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Solution spinning of cellulose carbon nanotube composites using room temperature ionic liquids

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ABSTRACT

Multiwall carbon nanotube (MWCNT)/cellulose composite fibers were processed from solutions in ethyl methylimidazolium acetate (EMIAc). Rheological percolation in MWCNT/Cellulose/EMIAc solution was observed above 0.01 mass fraction of MWCNT, while electrical percolation in oriented fibers was observed above 0.05 mass fraction of MWCNTs with respect to the weight of the cellulose. Cellulose orientation and crystal size were significantly higher in the composite than in the control cellulose fiber. In addition, in the composite fiber, carbon nanotube orientation was higher than cellulose orientation. At 0.05 mass fraction MWCNT, fiber tensile strength increased by about 25%, strain to failure increased by 100%, and modulus essentially remained unchanged. The composite fibers showed lower thermal shrinkage than the control cellulose fiber. The axial electrical conductivity at 0.1 mass fraction MWCNTs in these oriented fibers was more than 3000 S/m.

1. Introduction

Cellulose is amongst the most widely used natural fibers [1–3]. Recently, ionic liquids, have emerged as a new class of solvents that can dissolve and process biopolymers such as silk [4–8], wool [9], chitin and chitosan [10,11], lignocellulose and wood [12–15], and cellulose [16–28] with promising properties. Ionic liquids have very low vapor pressure [29], low flammability and low [2]toxicity and hence are considered to be "green solvents" compared to the traditional solvents used for processing cellulose. ^{13}C Nuclear Magnetic Resonance studies show that anion in imidazolium based ionic liquids form H-bond with the hydroxyl proton in cellulose and promote cellulose dissolution [19]. Cellulose/MWCNT paper processed using butyl methyl imidazolium chloride (BMICl) has been evaluated for supercapacitor application [30].

The most common method of making cellulose fibers is Viscose process which involves derivatizing of cellulose with carbon disulphide followed by dissolution in sodium hydroxide. This process involves use of aggressive chemicals such as carbon disulphide, sulfuric acid and sodium hydroxide. Fiber spinning of cellulose using ionic liquids offers advantage of a simple, one step dissolution process without use of aggressive solvents as compared to the traditional Viscous process. Recently, ethyl methyl imidazolium acetate [31] and 1-allyl-3-methylimidazolium chloride (AMIMCl) [25] have been used to produce regenerated cellulose fibers and cellulose nanocomposites. Hermanutz et al. [31] concluded that using ionic liquids as solvents to cellulose was easier and safer than dissolution of cellulose using *N*-methylmorpholine oxide (NMMO) as well as Viscous process. Moreover, they also concluded that fiber spinning of cellulose using ionic liquids allows design of both fibrillating and non-fibrillating fibers.

The goal of current work was to use room temperature ionic liquid to fiber spin cellulose based nanocomposites. Here we report

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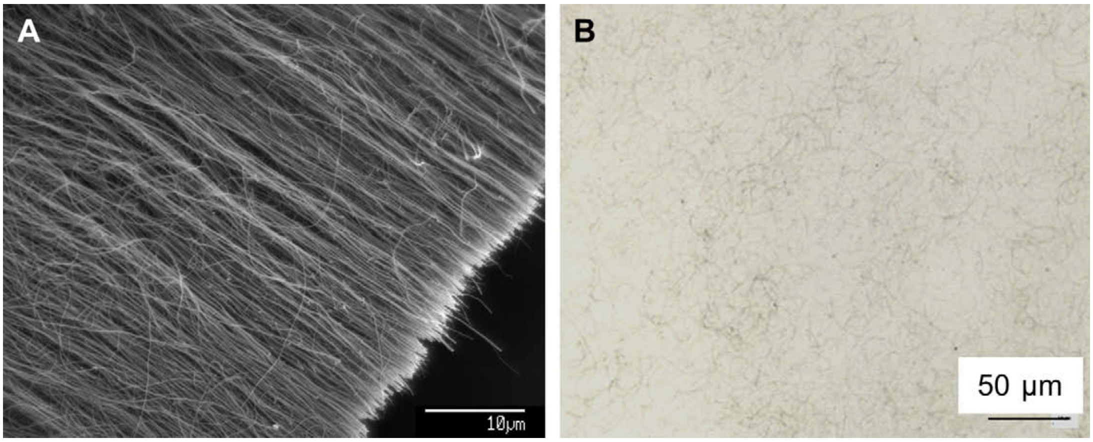

Fig. 1. A) Highly aligned MWCNTs grown by CVD growth process [31]. B) MWCNT dispersed in cellulose/EMIAc solution using high shear mixing does not show the presence of macroscopic aggregates.

the rheology and fiber spinning of cellulose, MWCNTs and Ethyl methyl imidazolium acetate solutions, and a detailed study of structure and properties of the resulting nanocomposites fibers. Cellulose/MWCNT fibers were electrically conductive with better thermal as well as electrical properties. Such fibers may find use in multifunctional materials such as electrically conducting textile fibers for electronic textiles applications.

2. Materials and methods[2]

Cellulose (degree of polymerization 820) was provided by Buckeye Technologies Inc. Multiwall carbon nanotubes forest (Fig. 1A), with average outer diameter of 80 nm and length well above 100 μm were synthesized by chemical vapor deposition at the University of Cambridge. The nanotube synthesis details as well their characterization is published elsewhere [32]. Ethyl methyl imidazolium acetate was purchased from Sigma–Aldrich Chemicals.

Cellulose-MWCNT solutions are prepared as follows: MWCNT is mixed with EMIAc using mortar and pestle till the mixture appears as homogenous paste. Separately, 1/5th of the total amount of cellulose to be dissolved is added to EMIAc and stirred at 80 °C till dissolution. To this cellulose/EMIAc solution, MWCNT/EMIAc paste is added and stirred for few hours (2–3 h) till the solution appears optically homogenous. The remaining cellulose is slowly added to this solution while stirring the solution at 80 °C until cellulose is completely dissolved and solution is optically homogenous (Fig. 1B). The amount of cellulose and MWCNT and their total mass fraction with respect to the EMIAc are given in Table 1.

Table 1
Amount of cellulose and MWCNT in various solutions prepared for fiber spinning.

MWCNT mass fraction with respect to cellulose	Amount of cellulose (g)	Amount of MWCNT (mg)	Solid content in EMI acetate (mass fraction)
0 (control cellulose)	4	0	0.08
0.01	4	40	0.07
0.03	2.9	90	0.06
0.05	2.4	125	0.055
0.07	2.1	157	0.05
0.1	2.0	225	0.045

The control fiber was spun from 0.08 mass fraction of cellulose solution in EMIAc. However, cellulose/MWCNT solution at 0.08 mass fraction of cellulose concentration exhibited poor spinnability at room temperature. Hence, the composite fibers were spun at lower solid concentration as given in Table 1. Fibers were processed using dry-jet wet spinning with 1 cm air-gap and using ethanol as coagulant. For all samples, a single hole spinneret of 120 μm was used except for the 0.1 mass fraction of MWCNT composite solution. The 0.1 mass fraction of MWCNT solution using 120 μm spinneret resulted in back flow of the solution, hence a 250 μm spinneret was used to spin this solution. All fibers were washed thoroughly using deionized water to remove EMIAc.

Rheological studies on the polymer solutions were conducted using TA instruments AR G2 rheometer. Both steady state (shear sweep) and dynamic (frequency sweep) measurements were carried out using parallel plate set up with nitrogen purge. The steady state shear testing of 0.01, 0.03, 0.05, 0.07, and 0.1 MWCNT mass fraction (mass fraction with respect to cellulose content) solutions (listed in Table 1) was conducted using ARES rheometer

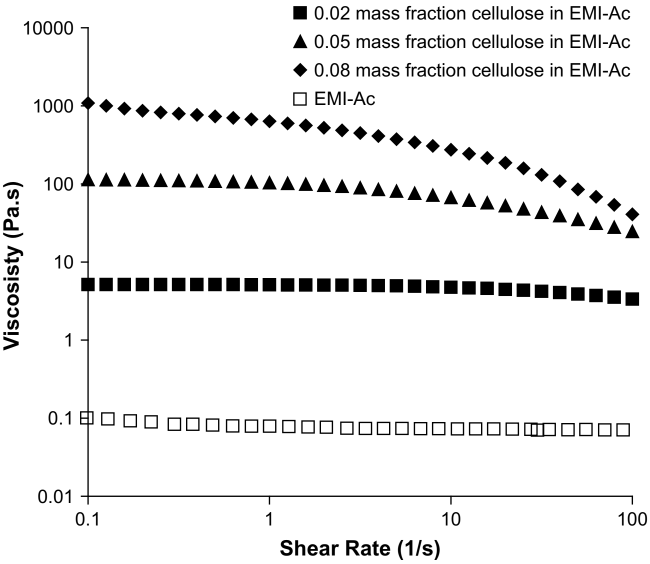

Fig. 2. Steady state shear viscosity of cellulose/EMIAc solution shows four orders of magnitude increase in the low shear viscosity of by addition of 0.08 mass fraction cellulose.

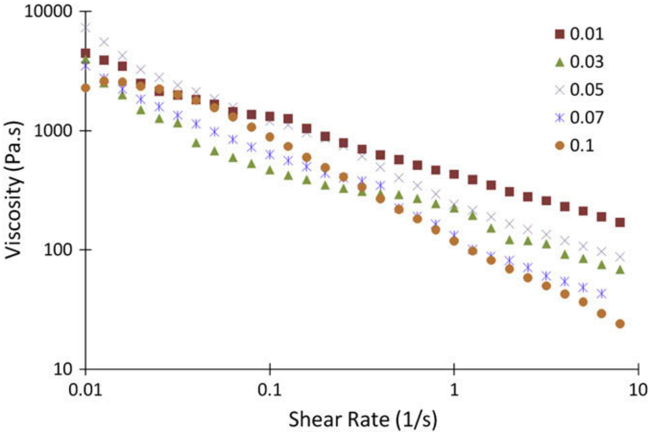

Fig. 3. Steady state shear viscosity of 0.01, 0.03, 0.05, 0.07, and 0.1 MWCNT mass fraction (with respect to cellulose) solutions used for fiber spinning. The solid content of various solutions is listed in Table 1.

(Advanced Rheometric Expansion System, TA Instruments Co.). SEM imaging of fibers was done on gold coated samples using a LEO 1530 Scanning Electron Microscope. Wide Angle X-ray Diffraction (WAXD) patterns were obtained on multifilament bundles on Rigaku Micromax-002 (X-ray wavelength, $\lambda = 0.15418$ nm) using Rigaku R-axis IV++ detection system. The diffraction patterns were analyzed using AreaMax V. 1.00 and MDI Jade 6.1. Fiber tensile tests were conducted on RSA III manufactured by Rheometric Scientific Co. at a gage length of 25 mm and the crosshead speed was 0.1 mm/s. At least 10 specimens of each fiber sample were tested. Thermomechanical analysis was carried out at a heating rate of 5 °C/min in air at an initial stress of 5 MPa, using TMA 2940 manufactured by TA Instruments. TA instruments Q500 thermogravimetric analyzer (TGA) was used for charring the samples at a heating rate of 10 °C/min in nitrogen.

3. Results

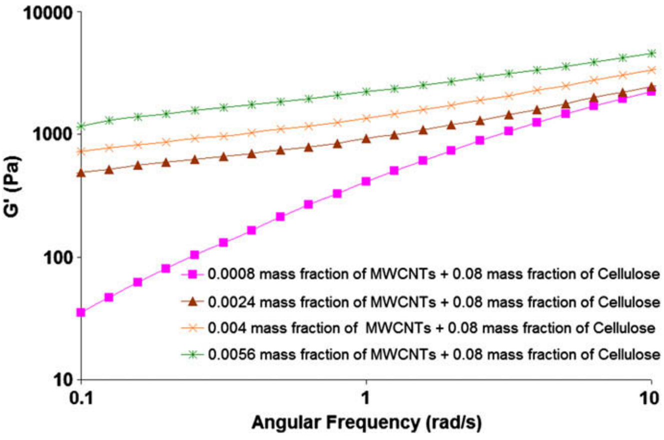

Fig. 4. Oscillatory shear measurement of elastic shear modulus (G') of MWCNTs suspended in cellulose/EMIAc solution shows network formation of MWCNTs above 0.0008 mass fraction of MWCNTs. All the mass fractions are with respect to the total amount of ionic liquid used.

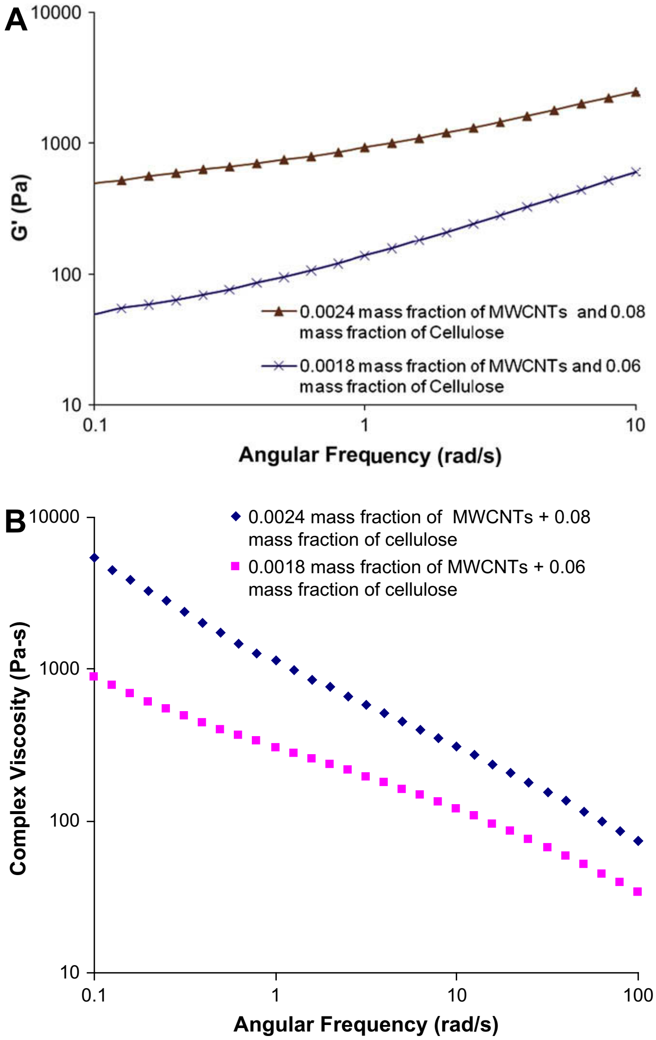

Fig. 5. Effect of reduction in the concentration of cellulose and MWCNT on the (A) shear elastic modulus and (B) on the complex shear viscosity. All the mass fractions are with respect to the total amount of ionic liquid used.

At room temperature, EMIAc exhibits relatively low viscosity (0.1 Pa s) with Newtonian behavior. At relatively low shear rate, the viscosity of 0.08 mass fraction of cellulose/EMIAc solution was three orders of magnitude higher than that of the EMIAc and the polymer solution exhibited the expected shear thinning behavior (Fig. 2). The 0.01, 0.03, 0.05, 0.07, and 0.1 MWCNT mass fraction solutions used for fiber spinning also showed a strong shear thinning behavior (Fig. 3). To study the effect of MWCNT dispersion in cellulose/EMIAc solutions, dynamic shear tests were carried out and results are shown in Fig. 4. In these experiments, cellulose concentration was maintained at 0.08 mass fraction and MWCNT concentration was varied. Elastic component of the shear modulus (G') 0.0008 mass fraction MWCNTs in cellulose/EMIAc solution does not show a plateau, whereas at 0.0024 mass fraction MWCNT in EMIAc solution) a plateau at low oscillation frequency is observed (Fig. 4). This plateau is characteristic of solid like behavior, suggesting that the rheological percolation for these solutions is achieved somewhere between (0.0008 and 0.0024) mass fraction of MWCNT. Network formation of MWCNTs using G' has been previously reported by number of researchers for both nanotubes dispersions in oligomers [33,34] as well as in polymers [35–37]. As mentioned in the fiber spinning section, cellulose fibers were spun at 0.08 mass fraction of cellulose. However, MWCNT containing solutions at 0.08 mass fraction of cellulose exhibited poor

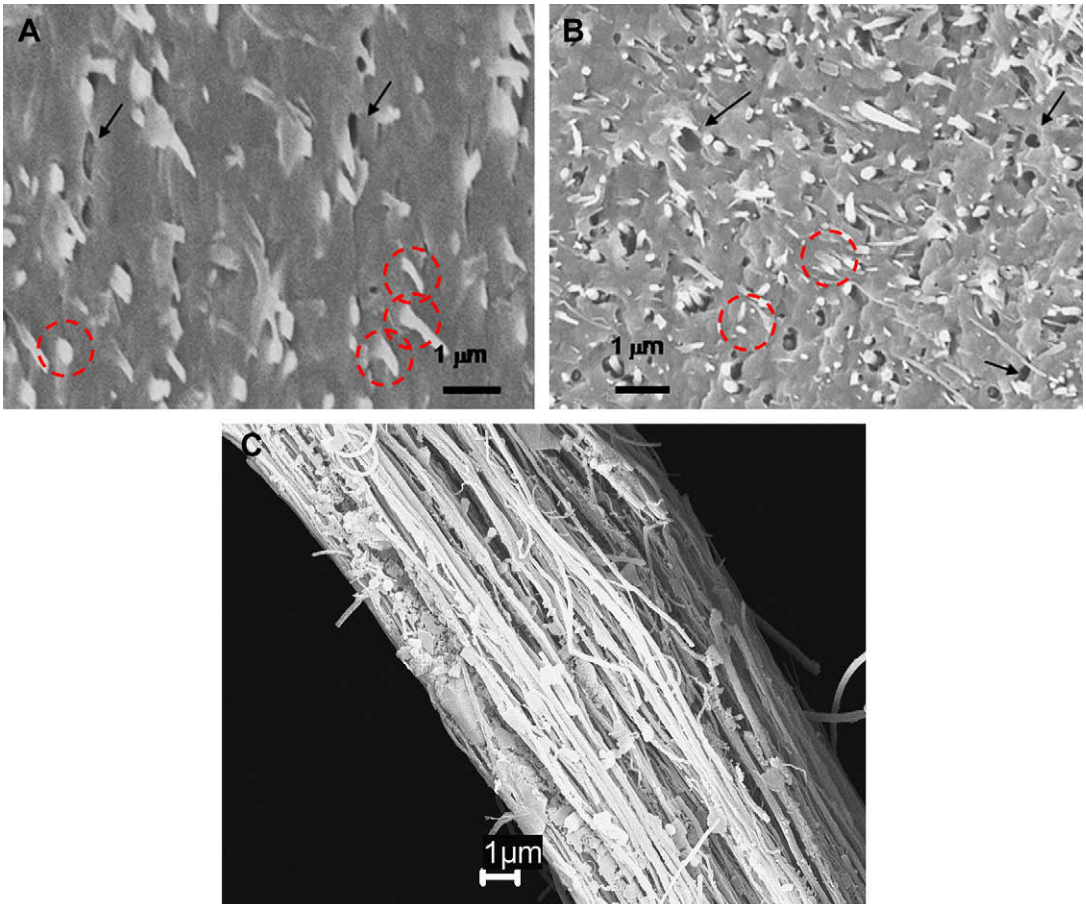

Fig. 6. SEM images of 0.05 mass fraction of cellulose/MWCNTs (A) and 0.1 mass fraction of MWCNTs (B) fibers. The arrows in figures indicate the defect sites due to pull out of MWCNTs during sample preparation. The dashed circles show the good wetting of MWCNTs with cellulose. (C) 0.07 mass fraction of MWCNTs in MWCNT/cellulose after charring up to 700 °C in nitrogen (to burn away the most of the polymer and show embedded MWCNTs). Image shows long length and high alignment of MWCNTs in the fiber direction.

spinnability. Therefore the composite fibers were spun at lower solid concentrations given in Table 1. This suggests that the presence of rigid fillers like MWCNTs with high aspect ratios can affect the spinnability of the cellulose/EMIAc solution. In order to successfully spin the MWCNT/cellulose solution, we had to drop concentration of both cellulose and MWCNTs in EMIAc. The actual solid contents of different amount of MWCNT containing solutions used for fiber spinning are listed in Table 1. Fig. 5 shows the significant reduction in the G' and complex viscosity (respectively) after reducing the concentration of MWCNTs from 0.0024 mass fraction to 0.0018 mass fraction and cellulose concentration from 0.08 mass fraction to 0.06 mass fraction in EMIAc. The reduction in the viscosity and shear modulus may explain why we were able to spin the cellulose/MWNT composites.

The SEM images of the composite fiber cross-sections show fairly uniform MWCNT dispersion in cellulose (Fig. 6). Composite fiber samples were also charred under N_2 atmosphere by heating from room temperature to 700 °C at a heating rate of 10 °C/min. Under these conditions, most of the cellulose is burned leaving a residue of only about 0.02–0.05 mass fraction [38], while most of the carbon nanotubes survive. SEM image (Fig. 6C) of the cellulose/MWCNT (93/7) fiber after charring showed highly aligned carbon nanotubes, suggesting nanotube alignment in the composite fiber.

Fig. 7 shows the WAXD pattern and integrated radial scan of the as received cellulose. Its diffraction pattern corresponds to the cellulose I structure [39–43]. Fig. 8 shows the WAXD patterns and integrated radial scans of regenerated control cellulose and various MWCNT/cellulose composite fibers. The diffraction patterns of these fibers correspond to the known cellulose II structure [40,42–45]. In addition, (002) graphitic peak at $2\theta = 26.2°$ corresponding to MWCNT is also observed in

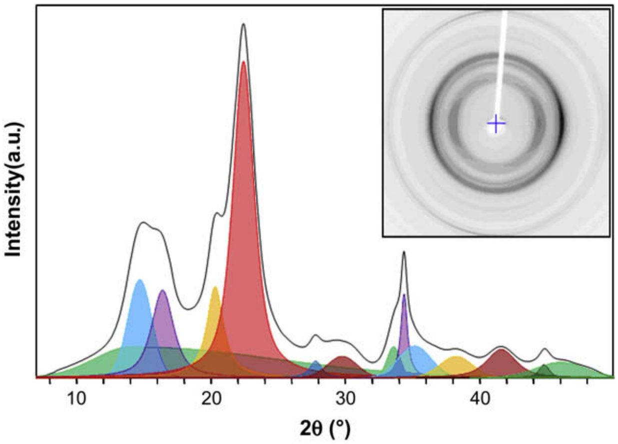

Fig. 7. WAXD pattern and integrated radial scan of the as received cellulose. The peaks have been deconvoluted to the best fit. The most intense peak at 22.5° corresponds to 002 peak of cellulose I structure.

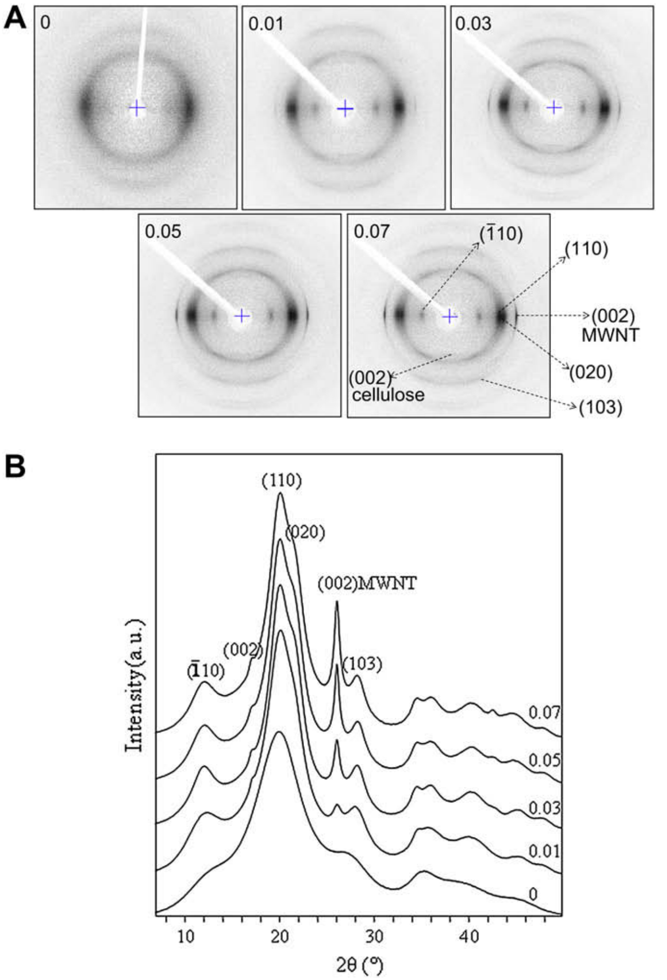

Fig. 8. A. WAXD patterns of (0, 0.01, 0.03, 0.05, 0.07, and 0.1) MWCNT mass fraction (with respect to cellulose) MWCNT/cellulose fibers. B. Integrated radial scans of (0, 0.01, 0.03, 0.05, 0.07, and 0.1) MWCNT mass fraction (with respect to cellulose) MWCNT/cellulose fibers.

the composite fibers as expected. The peak at around 12° corresponds to ($\bar{1}$10) plane, whereas the sharper peaks at 20° and 22° correspond to (110) and (020) planes, respectively (Fig. 8A). MWCNT containing fibers showed slightly higher crystallinity than control cellulose fiber. The cellulose crystal size was calculated using equatorial scans. The equatorial scans of control cellulose fiber and those of composite fibers are shown in Fig. 9. For control cellulose fiber, the crystal sizes were calculated from two peaks at around 12° and 20°. For MWCNT/cellulose composite fibers, the crystal sizes were calculated from three different peaks at around 12°, 20°, and 22°. Among different composite fibers, the MWCNT concentration did not have any significant effect on the overall crystallinity and crystal size.

The cellulose crystal orientation, based on the FWHM of the peak corresponding to (020) plane at $2\theta \sim 22°$, was much higher in the composite fibers than the control cellulose fiber (Table 2 and Fig. 10). Among different composite fibers, the MWCNT concentration did not have any significant effect on the cellulose crystal and MWCNT orientation. A lower FWHM of the MWCNT peak at $2\theta \sim 26°$ (as compared to FWHM of cellulose peak at $2\theta \sim 22°$) suggests that MWCNTs have higher orientation as compared to cellulose crystals.

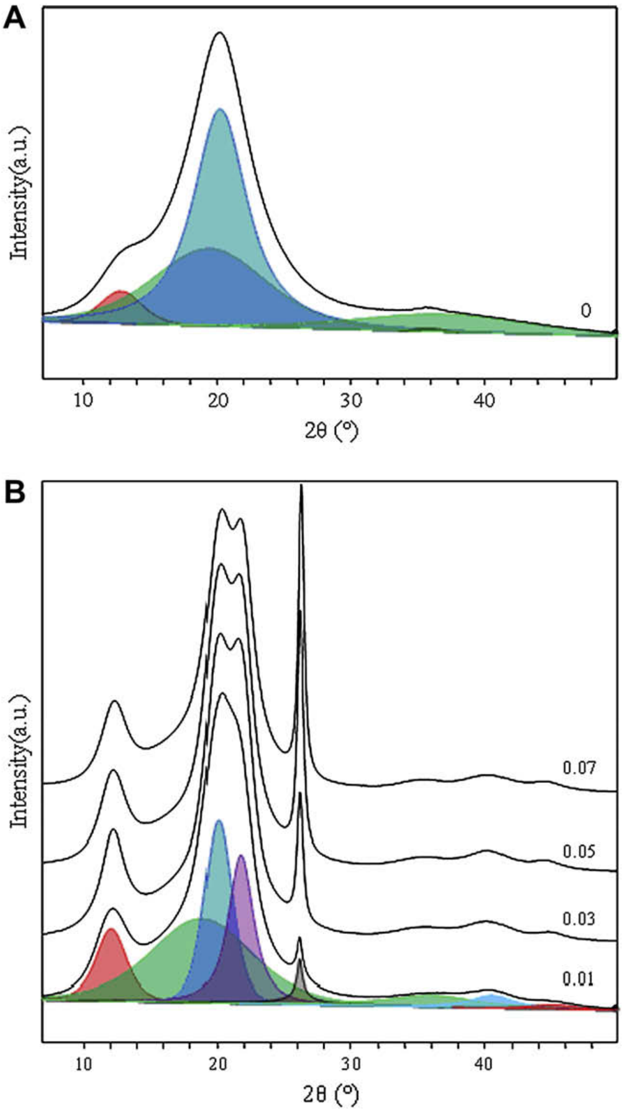

Fig. 9. A. Equatorial scan and the best fitted peaks of control cellulose fiber. B. Equatorial scans of (0.01, 0.03, 0.05, 0.07, and 0.1) MWCNT mass fraction (with respect to cellulose) MWCNT/cellulose composite fibers. Best fitted peaks in 0.01 MWCNT/cellulose fiber are also shown.

Table 2
WAXD analysis cellulose and cellulose/MWCNT fibers.

MWCNT mass fraction with respect to cellulose	Crystallinity[a] (%)	FWHM[b] ($2\theta \sim 22°$) (°)	FWHM[c] ($2\theta \sim 26°$) (°)	$L_{\text{Cellulose}}$[d] ($2\theta \sim 12°$) (Å)	$L_{\text{Cellulose}}$[d] ($2\theta \sim 20°$) (Å)	$L_{\text{Cellulose}}$[d] ($2\theta \sim 22°$) (Å)
0 (control cellulose)	62	43	–	22	17	–
0.01	68	25	14	30	33	36
0.03	68	24	14	37	42	44
0.05	70	27	13	37	38	42
0.07	70	25	12	37	36	41

[a] Crystallinity was calculated using 2θ scan in the range of 7°–50°.

[b] FWHM calculated from the azimuthal scan of cellulose peak at $2\theta \sim 22°$ indicate the orientation of cellulose.

[c] FWHM calculated from the azimuthal scan of MWNT peak at $2\theta \sim 26°$ indicate the orientation of MWCNT.

[d] Crystal size calculated using three different peaks from equatorial scan.

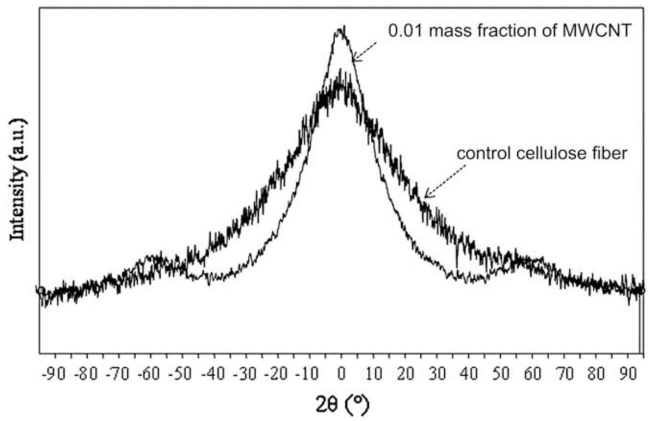

Fig. 10. Azimuthal scans of the $2\theta \sim 22^\circ$ peak for control cellulose and 0.01 MWCNT mass fraction MWCNT/cellulose composite fibers. All other composite fibers (with 0.03–0.1 mass fraction of MWCNT) showed similar scans as 0.01 MWCNT mass fraction fiber.

Tensile properties of various fibers are given in Table 3. Moderate enhancement in tensile strength is observed up to 0.05 mass fraction of MWCNTs. Further increase in nanotubes content (0.07 mass fraction) did not result in further enhancement in tensile strength and it decreased at 0.1 mass fraction of MWCNTs. No appreciable difference in tensile modulus was observed between control cellulose and the composite fibers, while the strain to failure at 0.05 mass fraction MWCNT was 100% higher than that for the control cellulose fiber. Improvements in polymer/carbon nanotube composite strain to failure as compared to the control polymer have often been reported [46–49]. The substantial increase in strain to failure suggests good polymer/carbon nanotube interaction. Carbon nanotube telescopic effect may also be responsible for the increased strain to failure. SEM images (Fig. 6A and B) show some debonding between the MWCNT and cellulose matrix (shown by arrows). However, there were also regions where MWCNT appeared to be very well adhered with the cellulose matrix (shown by dashed circles in Fig. 6A and B).

The axial electrical conductivity at (0.07 and 0.1) mass fraction of MWCNTs was 19 and 3075 S/m. Below 0.07 mass fraction MWCNT, fibers exhibited high electrical resistance and their conductivity could not be measured with our instrument. Based on these measurements, electrical percolation in these oriented fibers occurs between (0.05 and 0.07) mass fraction of MWCNT.

Thermomechanical analysis indicates reduced fiber shrinkage with the addition of carbon nanotubes (Fig. 11). At 140 °C, the shrinkage in the control cellulose fiber was about 0.8%, 0.6% with 0.01 mass fraction of MWCNT, and 0.35% at 0.03 mass fraction of MWCNT. No further reduction in shrinkage occurred at higher MWCNT concentrations. The shrinkage reduction is also consistent with good cellulose/MWCNT interaction.

Table 3
Tensile properties of cellulose and cellulose/MWCNT composite fibers.

MWCNT mass fraction with respect to cellulose	SDR	Diameter (μm)	Tensile strength (MPa)	Tensile modulus (GPa)	Strain to failure (%)
0 (control cellulose)	1.5	23.2 ± 1.8	198 ± 25	13.1 ± 1.1	2.8 ± 0.7
0.01	2	16.6 ± 0.8	244 ± 9	14.4 ± 0.8	3.7 ± 0.5
0.03	1.7	18.1 ± 1.4	239 ± 14	12.4 ± 0.9	5.5 ± 1.2
0.05	1.7	17.4 ± 0.9	253 ± 10	13.9 ± 0.7	5.8 ± 1.0
0.07	2	14.8 ± 1.1	257 ± 9	14.9 ± 1.3	4.2 ± 0.7
0.1	1	29.6 ± 3.2	179 ± 24	13.0 ± 0.2	3.2 ± 1.2

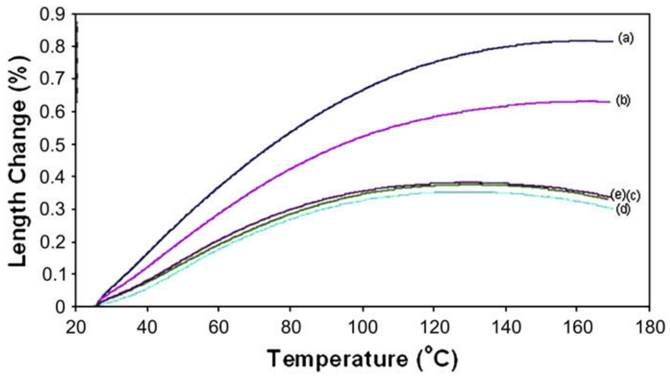

Fig. 11. Change in length (shrinkage) as a function of temperature for a) 0, b) 0.01, b) 0.03, d) 0.05, and e) 0.07 MWCNT mass fraction MWCNT/cellulose fibers.

4. Conclusions

This study reports dry-jet wet spinning of cellulose and cellulose/MWCNTs composites fibers using a room temperature ionic liquid, ethyl methyl imidazolium acetate as a solvent for cellulose. Rheological characterization of cellulose/EMIAc blends showed pseudoplastic shear thinning behavior. SEM images of MWCNTs/cellulose spun fibers showed good dispersion for all the concentration of MWCNTs ranging from 0.01 to 0.1 mass fraction. Wide angle X-ray diffraction of cellulose and cellulose/MWCNTs revealed that regenerated cellulose fibers show cellulose type-II crystal structure. WAXD data also showed high alignment of MWCNTs in cellulose fibers. There is moderate improvement in tensile strength with the addition of carbon nanotubes (up to 0.07 mass fraction), while strain to failure increased up to about 100%, and tensile modulus exhibited no significant change. The increased strain to failure does suggest sufficiently positive interaction between cellulose and MWCNT. High concentration of MWCNTs results in defects in the composite fibers (as seen in SEM images Fig. 6A and B) which could be the reasons for decrease in tensile properties of composite fibers at high MWCNT loading (0.1 mass fraction). Thermomechanical analysis data showed that addition of MWCNTs reduces the thermal shrinkage of cellulose fibers.

Room temperature ionic liquids such as ethyl methyl imidazolium acetate offer environmentally benign rout for fiber spinning of regenerated cellulose fibers as compared to NMMO and Viscose Process. Here we have shown that EMIAc can be effectively used for solution spinning of cellulose/MWCNTs composites fibers with enhanced tensile strength, reduced thermal shrinkage and good electrical conductivity. Such fiber could potentially be used in multifunctional materials such as electronic textiles or thermal barrier fabrics.

Acknowledgments

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