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Electrical and mechanical characteristics of buckypapers and evaporative cast films prepared using single and multi-walled carbon nanotubes and the biopolymer carrageenan

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Publication Details

Aldalbahi, A. & in het Panhuis, M. (2012). Electrical and mechanical characteristics of buckypapers and evaporative cast films prepared using single and multi-walled carbon nanotubes and the biopolymer carrageenan. Carbon, 50 (3), 1197-1208.

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Keywords

mechanical, characteristics, buckypapers, electrical, nanotubes, carbon, walled, multi, single, biopolymer, prepared, carrageenan, films, cast, evaporative

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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This journal article is available at Research Online: http://ro.uow.edu.au/scipapers/4327

[Title as published:

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Electrical and mechanical characteristics of buckypapers and evaporative cast films prepared using carbon nanotubes and the biopolymer carrageenan

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Abstract

The electrical and mechanical characteristics of composite materials prepared using evaporative casting and vacuum filtration of carbon nanotubes (CNTs) dispersed in the biopolymer τ-carrageenan (IC) are reported. It is demonstrated that the contact angle is proportional to the CNT mass and volume fraction, which is used to compare the properties of buckypapers with those of evaporative cast films. Multi-walled carbon nanotube films were found to exhibit higher conductivity values compared to those observed for single-walled carbon nanotubes composites at comparable contact angle values up to true nanotube volume fraction of 0.12. Buckypapers prepared by varying the absolute amount of CNT mass while keeping the IC amount of mass constant, were found to be more robust and conducting compared to evaporative cast films. In contrast, buckypapers prepared by changing the amount of IC mass while keeping the CNT amount of mass constant were found to be more conducting, but less robust compared to evaporative cast films. It is suggested that the electrical characteristics of these gel-carbon

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nanotube materials are determined by the relative amounts of mass (or volume) of CNTs and polymer, while the mechanical characteristics are governed by the absolute amounts of mass (or volume).

1. Introduction

Carrageenan is a generic name for a biopolymer family of water soluble, linear, anionic polysaccharides extracted from red seaweed, which is known for gel forming and thickening properties [1]. They have been extensively employed in the food industry and are commonly referred to as E407 (European Union specification) as well as being approved by the US Food and Drug Administration as a direct food additive. Furthermore, carrageenan has been used as additive in oil well drilling and in cosmetic and pharmaceutical formulations, while recent studies have shown that carrageenan blocks the human papilloma virus associated with the development of cervical cancer [2].

A range of biopolymers (including the carrageenans) have been proven to be effective in dispersing carbon nanotubes (CNTs) in water [3,4,5,6,7,8,9,10]. Many researchers are attracted to CNTs due to their phenomenal mechanical and electrical characteristics [11, 12]. Accessing the properties of single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) is essential for realising practical applications based on these fascinating structures. This requires organising carbon nanotubes into a material or a device, which can be achieved using either direct-growth or wet-processing methods [13, 14].

Most wet-processing methods involve two basic steps, dispersion of CNT in a solvent with or without a dispersant, followed by removal of solvent or solution. Vacuum filtration of nanotube

dispersions, resulting in so-called buckypapers, has been used to good extent in the fabrication of films consisting of densely packed CNT networks [15, 16, 17, 18, 19, 20, 21, 22]. Buckypapers can be thought of as porous membranes, with a free volume of 60-70% of the total volume of the paper [15]. It was found that such buckypaper membranes prepared using functionalised SWCNT and MWCNT are permeable to common gases such as oxygen, nitrogen, carbon dioxide and methane [21,22]. Intercalation of polymers into buckypaper resulted in mechanical reinforcement, while incorporating buckypapers into a polymer matrix resulted in demonstrations of their applicability as supercapacitor electrodes and strain sensors [15, 23, 24, 25].

It has been demonstrated that buckypaper film properties are affected by changing the conditions employed during preparation as well as the type of dispersant. For example, the in-plane Poisson's ratio of buckypapers could be tuned by combining SWCNT with MWCNT [18]. Changing the lengths of MWCNTs used to manufacture buckypapers has a significant effect on the diameter of the pores present in the final material [19]. In addition, changing the sonication time, final dispersion volume or membrane filter used all affected the mechanical properties and surface morphology of SWCNT buckypapers [20]. Furthermore, it has been established that electrical conductivity of buckypapers and mechanical characteristics decreases with increasing molecular mass of dispersant [20].

In evaporative casting, films are prepared by controlled evaporation of solvent from CNT dispersions leaving a composite film [10]. There are numerous examples in the literature related to the preparation of polymer-CNT composite films and their properties [12, 26, 27, 28]. The mechanical and electrical characteristics of these materials are generally dependent on the CNT:dispersant ratio, i.e. increasing the nanotube concentration usually increases the electrical

conductivity and also results in mechanical reinforcement [12, 28]. The use of biopolymers is a more recent approach, and it has been established that biopolymers such as chitosan, gellan gum and xanthan gum are all suitable matrix materials for polymer-CNT composites [10, 29, 30].

In this paper, we describe the electrical and mechanical characteristics of SWCNT and MWCNT composite materials prepared using evaporative casting and vacuum filtration. We show that the contact angle is proportional to the CNT mass and volume fraction, which is then used to compare the properties of buckypapers with those of evaporative cast films. We suggest that the electrical characteristics of these gel-carbon nanotube materials are determined by the relative amounts of mass (or volume) of CNTs and polymer, while the mechanical characteristics are governed by absolute amounts of mass (or volume).

2. Experimental

2.1 Materials

The biopolymer τ-carrageenan (IC, molecular weight 350,000 – 800,000 g/mol, Genuvisco type CI-123, lot # SK93842) was a gift from CP Kelco (USA). Single-walled carbon nanotubes (SWCNTs), produced by high-pressure decomposition of carbon monoxide (HiPco process) were purchased from Unidym Inc. (USA, lot # P0261). Catalytic chemical vapour deposition produced multi-walled carbon nanotubes (MWCNTs) were obtained from Nanocyl S.A. (Belgium, lot # 090901). Deionised “Milli-Q” water was used in all experiments and prepared using a Millipore filtration system (resistivity = 18.2 MΩ cm)

2.2 Solution and dispersion preparation

Solutions of IC were prepared by adding appropriate amounts of IC to 15 ml of Milli-Q water under stirring for 3 hours at ~70 °C. Different amounts of CNTs (in powder form) were added to IC solutions. Homogenous IC-CNTs dispersions (Fig.1a) were prepared using a digital sonicator horn (Branson 450, Ultrasonics Corp.) with a probe diameter of 10 mm, in pulse mode (0.5 s on/off) and amplitude = 12 W. The sample vial was placed inside a water bath to control solution temperature.

2.3 Preparation of composites by evaporative casting

Free-standing films were prepared by evaporative casting of IC solutions and composite dispersions (15 mL) into the base of cylindrical plastic containers which were then dried in the oven at 35°C for 24 hours. The resulting films were peeled off the substrate to yield uniform free-standing films (Fig. 1b).

2.4 Preparation of composites by vacuum filtration

Prior to the filtration, the composite dispersion was diluted by Milli-Q water up to a final volume of 50 mL. The dispersions were drawn through the membranes (5 μm pore size PTFE, Millipore) and filtration units by using a vacuum pump (Vacuubrand CVC2) that typically operated between 30 and 40 mBar. Once all of the dispersion had filtered, the buckypapers were washed with Milli-Q water, followed by methanol. After washing, the damp buckypaper was placed between absorbent paper sheets with a small flat glass sheet placed on top and left to dry for 24 hours at under controlled ambient conditions (21 C, 45% relative humidity, RH). The buckypaper (Fig. 1) was then peeled from the filtration membrane.

2.5 Characterization techniques

UV-visible absorption spectra of IC solutions and IC-CNTs composite dispersions were obtained with a dual beam UV-vis–NIR spectrophotometer (Cary 500) using quartz cuvettes (path length = 5 mm).

Flow curves (apparent viscosity as a function of shear rate) were determined using an Anton Paar Physica MCR 301 rheometer fitted with a PP25 head at 20 ºC.

Dispersions were imaged using an optical microscope (LEICA Z16) with Leica Application Suite (version 3.1.0 R1) software.

Current-voltage (*I*-*V*) characteristics were determined under controlled conditions in air (21°C, 45% RH) with a waveform generator (Agilent 33220A) and a digital multimeter (Agilent 34410A). For conductivity measurements films were cut into strips of 0.5 cm in width and 4 cm in length and contacted with copper electrodes. *I*-*V* measurements were made as a function of film length by cutting the end off the strip, contacting with copper electrodes, re-measuring the *I*-*V* characteristic and repeating. Films thickness was measured using a digital micrometer (Mitutoyo IP65).

The mechanical properties of all films were obtained using a dynamic mechanical analyser (Q800, TA instruments). Measurements were carried out under ambient conditions on rectangular strips (length = 10 mm) at a cross-head speed of 0.1 mm/min. Young's modulus, tensile strength, and extensibility were determined from the slope of the linear part of the stress-strain curve, the maximum stress and strain at break, respectively.

Scanning electron microscope (SEM) images were acquired using a JEOL JSM-7500FA. Samples were prepared by mounting small pieces of films onto a brass stub (11 x 5 mm^2) using conductive carbon tape.

Contact angle measurements were carried out using the sessile drop method on a goniometer (Data Physics SCA20), which was fitted with a digital camera. The contact angles of 1μL Milli-Q water droplets on the surface of the samples were calculated after 30 s using the accompanying Data Physics software (version SCA20.1). The mean contact angle was calculated based on measurements performed using at least 5 water droplets.

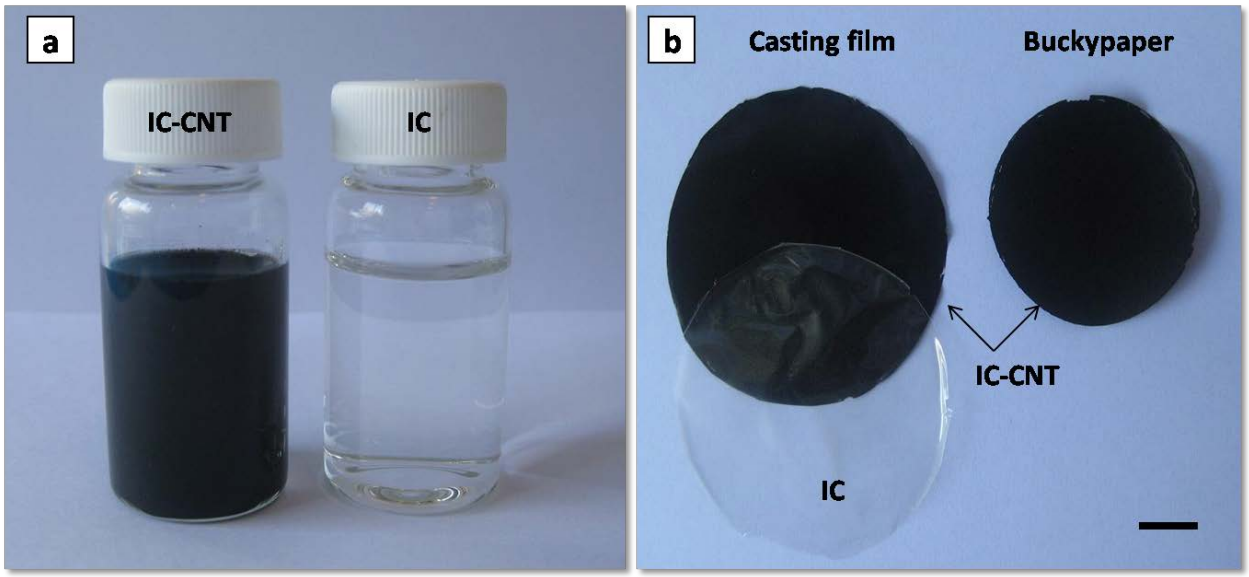

Fig. 1. Photographs of typical: (a) IC-CNT dispersion and IC solution, and (b) films prepared by evaporative casting and vacuum filtration. Scale bar indicates 1 cm.

3. Results and discussion

3.1 Dispersing carbon nanotubes

The optimum time of sonication required to effectively disperse CNTs was determined by monitoring the leveling of the UV-vis absorption intensity and the disappearance of visible

aggregates. The UV-vis spectra of the CNT dispersions as a function of sonication time are shown in Fig. 2. As IC absorbs minimally in the region shown, it can be assumed that the absorption bands observed are due solely to the presence of CNTs. Increasing the sonication time resulted in greater overall absorbance, indicating that an increasing amount of CNTs became dispersed. The optimum sonication time was defined as the minimum amount of time required to effectively disperse the CNTs, as excess sonication can shorten or cause defects to form in the tubes and thereby diminish their properties [31, 32, 33]. The absorbance of the dispersions at 660 nm was plotted as a function of sonication time (insets in Fig. 2). This particular wavelength was selected as it corresponds to the maxima of an absorption band arising from the van Hove singularities for SWCNT [34, 35, 36]. The inset in Fig. 2a clearly shows that the MWCNT absorbance becomes independent of sonication at 20 min. In contrast, the SWCNT absorbance did not show a clear plateau for sonication times of up to 60 min (inset, Fig. 2b). Instead it was noted that the rate of increase in absorbance started to decrease after approximately 35 min of sonication.

Based on the data shown in Fig. 2, sonication times of 20 and 35 min were selected as being optimal for ensuring that the MWCNT and SWCNTs were well dispersed, respectively. Optical microscopy revealed that there were no large aggregates present in the dispersions that had been subjected to these sonication times. Furthermore, dispersions prepared in this manner were found to be very stable, as they showed little change after 6 months standing under ambient conditions (21 ºC, 45% RH).

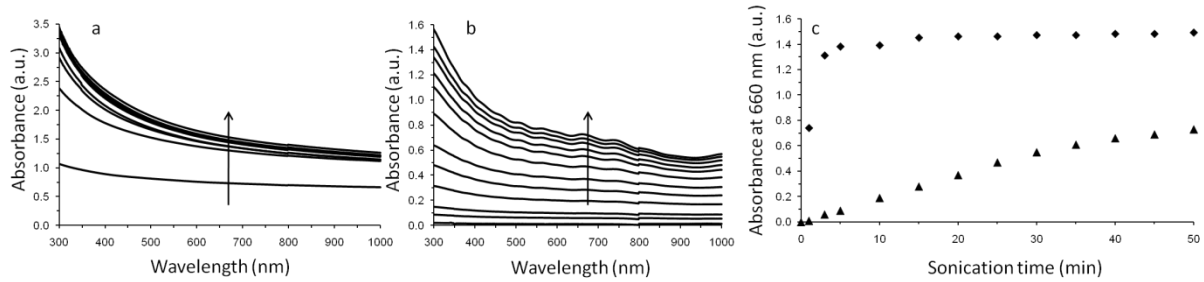

Fig. 2. Effect of increasing sonication time on the UV-visible absorption spectrum of a dispersion containing (a) 0.1% (w/v) MWCNT and 0.8% (w/v) IC, and (b) 0.1% (w/v) SWCNT and 0.8 % (w/v) IC sonication. Arrows indicate direction of increase in sonication time. (c) Absorbance at 660 nm versus sonication time for IC-MWCNT (diamonds) and IC-SWCNT (triangles) obtained from data shown in (a) and (b), respectively. All samples were measured after a 10-fold dilution.

The flow curves for selected IC solutions and IC-CNT dispersions are shown in Fig. 3a. All solutions and dispersions display shear thinning behaviour, i.e. viscosity (η) decreases with increasing shear rate (γ) which could be fitted to the well-known power-law model,

$$\eta = K\,\gamma^{n-1}, \qquad \text{(Eq. 1)}$$

where K and n indicate the 'consistency' and power law index, respectively. The apparent viscosity of IC solutions significantly decreases during sonication. For example, at a shear rate of 100 s^{-1} the measured viscosity of the as-prepared IC solution (0.8% w/v) is 48 mPa s compared to 4.5 mPa s after 35 min of sonication (Fig. 3b). With increasing sonication time, the IC solutions were found to become more shear thinning (n decreases), and thinner (K decreases, Table 1). This is in agreement with previous observations, i.e. sonolysis reduces the molecular weight of biopolymers, resulting in a decrease in viscosity [37, 38]. Addition of SWCNT (0.10% w/v) and MWNT (0.10% w/v) resulted in 2.3 and 2.0 fold increases in viscosity (at shear rate 100 s^{-1}), respectively, compared to the corresponding values for the sonicated IC solution (Table 1). In addition, increasing the CNT concentration from 0.6% w/v to 1.0% w/v leads to thickening (K

increases) of the dispersion. Thus, it is clear that sonolysis results in a decrease in apparent viscosity, while addition of CNTs results in the opposite effect.

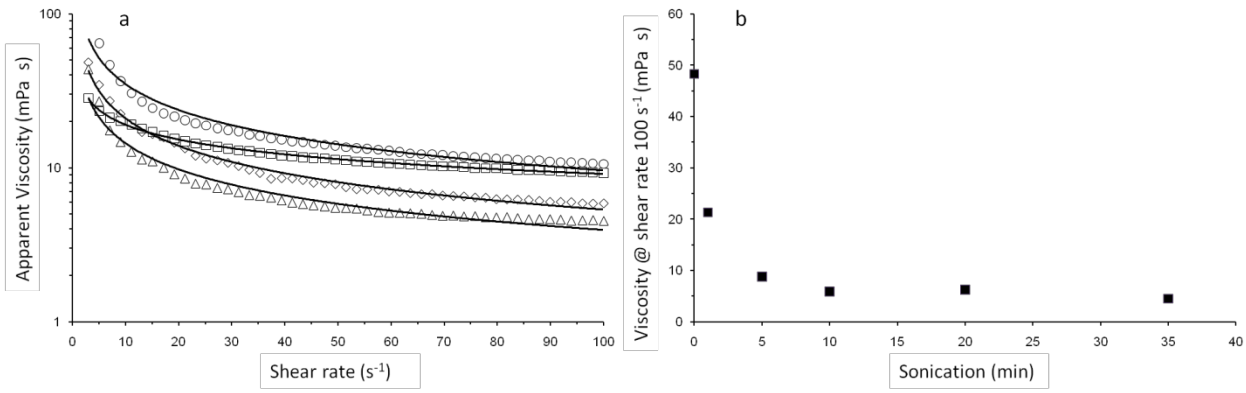

Fig. 3. (a) Apparent viscosity (at 20 °C) as a function of shear rate for typical IC solutions and IC-CNT dispersions. Diamonds and triangles indicate IC solution (0.8% w/v) after sonication for 20 and 35 min, respectively. Circles and squares indicate IC-SWCNT and IC-MWCNT dispersions with CNT concentration 0.10% w/v sonicated for 20 and 35 min, respectively. The lines are fits to Eq. 1. (b) Viscosity (at shear rate 100 s^{-1}) as a function of sonication time for a typical IC solution (0.8% w/v).

Table 1. Summary of flow curve analysis (at 20 °C) for biopolymer solutions and biopolymer-CNT dispersions. Consistency (*K*) and power law index (*n*) were obtained through curve-fitting with the power law model, Eq. 1. η_{100} represents the measured viscosity at shear rate 100 s^{-1}. The naming of the samples is as follows: biopolymer concentration-CNT concentration, e.g. "IC08-MW006" indicates a dispersion with τ-carrageenan (IC) and SWCNT (SW) concentrations of 0.8% w/v and 0.06% w/v, respectively.

Sample	***K* (mPa s^n)**	***n***	**η_{100} (mPa s)**
IC08 - no sonication	0.78 ± 0.03	122.1 ± 0.9	48.3 ± 2.4
IC08 – 1 min sonication	0.68 ± 0.04	61.3 ± 0.7	21.3 ± 1.6
IC08 – 5 min sonication	0.55 ± 0.02	60.4 ± 0.7	8.8 ± 1.0
IC08 – 10 min sonication	0.65 ± 0.03	25.9 ± 0.4	5.9 ± 0.4
IC08 – 20 min sonication	0.63 ± 0.01	31.6 ± 0.2	6.3 ± 0.1
IC08 – 35 min sonication	0.60 ± 0.02	26.7 ± 0.3	4.5 ± 0.2
IC08-MW006 – 20 min sonication	0.85 ± 0.01	13.5 ± 0.1	6.8 ± 0.2
IC08-MW01 – 20 min sonication	0.68 ± 0.01	39.8 ± 0.1	9.2 ± 0.2

IC08-SW006 – 35 min sonication	0.42 ± 0.01	95.6 ± 1.5	7.3 ± 0.4
IC08-MW01 – 35 min sonication	0.39 ± 0.01	155.0 ± 2.1	10.6 ± 0.5

3.2 Electrical characteristics.

Free-standing composite films were prepared by evaporative casting and vacuum filtration of IC-CNT dispersions. The current – voltage *(I-V)* characteristics of IC and IC-CNT films were investigated under ambient conditions (21°C, 45% RH). All composite films exhibited linear *I-V* characteristics, which indicate Ohmic behaviour. The calculated resistances are the total resistance (R_T), which includes a contribution of the electrode- film contact resistance (R_C). Previously, it has been shown that R_T scales with length l according to [10, 17, 20, 29]:

— , (Eq. 2)

where A and σ are the cross-section area bulk conductivity, respectively. The slope of the straight line fit to equation 2 can then be used to calculate the bulk conductivities (Fig. 4a and Table 2). Fig. 4b shows that increasing the CNT mass fraction ($M_f = mass_{CNT} / mass_{total}$) increases the conductivity of the composite films regardless of CNTs used. However, at equal M_f the conductivity values exhibited by SWCNT composite films are lower compared to those observed for MWCNT composite. For example, the values for SWCNT and MWCNT films with M_f = 0.111 are 1.2 ± 0.2 S/cm and 5.6 ± 0.9 S/cm, respectively. It is well-known that CNT mass fraction does not account for the difference in volume between SWCNT and MWCNT, as is evident from the difference in their density values, i.e. 1500 kg/m^3 (SWCNT) and 2150 kg/m^3 (MWCNT). [17, 39] Therefore, CNT volume fraction (V_f) is a more appropriate measure of comparison, which was calculated using the experimentally determined density value for IC (1630 ± 50 kg/m^3) and a rules-of-mixtures expression:

(Eq. 3)

where m_{CNT}, m_{IC}, ρ_{CNT}, and ρ_{IC} are the mass amounts and density values of CNTs and IC, respectively. Fig. 4c and Table 2 show that at similar V_f the conductivity values exhibited by SWCNT composite films are lower compared to those observed for MWCNT composites.

Table 2. Summary of the contact angle (θ), CNT mass fraction (M_f), density (ρ_{film}) and conductivity (σ) values for films (E1-10) prepared by evaporative casting. CNT volume (V_f) and true CNT volume (V_{ft}) fraction values are calculated using Eq. 3 and 5, respectively. The naming of the dispersions is as follows: biopolymer concentration-CNT concentration, e.g. "IC08-MW003" indicates a dispersion with τ-carrageenan (IC) and MWCNT (MW) concentrations of 0.8% w/v and 0.03% w/v, respectively.

Film	**Dispersion**	M_f	ρ_{film} **(kg/m^3)**	V_f	V_{ft}	θ **(º)**	σ **(S/cm)**
E1	IC08-MW003	0.0361	1361 ± 124	0.0276	0.0229	38.2 ± 1.2	0.36 ± 0.06
E2	IC08-MW006	0.0698	1435 ± 163	0.0538	0.0466	42.3 ± 1.1	0.82 ± 0.11
E3	IC08-MW010	0.1111	1499 ± 230	0.0866	0.0775	45.7 ± 0.8	5.58 ± 0.90
E4	IC10-MW010	0.0909	1573 ± 126	0.0705	0.0665	43.1 ± 0.7	4.20 ± 0.54
E5	IC12-MW010	0.0769	1618 ± 159	0.0594	0.0579	42.2 ± 0.8	2.60 ± 0.29
E6	IC08-SW003	0.0361	1320 ± 74	0.0754	0.0318	35.1 ± 0.9	0.00057 ± 0.00009
E7	IC08-SW006	0.0698	1386 ± 100	0.0392	0.0645	37.1 ± 0.6	0.25 ± 0.04
E8	IC08-SW010	0.1111	1418 ± 47	0.120	0.105	42.5 ± 0.4	1.18 ± 0.16
E9	IC10-SW010	0.0909	1475 ± 55	0.0980	0.0894	40.0 ± 0.9	0.82 ± 0.08
E10	IC12-SW010	0.0769	1540 ± 50	0.0830	0.0790	37.5 ± 0.8	0.060 ± 0.006

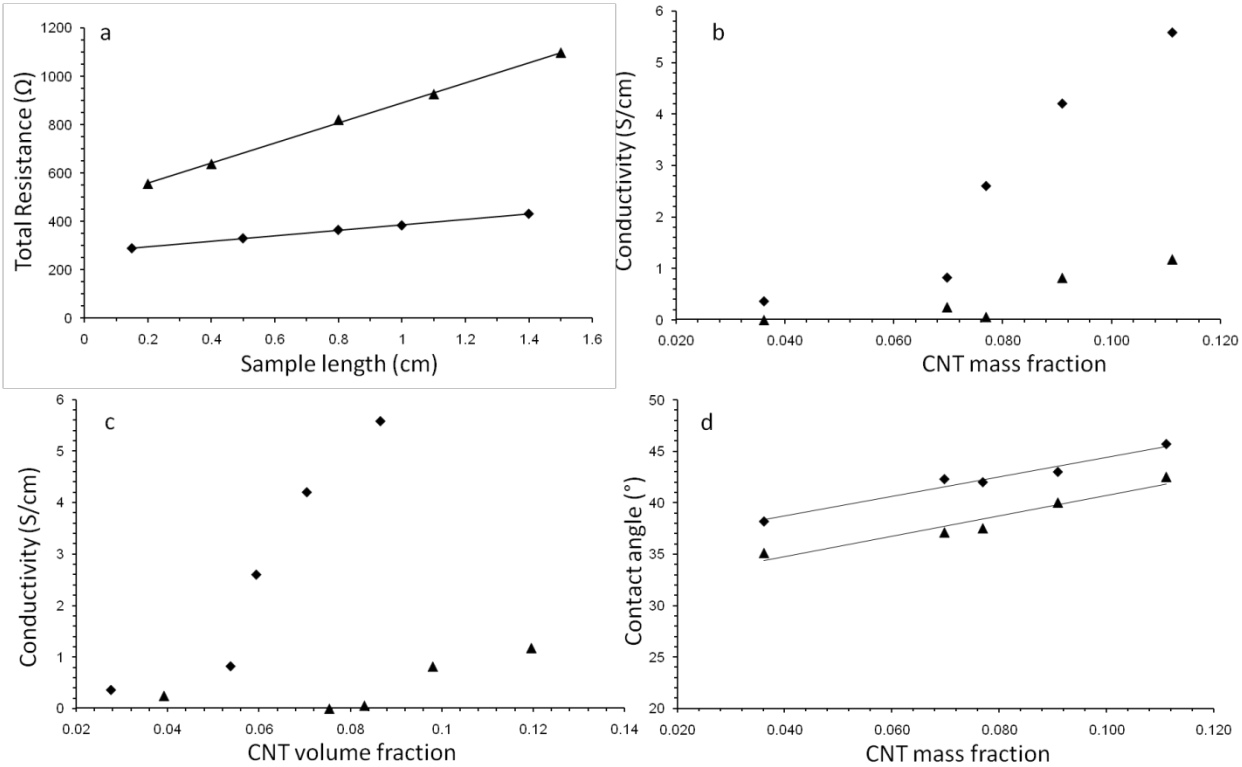

Fig. 4. Electrical conductivity and contact angle of films prepared by evaporative casting. (a) Resistance versus length for IC-MWCNT (diamonds) and IC-SWCNT (triangles) films with CNT:IC ratio = 0.10. The straight lines are fits to Eq. 2. (b) Electrical conductivity of IC-MWCNT (diamonds) and IC-SWCNT (triangles) films as a function of CNT mass fraction. (c) Electrical conductivity of IC-MWCNT (diamonds) and IC-SWCNT (triangles) films as a function of CNT mass fraction. (d) Contact angle of water with IC-MWCNT (diamonds) and IC-SWCNT (triangles) films as a function of CNT mass fraction. The straight lines are fits to Eq. 4.

It is not straightforward to relate the electrical conductivity values of buckypapers to CNT mass fraction due to the vacuum filtration process. To accurately determine the CNT mass fraction would require detailed spectroscopic analysis of the filtrate to determine what proportion of the CNTs and IC has passed through the membrane. This is a cumbersome and time-consuming process. Instead, it can be shown that the contact angle is proportional to the CNT mass fraction, which is then used to calculate the true nanotube volume fraction.

Fig. 4d shows that the contact angle (θ) increases with increasing CNT mass fraction, indicating that hydrophobicity increases with carbon nanotube content. Moreover, SWCNT and MWCNT films with the same CNT mass fraction exhibit comparable contact angles (Table 2). For example, the contact angle values for SWCNT and MWCNT composite materials at CNT mass fraction = 0.111 are 42.4 ± 0.4 º and 45.7 ± 0.8 º, respectively. Plotting contact angle versus conductivity (Fig. 5a), then clearly reveals that MWCNT composite materials yield higher conductivity values compared to SWCNT materials with comparable contact angle values. This demonstrates that SWCNT and MWCNT films with similar CNT mass fractions have comparable contact angles, but exhibit different conductivity values.

The data shown in Fig. 4d, can be used to demonstrate that the contact angle scales with CNT mass fraction according to:

(Eq. 4)

where k and θ_0 represents a proportionality constant and the contact angle at $M_f = 0$, respectively. The slope of the straight line fit to equation 4 (Fig. 4d), yield k values of 95 ± 10 ° and 100 ± 16 ° for MWCNT and SWCNT composites, respectively. The corresponding θ_0 values (evaluated from the intercept) are θ_0 = 34.9 ± 0.8 ° (MWCNT) and 30.8 ± 1.3 ° (SWCNT). This can be used to estimate the CNT mass fraction for films prepared by vacuum filtration.

The dependence of contact angle on conductivity for films prepared by vacuum filtration is shown in Fig. 5b. The contact angle data is then converted into estimated CNT mass fraction using Eq. 4 and the proportionality information for the CNTs. In contrast to evaporative cast

films, SWCNT composite films exhibit higher conductivity values compared to those observed for MWCNT composites at comparable contact angles and CNT mass fractions (Table 3 and Fig. 5c). For example, the conductivity values of SWCNT and MWCNT films with estimated CNT mass fraction of ~0.41 are 76 S/cm and 32 S/cm, respectively.

Table 3 illustrates that unlike for evaporative cast films; the vacuum filtrated films are more porous in nature as their density values are lower then either that of the polymer or the CNTs. The porosity is also evident from the SEM images. Fig. 6a-b shows that there is a significant difference in surface morphology between the two types of films. The difference in morphology can be attributed to the vacuum filtration process, which partially removes CNTs and IC. The carbon nanotubes are clearly visible in the buckypaper sample, but almost entirely covered by biopolymer in the sample prepared by evaporative casting. Furthermore, the SEM images confirm that an increase in contact angle for buckypaper samples corresponds to a decrease in biopolymer coverage, i.e. an increase in CNT mass fraction (Fig. 6b-d).

Therefore, the porosity needs to be accounted for in a calculation of the CNT volume fraction, rather then using a rules-of-mixtures expression (Eq. 3). The true CNT volume fraction (V_{ft}) can be calculated using contact angle information (Eq. 4) as follows:

(Eq. 5)

where V_{CNT}, V_{film} and ρ_{film} are the CNT and film volumes, and the film density, respectively. This yields V_{ft} values of 0.06 – 0.18 for the films prepared by vacuum filtration, and 0.02 – 0.10 for films prepared by evaporative casting. It is also evident that the CNTs occupy a larger volume in

the SWCNT composite materials at similar CNT mass fraction values. For example, SWCNT and MWCNT films with CNT mass fraction of ~0.41 exhibit V_{ft} values of 0.15 and 0.10, respectively. Fig 5d shows that up to true CNT volume fraction of 0.12 the conductivity of composite films prepared with MCWNT are higher compared to those prepared with SWCNT.

What happens at higher volume fraction? It has been determined that the conductivity of nanotube-only films consisting of SWCNT is higher than those consisting of MWCNT. For example, films prepared using an organic solvent instead of a polymer dispersant yielded conductivity values of ~55 S/cm and ~200 S/cm for MWCNT and SWCNT materials, respectively [40, 41]. Hence, the MWCNT films with V_{ft} = 0.12 and σ = 38 S/cm is already approaching this limiting conductivity value. Based on the higher conductivity values (> 55 S/cm) observed for SWCNT films, it would be reasonable to assume that these films will outperform the MWCNT films for V_{ft} > 0.14 (Fig. 5d).

It is not entirely clear at present why MWCNT films are more conducting then SWCNT film for true nanotube loading fractions below 0.12. It is likely that the observed difference in conductivity of composite materials may be related to the biopolymer being able to achieve a more complete coating of the SWCNT surface compared to that of MWCNT. This in turn would affect the resistance of the intra-CNT and CNT-polymer-CNT junctions as previously observed [8, 10, 29, 42, 43]. Furthermore, it has been shown that in gel-CNT films and hydrogels, the CNT–polymer–CNT junctions can act as a tunnelling barrier [8]. Hence, the difference in conductivity and contact angle of films prepared by evaporative casting and vacuum filtration, suggests that CNT-polymer-CNT junctions may play a more significant role in evaporative cast films then in buckypapers.

Previously, it was observed that percolation scaling can persist beyond the percolation threshold up to higher volume fractions, obeying the scaling law [17] :

(Eq. 6)

where σ_0 is related to the conductivity of the CNTs and t is the conductivity exponent. Percolation scaling was observed for all MWCNT films, with t = 2.9 ± 0.6 and log (σ_0) = 4.2 ± 0.7. Although this t value is higher then the calculated for a 3D percolative system (t = 2.0), it is in reasonable agreement with a previously reported value (t = 2.22).[17] In contrast, applying this percolation scaling to the SWCNT data did not yield a realistic value (t = 7.9 ± 1.5), suggesting that scaling does not apply up volume fraction value of 0.20. We feel that this difference in percolation scaling may also be related to the observed difference in conductivity values for our CNT films. Further research is necessary to fully understand this.

Table 3. Summary of the contact angle (θ), film density (ρ_{film}), CNT mass (M_f) and conductivity (σ) values for films (BPs) prepared by vacuum filtration. CNT volume fraction (V_f) and true CNT volume (V_{ft}) fraction values are calculated using Eq. 4 and 5, respectively. The naming of the dispersions is as follows: biopolymer concentration-CNT concentration, e.g. "IC024-MW002" indicates a dispersion with τ-carrageenan (IC) and MWCNT (MW) concentrations of 0.24% w/v and 0.02% w/v, respectively.

Film	**Dispersion**	M_f	ρ_{film} **(kg/m^3)**	V_f	V_{ft}	θ **(º)**	σ **(S/cm)**
B1	IC024-MW002	0.388	332 ± 99	0.325	0.0600	71.9 ± 2.1	28.8 ± 5.0
B2	IC024-MW0033	0.411	504 ± 23	0.346	0.0963	74.1 ± 1.7	33.2 ± 5.0
B3	IC024-MW0039	0.447	575 ± 12	0.380	0.120	77.5 ± 1.4	37.5 ± 5.0
B4	IC030-MW0033	0.387	562 ± 36	0.324	0.101	71.8 ± 1.6	21.6 ± 2.3
B5	IC036-MW0033	0.311	637 ± 119	0.255	0.0922	64.6 ± 1.5	11.5 ± 2.1

B6	IC024-SW002	0.390	452 ± 12	0.410	0.118	69.6 ± 2.1	39.8 ± 7.0
B7	IC024-SW0033	0.409	522 ± 38	0.429	0.142	71.5 ± 2.3	76 ± 10
B8	IC024-SW0039	0.440	608 ± 31	0.461	0.179	74.6 ± 2.3	117 ± 16

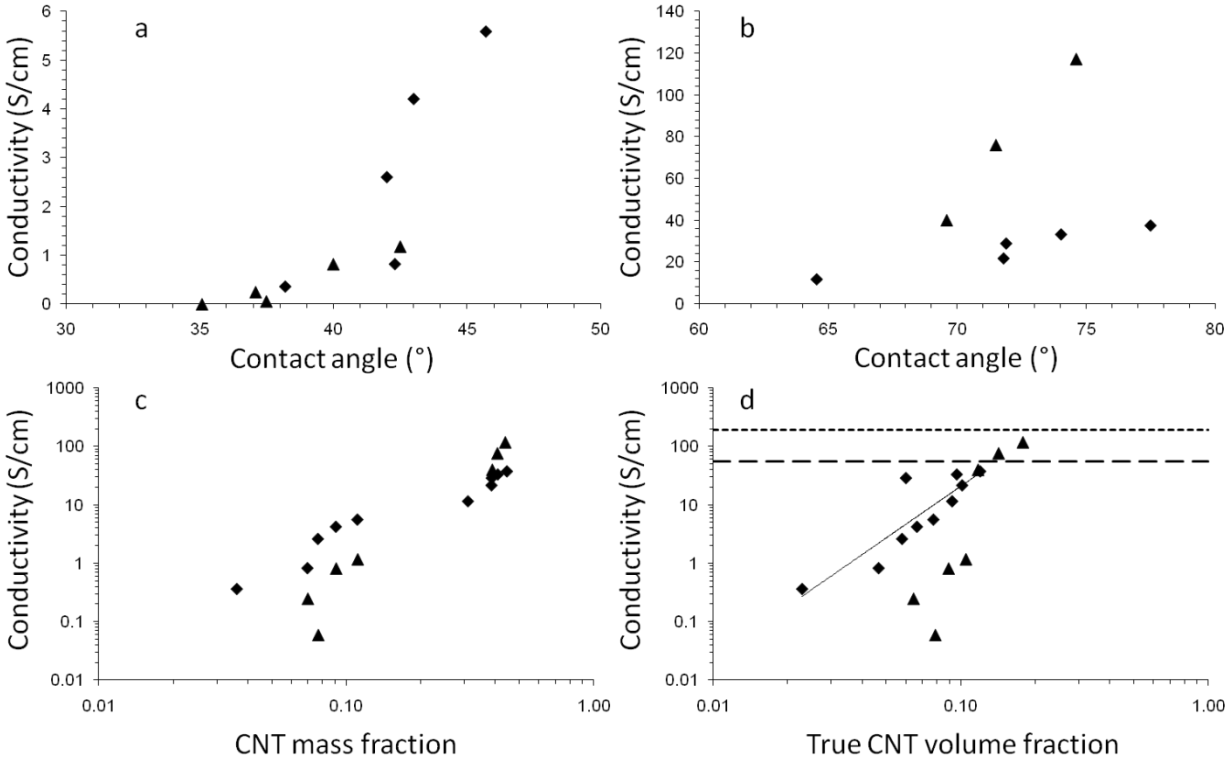

Fig. 5. Electrical conductivity versus contact angle for films prepared by (a) evaporative casting and (b) vacuum filtration. Electrical conductivity versus (c) CNT mass fraction and (d) true CNT volume fraction for films prepared by evaporative casting and vacuum filtration. The small and large dashed lines in (d) indicate the limiting conductivity of nanotube-only films using SWCNT and MWCTN, respectively. The solid line is a fit to Eq. 6. Diamonds and triangles indicate IC-MWCNT and IC-SWCNT films, respectively.

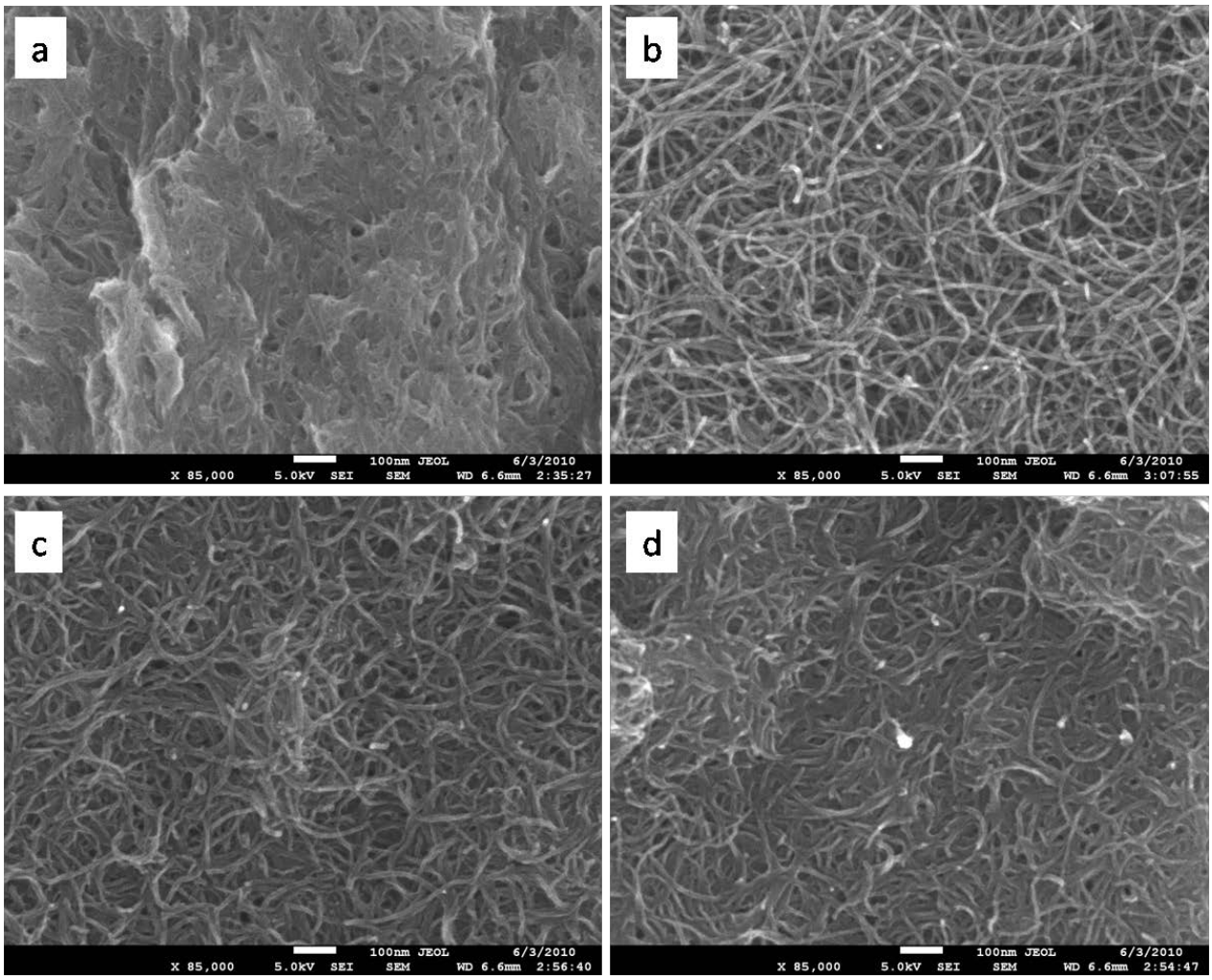

Fig. 6. Scanning electron microscopy images of IC-CNT composite materials. Image (a) represent a typical sample prepared by evaporative casting (contact angle = 46º). Images (b), (c) and (d) correspond to typical samples prepared by vacuum filtration with contact angles 74º, 72º and 65º, respectively. Scale bars indicate 100 nm.

3.3 Mechanical characteristics.

The CNT mass or volume fraction in composite materials can be modified by changing the concentration of the constituents in the dispersion using two methods: (i) changing CNT concentration, while keeping the IC concentration constant; and (ii) modifying the IC concentration, while keeping the CNT concentration constant. Fig. 7a shows that for IC-MWCNT composites prepared by evaporative casting the overall trend of decreasing

conductivity with decreasing CNT mass fraction is independent of methods used to change this ratio. However, Young's modulus and tensile strength values display different trends (Fig. 7b-c and Table 4). They increase with decreasing CNT mass fraction for materials prepared by modifying the ratio via method (i), while they decrease upon changing the ratio through method (ii). This suggests that the electrical characteristics of these materials are determined by the relative amounts of mass of CNTs and polymer, while the mechanical characteristics are governed by absolute amounts of mass.

Here it is suggested that this behaviour can be explained as follows. It is well-known that incorporating CNTs can result in mechanical reinforcement of a polymer matrix, which scales with the CNT concentration [12]. Therefore, decreasing the CNT mass or volume fraction by reducing the amount of CNTs (while keeping the IC concentration constant), will reduce this reinforcement effect. This results in the observed decreases in Young's modulus and tensile strength values. Furthermore, it is well-known that the modulus of elasticity scales with polymer concentration. Decreasing the CNT mass or volume fraction by increasing the amount of IC (while keeping CNT concentration constant) will therefore results in the observed increase in stiffness (Young's modulus).

The effect on the electrical conductivity is the same in both cases of changing the CNT mass or volume fraction, i.e. decreasing the concentration of CNTs (at constant IC amount) results in a decrease in the number of intra-CNT junctions with respect to the number of CNT-polymer-CNT junctions. Increasing the IC concentration (at constant CNT amount) has the same effect on the number of junctions. Both approaches reduce the number of conducting pathways resulting in lower conductivity.

Table 4. Mechanical characteristics and contact angle (θ) of IC-MWCNT composite films prepared by evaporative casting and vacuum filtration. E1-5 and B1-5 refer to IC-CNT films as listed in Tables 2 and 3.

Film	θ	**Young's modulus (MPa)**	**Tensile strength (MPa)**	**Extensibility (%)**
E1	38.2 ± 1.2	859 ± 105	15.0 ± 1.0	4.0 ± 1.0
E2	42.3 ± 1.1	935 ± 93	16.0 ± 2.0	5.0 ± 1.0
E3	45.7 ± 0.8	1341 ± 95	32.3 ± 6.5	7.6 ± 2.7
E4	43.1 ± 0.7	2466 ± 272	37.8 ± 8.6	6.0 ± 0.4
E5	42.2 ± 0.8	2602 ± 174	39.5 ± 6.0	6.5 ± 0.6
B1	71.9 ± 2.1	1415 ± 62	7.2 ± 1.0	1.2 ± 0.3
B2	74.1 ± 1.7	1449 ± 36	12.0 ± 0.4	2.3 ± 0.2
B3	77.5 ± 1.4	2665 ± 71	23.9 ± 1.3	3.4 ± 0.6
B4	71.8 ± 1.6	1515 ± 41	13.5 ± 0.9	2.6 ± 0.4
B5	64.6 ± 1.5	1832 ± 48	22.5 ± 3.5	3.3 ± 1.0

In the previous section it was demonstrated that contact angle increases with increasing CNT mass and volume fraction. This allows a comparison between films prepared by evaporative casting and vacuum filtration (Fig. 8 and Tables 2-4). Conductivity, Young's modulus and tensile strength values increase with contact angle, coupled with a decrease in extensibility for films prepared via method (i). Buckypapers prepared via this method are more robust and conducting, but less ductile compared to evaporative cast films. Films prepared via method (ii) behave differently; conductivity still increases with contact angle, but now Young's modulus, tensile strength and extensibility values all decrease with contact angle. Buckypapers prepared via this

method are more conducting, but less robust and ductile compared to evaporative cast films. Hence, it is clear that the observed trends for electrical and mechanical properties are independent of the method of film preparation (Fig. 8e-f).

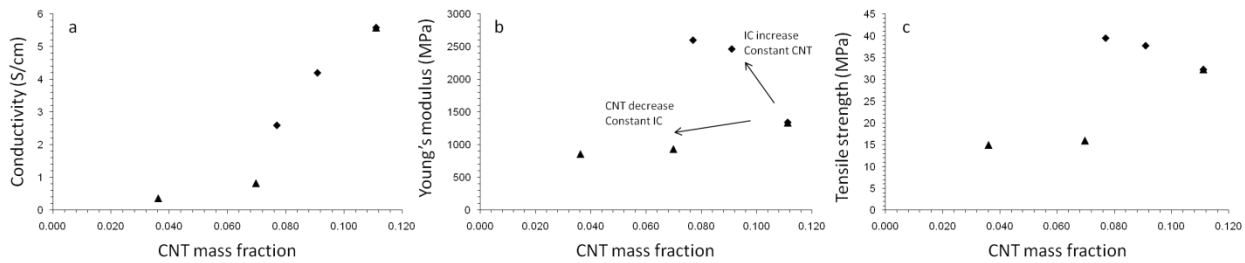

Fig. 7. Young's modulus (a), tensile strength (b) and electrical conductivity (c) versus CNT mass fraction for IC-MWCNT films prepared by evaporative casting. Diamonds and triangles indicate films for which the CNT mass fraction was modified by varying the amount of IC at constant CNT amount and varying the amount of CNT at constant IC amount, respectively.

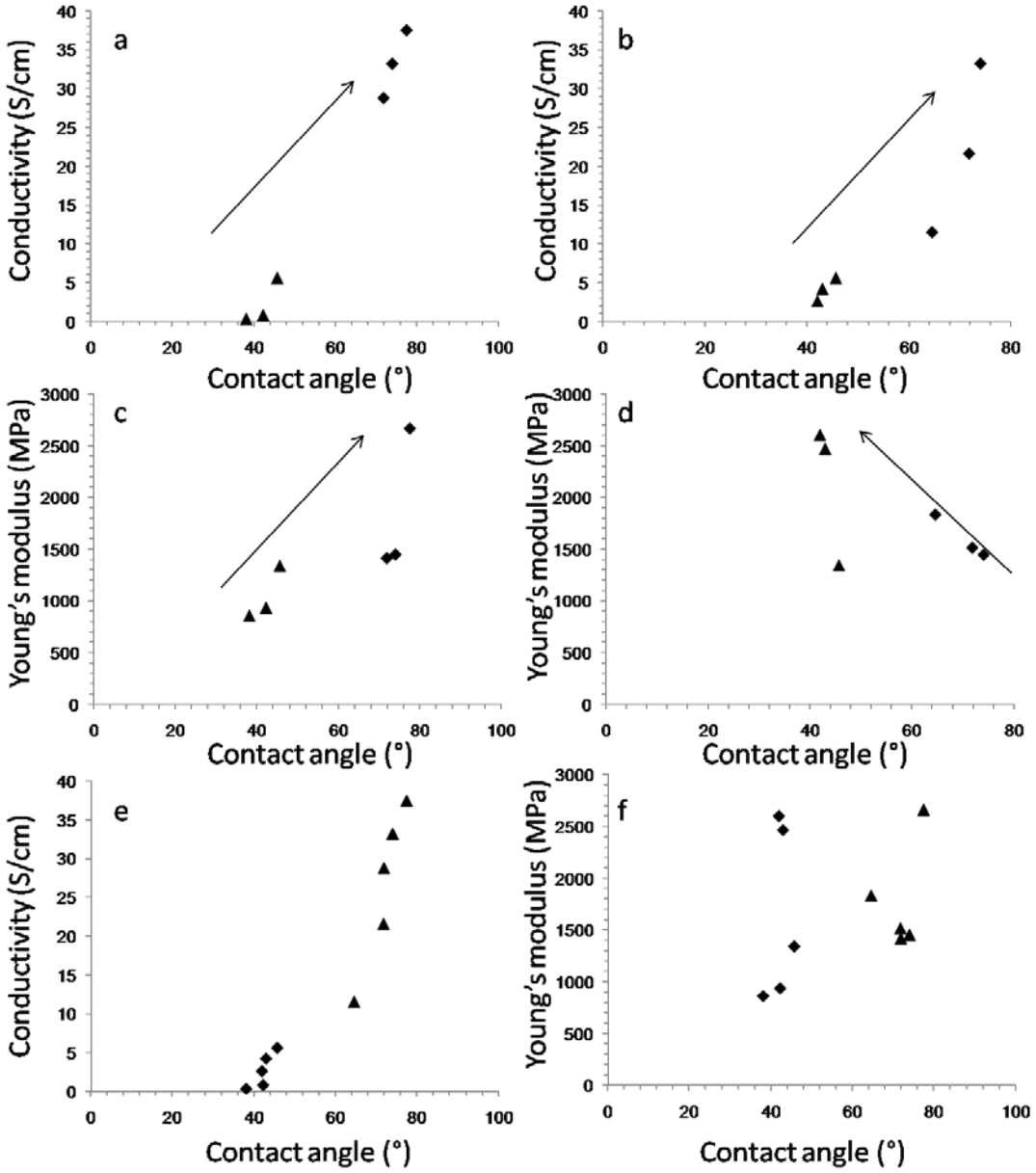

Fig. 8. (a) Electrical conductivity and (c) Young's modulus of films prepared by varying IC concentration at constant MWCNT concentration. (b) Electrical conductivity and (d) Young's modulus of films prepared by varying MWCNT concentration at constant IC concentration. (e) and (f) show conductivity and Young's modulus for all samples. Triangles and diamonds indicate films prepared by evaporative casting and vacuum filtration, respectively. Arrows indicate trend with contact angle.

4. Conclusion

The electrical and mechanical characteristics of composite materials prepared using evaporative casting and vacuum filtration of CNTs dispersed in the biopolymer τ-carrageenan (IC) has been investigated. SWCNT and MWCNT evaporative cast films with similar CNT mass and volume fractions were found to exhibit different conductivity values. For example, the values for SWCNT and MWCNT composites with CNT volume fraction = 0.125 are 1.2 ± 0.2 S/cm and 5.6 ± 0.9 S/cm, respectively.

It is not straightforward to determine the CNT mass (or volume) fraction for buckypapers due to the vacuum filtration process. Instead, it was demonstrated that the contact angle is proportional to the CNT mass fraction, which is used to estimate the true CNT volume fraction values. MWCNT composite films exhibit higher conductivity values compared to those observed for SWCNT composite at true nanotube volume fractions < 0.12. It is suggested that the high conductivity values (> 75 S/cm) observed for SWCNT composites with true nanotube volume fraction > 0.14 will outperform MWCNT films due to the difference in limiting conductivity values for nanotube-only SWCNT and MWCNT films. For example, the observed conductivity of 38 S/cm for a MWCNT film with true nanotube volume fraction 0.12 is already close to its limiting conductivity value (55 S/cm).

Furthermore, contact angle analysis was used to compare the properties of BP with those of evaporative cast films. Buckypapers prepared by varying the absolute amount of mass of CNTs while keeping the IC amount of mass constant, were found to be more robust and conducting compared to evaporative cast films. In contrast, buckypapers prepared by changing the amount of

IC mass while keeping the CNT amount of mass constant were found to be more conducting, but less robust compared to evaporative cast films.

These observations led us to suggest that the electrical characteristics of these materials are determined by the relative amounts (mass or volume) of CNTs and polymer, while the mechanical characteristics are governed by absolute amounts (mass or volume). This work contributes to the understanding of gel-carbon nanotube materials.

Acknowledgments

This work was supported by the University of Wollongong (URC Small Grant), King Saud University (A. Aldalbahi), Australian Research Council (ARC), and ARC Future Fellowship (M. in het Panhuis). We thank M. Collins, R. Clark and P. Jackson (all CP Kelco) for provision of materials and T. Romeo (University of Wollongong) for assistance with SEM measurements, respectively.

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