 2.4×10^{-4} to 3.8×10^{-4} S cm^{-1} with polypyrrole).[33] In addition to the higher conductivity of the sheet obtained, the SWCNT–cellulose composite paper produced did not suffer from instability issues often associated with conductive polymer-based papers.

It is also important to report that there were no other metals present in the SWCNT samples that were not present in the control sheets that could be contributing to the conductivity of SWCNT-containing sheets. Of the two most prevalent metals detected by ICP other than cobalt and nickel, neither aluminium (from alum) nor iron can explain the increased conductivity of SWCNT-containing sheets as both the control sheets (35% alum and 37% CMC) and the PK-6 and PK-8 containing sheets had similar concentrations: 0.05 ± 0.02 g kg^{-1} of iron and 9.4 ± 1.9 mg kg^{-1} of aluminium (readings are mean concentrations of control, PK-6 and PK-8 containing sheets and standard deviation).

SWCNT films

Higher conductivities than those measured in the paper composites were obtained with films of SWCNT prepared from PK-8 or PK-6. Table 2 shows that conductivities as high as 4.3×10^{-1} S cm^{-1} were measured in PK-8 films prepared with Triton X-100. Although addition of Triton X-100, starch, latex, PVOH and NCC reduced the conductivity of the films, it prevented cracking and breakage of the films. Again, incorporation of PK-6 in films gave inferior results to those films made with PK-8. Thin films were also made by coating Mylar® (a polymer commonly used for glossy coatings on paper) sheets (not shown). For coating the Mylar® sheets, it was necessary to add a surfactant (Triton X, 0.13 wt%) to lower the surface tension of the SWCNT suspension. The surfactant permitted wetting of the Mylar® sheet and prevented cracking of the sheet upon drying. The limiting factor in using the SWCNT samples as coating was the low 1% solid content of the suspensions. Typically solid contents of coating solutions are much higher, in the order of 20–25%.

Microscopy of SWCNT–cellulose paper composites

To determine the effect that alum had on CMC-stabilized SWCNT (PK-8), we filtered the precipitates on filters and examined them under light and electron microscopes. Light micrograph and FESEM images of precipitates without cellulose fibres present can be seen in Fig. 2a–d. Fig. 2a shows clusters of precipitates of CMC–SWCNT–alum at varying dimensions. Closer examination of the clusters in Fig. 2b–d shows the presence of amorphous carbon spheres, with large fused areas and what we believe are ropes of SWCNT. The ropes between 14 and 19 nm in width can be up to 1.2 μm in length. Due to the limits of the microscope, individual SWCNTs of 1–2 nm wide would not be visualized as the minimum resolution in size is 8 nm.

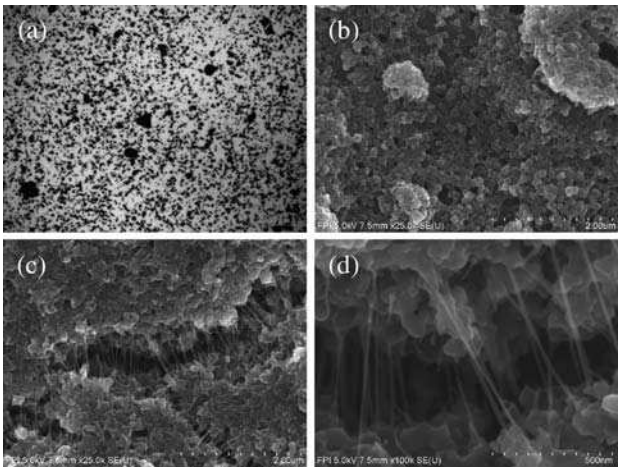

Fig. 2 Microscopy of SWCNT (PK-8) with alum in the absence of fibre. Light micrograph image (a) shows precipitation of alum and SWCNT. FESEM images (b–d) show precipitates at different magnifications. At fracture points (c and d), amorphous carbon with SWCNT ropes of 1.2 μm long and 14–19 nm wide is visible.

To visualize the effect of alum and CMC-stabilized SWCNT as PK-8 on kraft fibres, we examined the sheets under light and electron microscopes. Fig. 3 shows fibre and alum (a) and fibre, alum and 35% PK-8 (b–d). It is evident in photo (b) that the PK-8 has coated the fibre as further seen in (c). Enlarged areas of PK-8 coated fibre show the same elements observed in the precipitates of CMC–SWCNT–alum shown in Fig. 2c and d containing both SWCNT ropes and amorphous carbon particles. While not as efficient conductors as an individual metallic SWCNT, SWCNT ropes are still good electrical conductors.

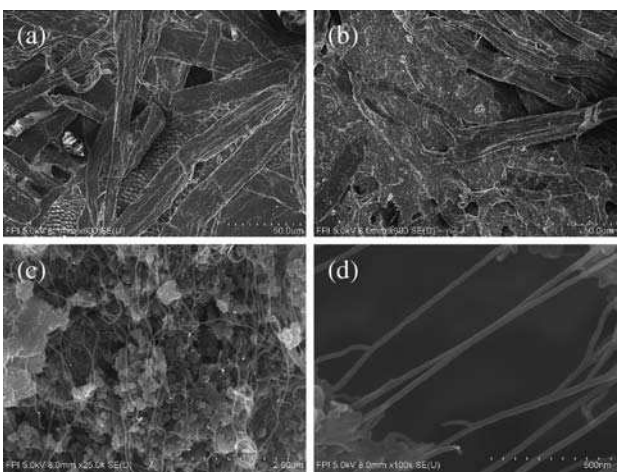

Fig. 3 FESEM images of SWCNT : cellulose paper composites: (a) hardwood kraft fibres with alum, (b–d) hardwood kraft fibres with alum and SWCNT as PK-8. Images (c) and (d) show cross-sectional area of paper sheet with amorphous carbon coating of fibres with SWCNT ropes of 1.2 μm long and 14–19 nm wide.

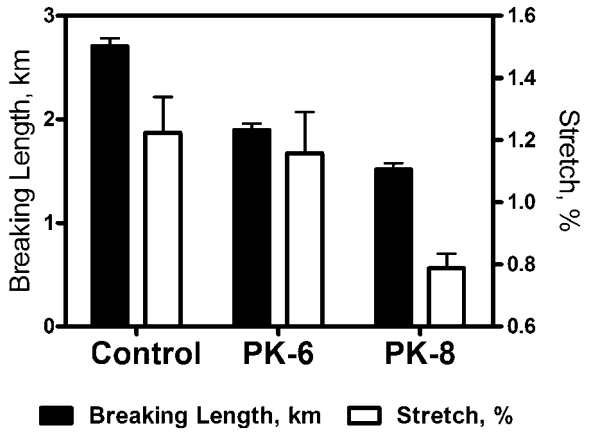

Fig. 4 Strength properties of handsheets prepared with hardwood Kraft fibres and alum (control) or with 35% SWCNT as PK-6 or PK-8.

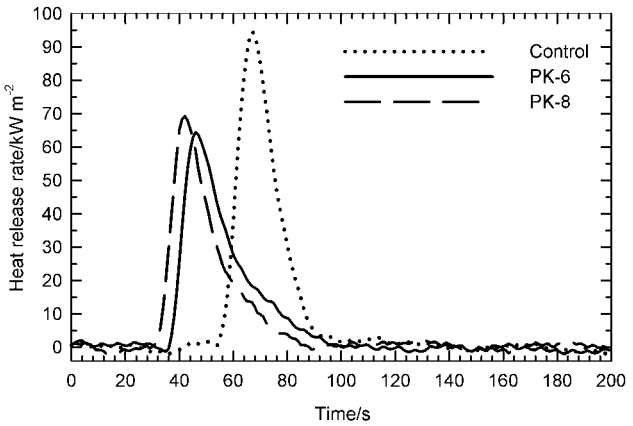

Fig. 5 Heat release rate of SWCNT-paper composites. Lines are means of triplicate samples.

SWCNT–cellulose paper properties

If paper is to be used as a matrix to support SWCNT semi-conductive or conductive material, maintenance of the strength properties will be important as we increase the SWCNT loading in the sheet. Since we are using surfactant (CMC)-wrapped SWCNT which are not chemically bonded to the cellulose fibres, we did not expect an enhancement in strength and indeed we did not find one. Fig. 4 compares the breaking length and stretch of the paper at 35% loading of SWCNT as PK-6 or PK-8. Incorporation of PK-8 into the kraft fibre sheets reduced the breaking length of paper by 48% and the stretch by 45%. In comparison, the effects of the purer SWCNT preparation, PK-6, on sheet properties were less pronounced with a reduction of 28% breaking length and 7% stretch when compared to the control sheets. Many factors could explain why sheets prepared with PK-8 were weaker than sheets prepared from PK-6 suspensions. Compared to PK-8 suspensions, PK-6 suspensions contained twice the amount of CMC, which is known to improve paper dry tensile strength. Also, the amorphous carbon content of unpurified PK-8 (~60 wt%) is twice that of purified PK-6 (~30%). The large amount of amorphous carbon and the aggregates it and SWCNTs form could potentially interfere with fibre to fibre bonding.

Flame retardant properties of SWCNT–cellulose paper composites

Triplicate cone calorimetry tests at the incident flux of 25 kW m^{-2} were conducted for each of the SWCNT-paper and blank paper samples. The results are summarized in Table 4 and the heat release rates are shown in Fig. 5. Fig. 5 shows the time for each sample to ignite on the x axis, the heat release rate on the y axis and the total heat release is the area under each curve. Parameters such as heat release rate, total heat release, and effective heat of combustion are scaled either in terms of specimen area or in terms of specimen mass.

All test specimens were ignited at the radiant flux of 25 kW m^{-2}. The SWCNT-paper samples ignited quicker than the blank paper samples. But the total burning times with visible flames were one-third shorter and the peak heat release rates were also one-third lower for the SWCNT-paper samples. This is not surprising as the carbon nanotube preparations replaced 35% of the cellulose. What is more important is that during the flaming combustion (from ignition to flameout), the total heat releases for the SWCNT-paper samples were half that obtained for the blank paper samples, as shown in Table 4. Each of the SWCNT-paper samples produced a lower effective heat of combustion than the blank paper samples. This suggests that SWCNT materials can improve flame retardant properties.

Table 4 Cone calorimeter results for SWCNT-paper composites

Sample	Units	Control	PK-6	PK-8
Heating flux[a]	kW/m^2	25	25	25
Initial mass[b]	g	1.14 ± 0.01	1.16 ± 0.05	1.23 ± 0.03
Ignition time[c]	s	52 ± 3	35 ± 2	32 ± 2
Flameout time[d]	s	82 ± 2	55 ± 2	50 ± 2
Burning time[e]	s	30 ± 4	20 ± 1	18 ± 2
Peak HRR[f]	kW/m^2	94.4 ± 3.6	61.6 ± 5.2	65.0 ± 3.8
HR[g]	MJ/m^2	1.53 ± 0.03	0.8 ± 0.08	0.76 ± 0.06
Effective heat of combustion[h]	MJ/kg	13.4 ± 0.3	6.9 ± 0.5	6.2 ± 0.6

[a] Heating flux—incident flux imposed by cone heater. [b] Initial mass—mass of 100 mm × 100 mm specimen. [c] Ignition time—time to sustained flaming. [d] Time flameout—time at which no longer visible flames. [e] Burning time—time from ignition to flameout. [f] Peak HRR—peak heat release rate. [g] HR—heat release measured between ignition time and flameout. [h] Effective heat of combustion—the measured heat release per unit mass lost between ignition time and flameout.

Acoustic properties of SWCNT–cellulose paper composites

To assess the suitability of using these composites for noise control materials, the acoustic properties of the SWCNT–cellulose papers were investigated. The measurements were made using an impedance tube with a 4.5 cm diameter. An acoustic driver at one end provides acoustical excitation and the sample is mounted at the other end of the tube. Since the acoustic wavelengths are much larger than the tube's internal diameter, plane waves propagate along the tube. A microphone probe traverses the length of the tube and gives the sound pressure as a function of position $p(x)$, known as the standing wave pattern.

Table 5 Reflection coefficients from acoustic tests

	Frequency/Hz	Rigid backing	Open backing
PK-6	500	0.992	0.971
PK-6	1000	0.985	0.950
PK-6	2000	0.983	0.972
PK-8	500	0.989	0.949
PK-8	1000	0.991	0.954
PK-8	2000	0.989	0.979
Control	500	0.989	0.976
Control	1000	0.999	0.943
Control	2000	0.991	0.975

Analysis of the standing wave pattern illustrates how the sample absorbs sound. If there is perfect absorption (a characteristic of a good soundproofing material), then there is no reflected wave in the tube and the magnitude of the sound pressure is constant along the tube. Here the reflectance coefficient would be equal to 0. Alternatively, if there is perfect reflection (characteristic of a material poorly suited for soundproofing applications), then there is a reflected wave traveling in the direction to that of the incident sound wave. For a highly reflective material the reflectance coefficient is 1.

Two different mounting methods were used, so that the absorption results would be unequivocal. One method uses a rigid backing behind the sample, mimicking a typical configuration for mounting noise reduction panels on a wall. This configuration elucidates whether the sample is acoustically highly absorbing or transparent. For a highly absorbing material, the backing makes no difference. The standing wave pattern will show this and have shallow minima. If the sample is acoustically transparent then the incident energy passes through, reflecting off the backing and propagates back through the sample. In the second configuration the sample is open to the atmosphere. A transparent sample will allow all the incident energy to pass through, not reflecting anything. This will appear as highly absorbent and the standing wave patterns would have shallow minima.

The results in Table 5 show that the three samples are all highly reflective at all test frequencies. Even with the open backing, the reflection coefficient is always greater than 0.943. It is noted that results for the rigid backing are all slightly greater than for the open backing. What little sound does get through a sample is reflected back into the impedance tube by the rigid backing, making the combination more reflective. Comparing the three different samples, there are no significant differences. Any variations fall within our estimated uncertainty of ± 0.01. The introduction of nanotubes into these samples had no measurable effect. While no improvements were observed with SWCNT addition, importantly the paper's acoustic properties did not worsen. To achieve higher absorption, samples must be porous with lots of connected open spaces such as foams or fibreglass. Though outside of the scope of this project, SWCNT-paper might be made into a viable soundproofing material by experimenting with thicker, multi-layered, and/or more porous composites.

Conclusion

We have succeeded in producing a multifunctional SWCNT-paper composite that is electrically conductive and has flame retardant properties. Paper composites prepared from unpurified SWCNT (PK-8) exhibit increasing conductivity with increasing SWCNT concentration. Changing the composition from 0% to 35% PK-8 increased the conductivity of the sheet by eight orders of magnitude to ranges typical of low doped semiconductors. Wrapping of the hydrophobic SWCNT with CMC permitted their dispersion in water and gave nanotubes a negative charge. After mixing the CMC-stabilized SWCNT with fibre, addition of a positively charged papermaking additive, alum, acted as a bridge between two anionic surfaces (fibre–fibre, fibre–CMC, CMC–CMC). When compared to layer-by-layer additions reported in the literature, this method is simpler and may convey enough conductivity to be used in many packaging and electrical and magnetic shielding applications.

In flaming combustion tests (from ignition to flameout), the total heat releases for the SWCNT-paper samples were half that obtained for the blank paper samples even though SWCNT as PK-8 replaced only one-third of the cellulose substrate. Each of the SWCNT-paper samples produced a lower effective heat of combustion than the blank paper samples. This suggests that SWCNT materials can improve flame retardant properties.

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