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Abstract
In this work, kappa-carrageenan (KC) is used to prepare composite dispersions consisting of single-walled (SWNTs) and multi-walled (MWNTs) carbon nanotubes. Free-standing composite films were prepared by evaporative casting and vacuum filtration of these dispersions.

Keywords
carbon, nanotube, biopolymer, composite, characterisation, materials, preparation, conducting

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PREPARATION AND CHARACTERISATION OF CONDUCTING BIOPOLYMER-CARBON NANOTUBE COMPOSITE MATERIALS

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Introduction

Carbon nanotubes (CNTs) have unique electronic, mechanical, optical and thermal properties which make them interesting as a material for nanotechnology applications [1]. Many different processing methods for fabrication of conducting CNT materials have been used including filtration, fiber spinning, inkjet printing and drop casting [1,2]. Carrageenan is a generic name for the biopolymer family of water soluble, linear sulphonated galactans extracted from red seaweed which are known for their gel forming and thickening properties [3].
In this work, kappa-carrageenan (KC) is used to prepare composite dispersions consisting of single-walled (SWNTs) and multi-walled (MWNTs) carbon nanotubes. Free-standing composite films were prepared by evaporative casting and vacuum filtration of these dispersions.

Experimental

Preparation of dispersions
Solutions of KC (CP Kelco, Genuvisco CI-102, 0.5 % w/v) were prepared by adding 75 mg of IC to 15 ml of Milli-Q water (18 MΩ cm) under stirring for 3 hours at ~70 °C. Homogenous KC-CNT dispersions (Fig. 1 A) of MWNT (Nanocyl S.A., lot# 090901) and SWNT (Unidym Inc, lot# P0348) were prepared using a Branson 450 (400 W, Ultrasonics Corp.) digital sonicator horn with a probe diameter of 10 mm, in pulse mode (0.5 s on/off) and amplitude of 120 W. The sample vial was placed inside a water bath to control the solution temperature.

Preparation of films by evaporative casting method
Free-standing films were prepared by evaporative casting of composite dispersions (15 ml) into the base of square PVC 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 1 B).

Preparation of films by vacuum filtration method
The composite dispersions were drawn through a PTFE membranes (5 μm pore size, Millipore) and filtration units by using a Vacuubrand CVC2 vacuum pump. Once all of the dispersion had filtered, the films were washed and placed between absorbent paper sheets to dry for 24 hours at room temperature. The film was then peeled off from the filtration membrane (Fig.1 B).

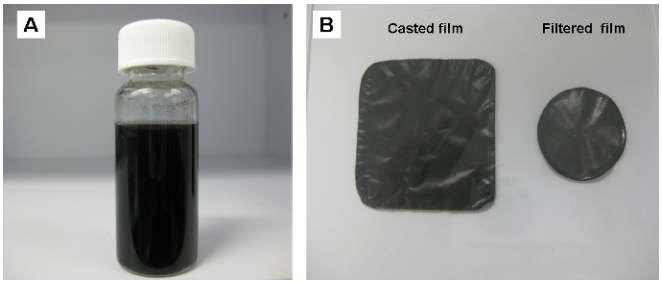

Fig. 1 Photographs of: (A) a composite dispersion and (B) composite casted and filtered films.

Characterization techniques
The UV-vis-NIR spectra of KC-CNTs composite dispersions were obtained with a Cary 500 UV-vis–NIR spectrophotometer using a quartz cuvette (path length = 5 mm). Viscosity as a function of shear rate was measured using a Physica MCR 301 Rheometer (Anton Paar) at 23°C. For electrical resistance measurements, films were contacted with copper electrodes. Current (*I*) – voltage (*V*) characteristics were determined under controlled ambient conditions in air (21 °C, 45 % relative humidity) using a waveform generator (Agilent 33220A) interfaced with a digital multimeter (Agilent 34410A). Thickness was determined using a Mitutoyo IP65 digital micrometer. Scanning electron microscopy (SEM) was carried out using a JEOL JSM-7500FA.

Results and Discussion

The optimum time of sonication required to effectively disperse MWNTs and SWNTs in KC solution was determined. Absorbance at 660 nm was monitored. Our result shows that the MWNTs absorbance becomes independent of sonication time at 20 minutes. The SWNTs absorbance shows an increase in intensity of 1.2 au over first 30 minutes of sonication, followed by an increase of 0.02 au between 35-50 minutes. The optimum sonication time for MWNTs and SWNTs were determined as 20 and 35 minutes, respectively.
The apparent viscosity of KC solutions decreases during sonication, while addition of CNT increases viscosity significantly (Fig. 2). For example, at a shear rate of 100 s^{-1}, the viscosity of the as-prepared KC solution (0.5% w/v) is 39 mPa·s, compared to 2.5 mPa·s after 35 min of sonication.

Addition of (0.1% w/v) MWNTs and SWNTs resulted in 7.8 and 9.9 fold increases in viscosity (at shear rate $100s^{-1}$), respectively, compared to the corresponding values for the sonicated KC solution. This can be seen in Fig.2, below. All solutions and dispersions display shear thinning behaviour, i.e. viscosity decreases with increasing shear rate (results not shown).

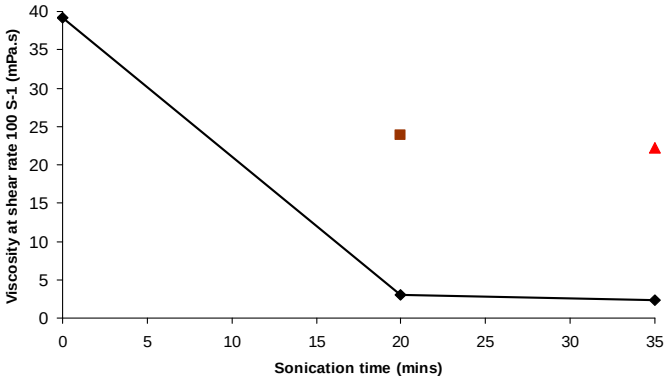

Fig. 2 Viscosity as a function of sonication time of KC solutions (diamonds), KC-MWNT (square) and KC- SWNT (triangle).

Free-standing composite films were prepared by evaporative casting and vacuum filtration of IC-CNT dispersions. The resistance values increased with channel length (Fig. 2). The total resistance (R_T) was found to scale linearly according to:

$$R_T = (l / \sigma A) + R_C , \qquad (1)$$

where l, A, σ and R_C are the sample's length, cross-sectional area, electrical conductivity and contact resistance, respectively. The slope of the straight line fit to equation 1 can then be used to calculate the bulk conductivities (Table 1). It was found that the conductivity of MWNTs composite films, prepared by an evaporative casting process, were similar compared to those of the SWNT composite films (7-9 S/cm).In contrast, the conductivity values of SWNTs composites films (25.4 ± 2.8 S/cm), prepared by vacuum filtration process were higher compared to those of the MWNTs composite films (16.4 ± 1.6 S/cm). This can be attributed to the KC acting as a barrier to electrical transport and being able to achieve a more complete coating of CNTs surface in casted composite films compared to that of composite films, prepared by vacuum filtration process, which partially remove KC during the filtration which can be seen in the SEM images (Fig. 3). These reveal that the difference in conductivity is due to the KC coverage of the CNT-CNT junction in the CNT network**.** Addition of glycerin to the composite films reduced their conductivity (Table 1), but increased their flexibility.

Table 1 Effect of preparation method and addition of glycerin (G) on the conductivity (σ) of composite casted and filtered films.

Film	Preparation method	σ (S/cm)	σ (S/cm)after adding 50 % w/v G
KC-0.1 MWNT	evaporative casting	8.6 ± 1.6	5.0 ± 0.9
KC-0.1 SWNT	evaporative casting	7.4 ± 0.9	2.9 ± 0.5
KC-0.1 MWNT	vacuum filtration	16.4 ±1.6	14.5 ± 1.7
KC-0.1 SWNT	vacuum filtration	25.4 ± 1.6	17.9 ± 1.9

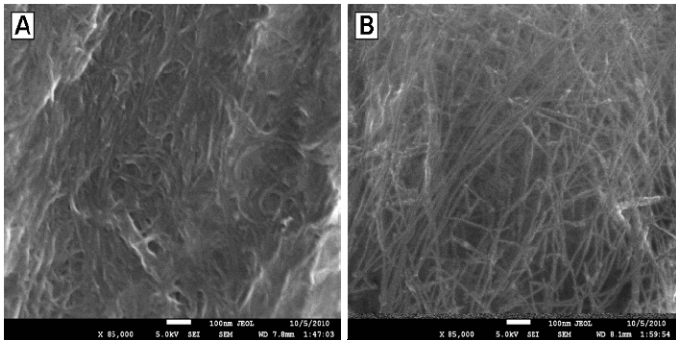

Fig. 3 SEM images of films prepared by (A) evaporative casting and (B) vacuum filtration methods.

Conclusion

MWNTs and SWNTs were successively dispersed using KC. Our results indicated that MWNTs require less sonication time compared to SWNTs, i.e. 20 minutes versus 35 minutes. Rheology results showed that increasing the sonication time reduced the apparent viscosity of KC solutions, while addition of CNT increased viscosity significantly. The conductivity of MWNT composite films prepared by an evaporative casting process were similar compared to those of the SWNT composite films (7-9 S/cm). In contrast, the conductivity values of SWNTs composite films (25.4 S/cm) prepared by a vacuum filtration process were higher compared to those of the MWNTs composite films (16.4 S/cm). Addition of glycerin to the composite films reduced their conductivity, but increased their flexibility. This work contributes to the development of conducting biopolymer composite materials.

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