Wet Spun Fibers from Solutions of Cellulose in an Ionic Liquid with Suspended Carbon Nanoparticles

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ABSTRACT: Wet spun fibers from solutions of dissolving pulp in 1-ethyl-3-methylimidazolium acetate (EmimAc) with up to 50 wt % (based on cellulose) suspended carbon black and graphene nanoplatelets particles were studied. Carbon fillers were dispersed by simple shearing in a Couette type mixer and the resulting spin dope was extruded into a hot water coagulation bath from a single hole spinneret. Microstructure, mechanical properties, and electrical conductivity were assessed as a function of filler loading and discussed in comparison to melt spun fibers with similar fillers. The coagulation process and subsequent drying of wet spun fibers was found to produce a significant microporosity, more so the higher the filler loading. The electrical percolation threshold was quite high in the wet spun fibers and relatively modest values of conductivity were obtained with regard to the high filler loadings. Carbon black was found to be superior to graphene nanoplatelets. This was related to flow-induced orientation effects. The mechanical properties of the carbon-filled fibers were found to be similar or lower compared to the pure cellulose fibers because of low interfacial interactions and formation of microporosity. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41417.

INTRODUCTION

Electrically conductive textile fibers may bring new functionalities to fabrics, like transfer of signals and power, heating and EMI shielding.[1] The development of melt spun synthetic fibers incorporating conductive fillers like carbon black (CB), carbon nanotubes (CNT) and graphene nanoplatelets (GNP) has recently attracted research efforts by our group[2–4] and others.[5–12] Less attention has been paid to conductive fibers based on bio-based renewable resources like cellulose. Cellulose cannot be melted and fiber manufacture is therefore accomplished by wet spinning (with or without an air gap) of cellulose solutions.[13] A relatively new class of solvents for cellulose is the ionic liquids.[14] An efficient ionic liquid for dissolving cellulose is 1-ethyl-3-methylimidazolium acetate (EmimAc), dissolving cellulose up to at least 25 wt %.[15] A few studies are available on wet spun cellulose fibers from ionic liquids incorporating CNT. Very recently Zhu et al.[16] studied wet spinning of a solution of dissolving pulp in EmimAc with 10 wt % (based on cellulose) suspended CNT. A short air gap was used and the fibers were coagulated in water. Conductivities in the

range 0.0024–0.0004 S/cm was obtained depending on extrusion speed. Similar experiments with cellulose dissolved in EmimAc with up to 10 wt % CNT based on cellulose were done by Rahatekar et al.[17] Coagulation was done in ethanol and the conductivity of the fibers, with 7 and 10 wt % CNT, was 0.19 and 31 S/cm, respectively, while tenacity was 12 and 17 cN/tex. Zhang and co-workers[18] used 1-allyl-3-methylimidazolium chloride (AmimCl) to dissolve pulp and fibers were spun with an air gap into water. The highest conductivity (0.008 S/cm) and tenacity (22 cN/tex) were obtained for 4 wt % CNT based on cellulose. Both higher and lower CNT concentrations showed lower conductivity and strength. Cai[19] used 1-butyl-3-methylimidazolium chloride (BmimCl) to dissolve pulp and added single wall CNT. Fibers were air gap spun into an aqueous coagulation bath. The highest tenacity (25 cN/tex) was obtained for 3 wt % CNT based on cellulose. Both higher and lower CNT concentrations gave lower strength. Conductivity was not reported.

This study investigates the microstructure, strength, and conductivity of fibers wet spun from solutions of dissolving pulp in
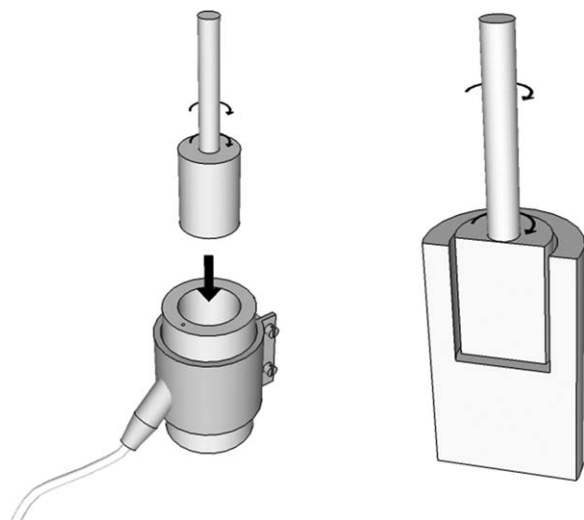
Figure 1. Schematic picture of the Couette type shear mixer.

EmimAc with up to 50 wt % (based on cellulose) suspended CB and GNP fillers.

EXPERIMENTAL

Materials
The cellulose source was a dissolving pulp from Domsjö Fabriker AB, Sweden. Viscosity of the dissolving pulp was in the range 500–900 mL/g, measured according to the standard SCAN-C15:88 and DP_v was between 620 and 1360 (according to the supplier). The ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) Lot# STBC3627V $\geq$ 90% was purchased from Sigma-Aldrich, USA. The CB was Ensaco 250G from Timcal, Switzerland, with a specific gravity of 1900 kg/m^3, bulk density of 185 kg/m^3, and BET surface area of 68 m^2/g. GNP was obtained from XG Sciences, USA, with a specific gravity of 2200 kg/m^3, bulk density of 30–100 kg/m^3, and BET surface area of 120–150 m^2/g. The platelet thickness was 6–8 nm with an average diameter of 5 μm. All data were given by the suppliers and all chemicals were used as delivered.

Methods
The dissolving pulp was cut and milled with a 0.75 mm sieve. Prior to dissolution the pulp was dried in a vacuum oven at 80°C for 12 hours. For dissolution and mixing a simple shear mixer of the Couette type was constructed, see Figure 1. The diameter of the rotating cylinder was 40 mm and the shear gap 6 mm. The mixer was operated at a constant rpm producing a shear rate of 50 s^{-1} in the gap. The milled pulp and EmimAc was placed in the mixer and sheared at 70°C until all of the pulp was dissolved, and a homogenous solution obtained. This took about 2 hours. The cellulose concentration was always 6 wt % at this stage. The CB or GNP filler was then added and the mixture was continuously sheared at 70°C until a smooth homogenous suspension (spin dope) was again obtained, which took about 3–5 hours. Homogeneity was checked visually. The CB loading was varied from 15 to 50 wt % and the GNP was varied from 30 wt % to 50 wt %, based on the total amount of cellulose and filler.

Wet spun fibers were produced with a single hole spinneret with 0.5 mm in diameter, and with a length to diameter ratio of 1. The extrusion velocity was 2.0 m/min and the fibers were spun into a coagulation bath containing 60°C water and then wound up on a winder, see Figure 2 for schematic picture. The apparent wall shear rate in the spinneret was 533 s^{-1}. The piston extruder was operated at 60°C and before entering the spinneret the spin dope passed a metal filter fleece with a nominal filter value of 20 μm. The force on the piston remained essentially constant during spinning indicating that there was no filter cake accumulated. The fibers were drawn between the winder and the spinneret at a draw ratio of 2, by setting the winder velocity to 4.0 m/min. The spun fibers were transferred to individual rolls and submerged in water for 12 hours and then dried at 20°C and 65% RH for 12 hours, still being on the rolls.

Tensile testing of single fibers was conducted on a Vibroskop/Vibrodyn device (Lenzing AG, Austria) in accordance with SS-EN ISO 5079:199, the gauge length being 20 mm and the speed 20 mm/min. The samples were conditioned at 20°C and 65% RH for at least 24 hours before testing. The results given are an average of 10 samples tested.

Resistance measurements were done on 10 fibers put in parallel into a bundle with fiber ends silver painted together. Volume resistivity (often denoted as ρ) is given by

$$\rho = (R \times A)/l \tag{1}$$

where R is the resistance measured over the length l of a fiber with cross sectional area A. Volume conductivity, denoted by σ, is the reciprocal of volume resistivity and therefore given by

$$\sigma = l/(R \times A) \tag{2}$$

and is expressed in Siemens per centimeter [S/cm]. The resistance measurements were done by means of a digital multimeter (Fluke 8846A, USA) on 1 cm long samples, using the two-probe method. Samples showing conductivities lower than $< 10^{-5}$ S/cm could not be assessed properly by the used measurement technique. The area A in Eq. (2) was calculated from the measured linear density of the fiber bundle and the calculated density of the fibers based on the assumption that densities of
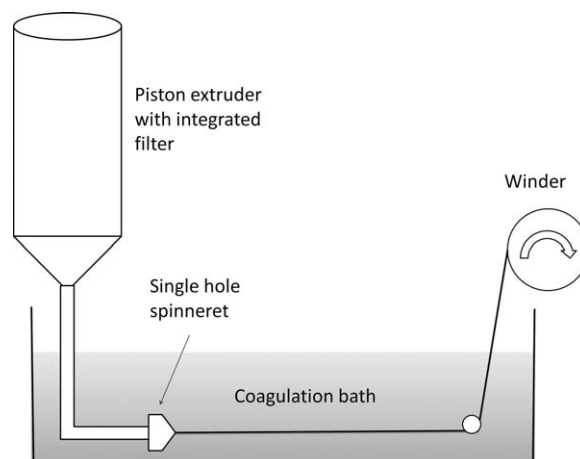

Figure 2. Schematic picture of lab-scale wet spinning equipment.

cellulose, CB and GNP are 1500, 1900, and 2200 kg/m³, respectively.

The morphology of the fibers was evaluated with Scanning Electron Microscopy (SEM). The fibers were embedded in epoxy and cross sections perpendicular to the fiber directions were prepared by ion etching using a Gatan Ilion+ PIPS (Precision Ion Polishing System) Gatan, USA, with cooling to −80°C and an ion beam energy of 5 kV. Imaging was performed by Field Emission SEM (FE-SEM) using a JEOL JSM-7800F instrument (JEOL, USA). The images were taken at 2 kV in the Gentle Beam (GB) mode, i.e. using a low landing voltage on the specimens to minimize charging.

The rheological properties of the spin dopes were characterized by means of a Bohlin Rheometer CS 30 (Malvern Instruments, UK). The measurements were conducted using a cone-and-plate geometry with a diameter of 25 mm and a cone angle of 5.4° at 60°C. The magnitude of the complex viscosity was measured in the angular frequency range 0.0628 to 188.5 rad s⁻¹, and the strain amplitude during oscillatory shear was set to 1%.

RESULTS AND DISCUSSION

Microstructure

SEM micrographs of the cross sectional areas of the fibers reveal very different morphologies for the spun fibers, as can be seen in Figure 3(A–F), where Figure 3(A–C) are SEM micrographs of 50 wt % CB and Figure 3(D–F) 50 wt % GNP, respectively. The CB is in granular form; small primary particles are organized in spherical aggregates. The granular form of the CB can clearly be seen in Figure 3(C) as spherical particles imbedded in the cellulose matrix. Figure 3(A) also reveals a few larger agglomerates of carbon aggregates with diameter up to about 5 μm indicating a not entirely perfect distribution of CB. The GNP are nanoparticles consisting of short stacks of graphene sheets having a platelet shape, with a thickness of 6–8 nm and an average diameter of 5 μm. These platelets can be seen in Figure 3(D–F) as the disk shaped particles, which are most likely made up of several platelets agglomerated together, with the cellulose matrix surrounding them.

In contact with the coagulation bath water is diffusing into the strand, diluting the EmimAc and rendering the dissolved cellulose to precipitate (coagulation). Simultaneously, and during subsequent washing, EmimAc is diffusing out from the extruded strand into the surrounding water driven by the concentration gradient. It was visually observed that the strand to a great extent kept its diameter (about 0.5 mm) in the coagulation bath and subsequent washing, forming a gelled or swollen structure holding a lot of water. Upon drying the strand diameter shrunk substantially to about 0.1 mm forming a solid fiber. It seems likely that such a consolidation process involving the evaporation of water and self-assembly of cellulose aggregates in combination with a rather high amount of filler particles may create micropores. Indeed, the SEM micrographs seem to reveal quite a few micropores surrounding the filler particles, see Figure 3(B,C,E,F).

This is supported by the measured fiber titer (linear density) expressed in units of dtex (g/10,000 m) compared to the theoretical titer calculated from the extrusion rate, cellulose

concentration, winding speed and theoretical fiber density assuming zero porosity. The densities used for calculation were 1900, 2200, and 1500 kg/m³ for CB, GNP, and cellulose, respectively. Measured titers are pretty much constant and independent of the filler loading indicating an increased porosity with increasing filler loading, see Figure 4.

The measured fiber diameters of the samples filled with 50 wt % CB and 50 wt % GNP were 131 ± 5 and 110 ± 8 μm, respectively. The corresponding calculated fiber diameters assuming zero porosity were 96 and 93 μm, again indicating a substantial porosity.

In Figure 3 it can also be seen that the fiber cross section was circular and smooth for the fibers containing CB, while the GNP filler produced fibers with a very irregular shape. This can be explained by the big difference in size of the CB aggregates, being submicron, compared to rigid GNP stacks with lateral dimensions in range of several microns for which steric interactions overrule the surface tension promoting a circular cross section. A similar irregular cross sectional shape was seen in melt spun bi-component fibers where the core was a polypropylene/GNP composite and the sheath polyamide.[2]

Spin Dope Rheology

Figure 5 shows the magnitude of the complex viscosity as a function of angular frequency for all investigated spin dopes.

The shape of the curves are consistent with that reported by others[20–22] for similar systems, showing a pronounced shear thinning behavior typical for entangled polymer solutions and polymer melts. As expected, the viscosity increases as the carbon filler content is increased. However, there is a difference between the two fillers especially at lower frequencies. This difference is more clearly seen in Figure 6, showing the viscosity at the lowest angular frequency as a function of filler concentration.

Up to about 1.3 vol % of filler the viscosity is virtually unaffected. For filler concentrations higher than about 1.5 vol %, CB produces a significantly higher viscosity compared to GNP. A similar behavior was found for CB and GNP filled polycarbonate-based composites.[23] The difference in viscosity between CB and GNP, especially at high filler loadings, can tentatively be explained by slip at the interface between GNP and polymer matrix.[2,24] At about 3 vol % CB there is a sharp upturn in viscosity at lower frequencies, clearly seen also in Figure 6, indicating the formation of a percolated network of carbon particles (rheological percolation). For the process of melt spinning the formation of such a network is detrimental for spinnability, as discussed by e.g. Strååt and White, because of the associated appearance of a yield stress for viscous flow.[4,25] For polymer melts filled with high structure CB or carbon particles with high aspect ratio (e.g. CNT or GNP) the rheological percolation threshold is low and often found at filler concentrations lower (often much lower) than 5 vol %.[4] In the present case the rheological percolation threshold appears to be at about 3 vol % for CB in the spin dope. For GNP no signs of rheological percolation were seen at the studied particle concentrations.

Electrical Conductivity

As already mentioned, the spinnability of a polymer melt containing filler particles is negatively affected at filler
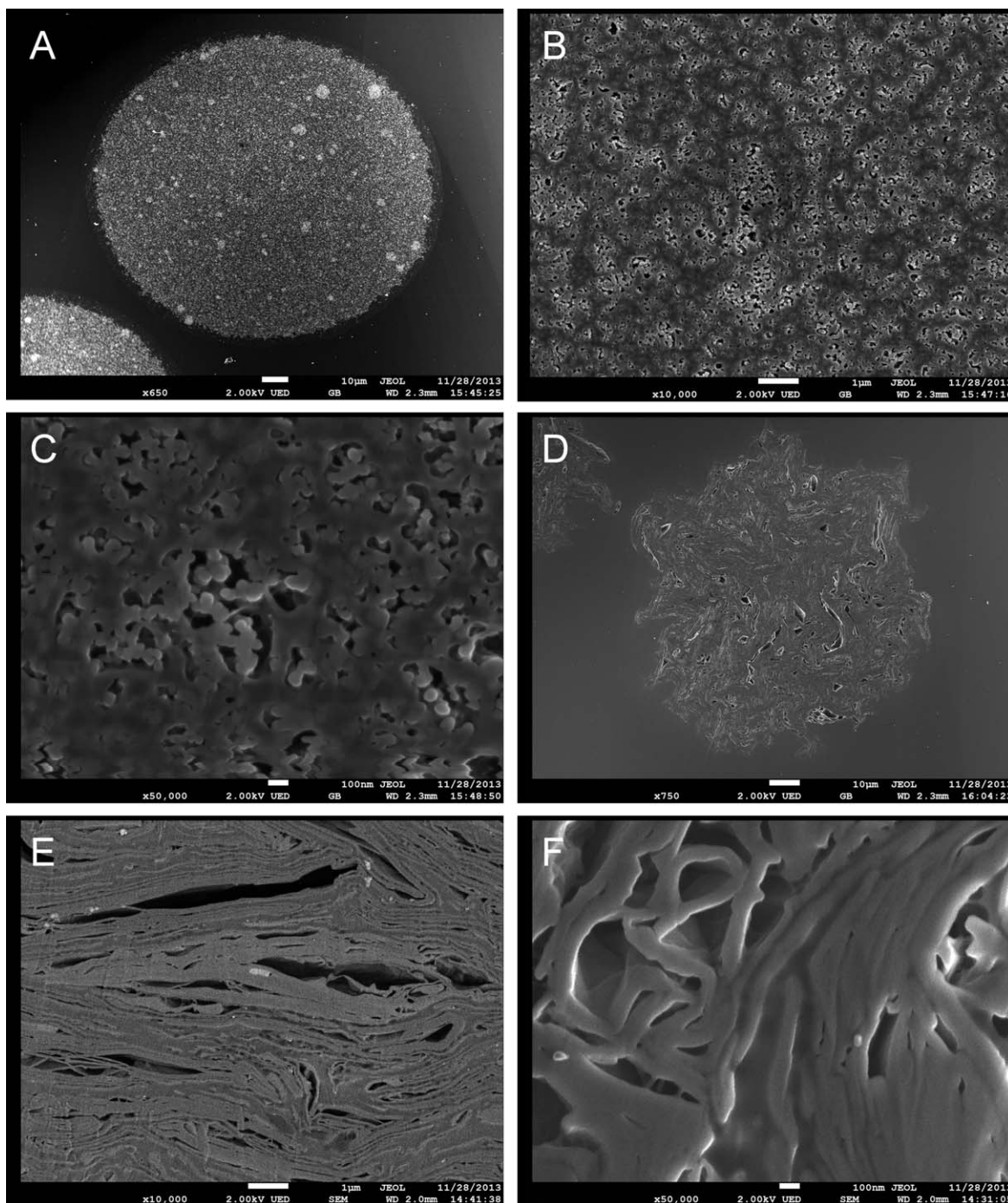
Figure 3. SEM micrographs of wet spun fibers. CB 50 wt % at (A) 650×, (B) 10,000×, and (C) 50,000x magnification, respectively. GNP 50 wt % at (D) 750×, (E) 10,000×, and (F) 50,000× magnification, respectively. E was taken by back scatter detector.

concentrations approaching the rheological percolation threshold. At higher filler concentrations conventional melt spinning is virtually impossible. In solution spinning, on the other hand, the final filler concentration in the solidified fiber may be an order of magnitude higher than in the spin dope processed. Thus, the processing of a relatively low concentration of carbon particles in solution spinning may result in very high particle concentrations in the finished fiber upon removal of the solvent. This may be a great advantage of the solution spinning process compared to the melt spinning process, provided that the high particle concentration leads to the desired functionality, here high electrical conductivity.

In the present case, using spin dopes of up to 3.4 vol % carbon filler, did not affect the spinning process negatively. In this way, fiber containing 50 wt % carbon filler could be produced in a stable fashion. However, despite the high content of carbon
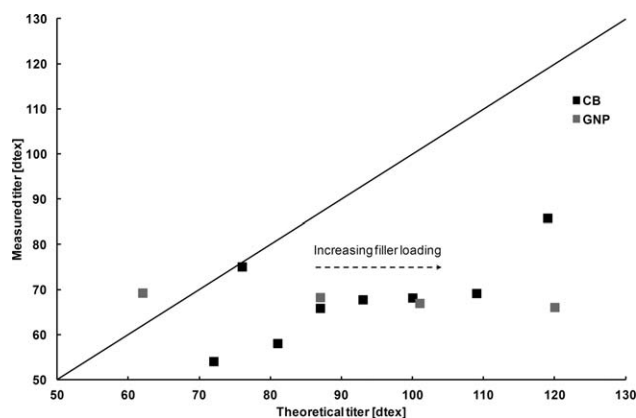
Figure 4. Measured titer vs. theoretical titer assuming zero porosity. The straight line is the identity line while the dashed arrow indicates increasing filler loading.

Figure 6. Complex viscosity at low frequency vs. vol % filler in spin dope.

fillers in the final fiber the conductivity was found to be modest in case of CB and totally lacking in case of GNP. For CB only the very highest concentrations showed measurable conductivities; see Figure 7.

When the very same CB is melt compounded into a high-density polyethylene (HDPE) a conductivity of about 2.5 S/cm at 40 wt % CB (26 vol %) was found.[26] At 40 wt % CB (36 vol %) in the cellulose fiber the conductivity is about 0.004 S/cm. We estimate the electrical percolation threshold for CB in the produced cellulose fibers to be at a volume fraction of about 0.34 where a network of conductive particles starts to build within the composite. The same CB in HDPE gave an electrical percolation threshold an order of magnitude lower (0.04).[26] This indicates that aggregates of primary carbon particles and larger agglomerates remain isolated and are largely separated by cellulose even if the CB content in the fiber approaches 50 wt %. This view is supported by the micrograph in Figure 3(C) showing isolated islands of CB aggregates in the cellulose matrix. The reason for the high percolation threshold may be related to the nature of the coagulation and drying process during fiber formation. The influx of water and outflow of EmimAc happen simultaneously leaving the strand diameter relatively constant as already mentioned. Cellulose probably precipitates
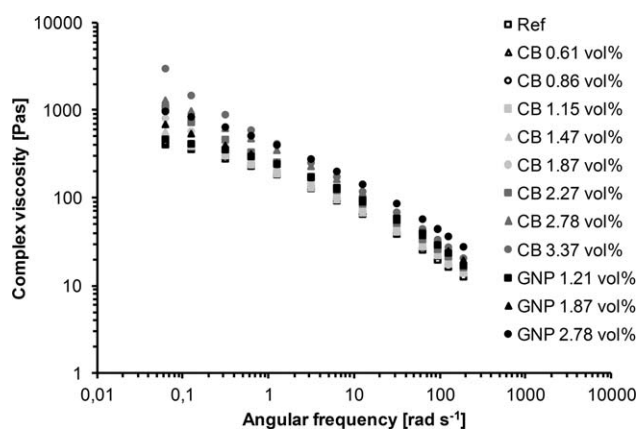
on the surface of the carbon aggregates surrounded by water. During drying the structure is consolidated by shrinking, leaving the carbon aggregates separated by a thin layer of cellulose. This will not lead to percolation of carbon particles during the consolidation process. Instead, the percolated network structure of conductive particles needs to be formed already in the diluted state upfront precipitation and drying, to be efficient. The rheological properties seem to support this view. The fiber with the highest conductivity (50 wt % CB) resulted from a spin dope showing clear signs of rheological percolation in the spin dope, see Figure 6. A contributing factor to the low conductivity may be that the "consolidation" of the swollen gel like strand structure into a solid fiber during drying, took place in the radial direction at constant fiber length. This will maintain the distance between conductive particles in the fiber direction.

As already mentioned, the fibers filled with 50 wt % GNP did not show any measurable conductivity at all, despite the high inherent conductivity of graphene. As can be seen in Figure 3(E,F) the GNP platelets appear to be oriented along and parallel to the fiber direction and being separated by cellulose. The high conductivity of graphene is limited to the in plane direction and the conductivity in the perpendicular direction across the graphene sheets is low. In addition, being isolated by cellulose, electrical contact between stacks of nanoplatelets will thus be negligible. It should also be pointed out that the electrical percolation threshold of oriented high aspect particles will be
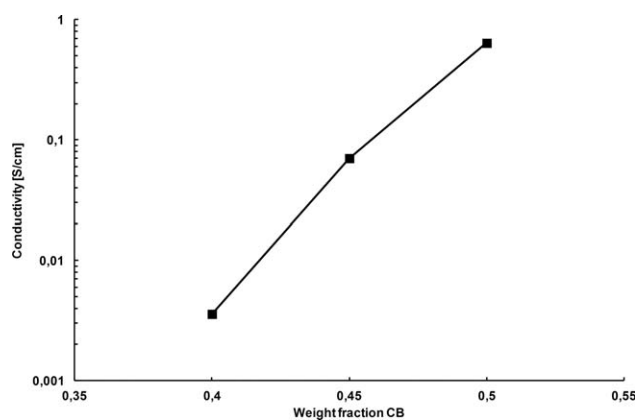

Figure 5. Viscosity as a function of angular frequency.

Figure 7. Conductivity of wet spun cellulose fibers with CB.

Figure 8. Tenacity of wet spun cellulose fibers with different amount of filler (CB or GNP). The standard deviation was 11%.
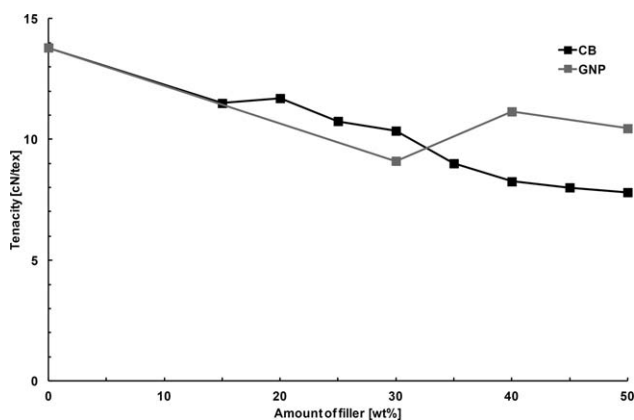

Figure 9. Elongation of wet spun cellulose fibers with different amount of filler (CB or GNP). The standard deviation was 32%.

higher than for the corresponding particles randomly oriented. In a recent work by Zhu and co-workers,[16] fibers and films coagulated from a solution of dissolving pulp in EmimAc with 10 wt % (based on cellulose) suspended multi-walled CNT (MWCNT) were studied. A film with random MWCNT orientation showed a conductivity of 0.18 S/cm while the extruded fibers showed conductivities in the range 0.0024–0.0004 S/cm, depending on extrusion speed.[16] The flow-induced orientation of the MWCNT in the fibers thus significantly reduces conductivity. The same will apply for GNP being susceptible to flow induced orientation as a result of their high aspect ratio. CB has a low aspect ratio and is much less sensitive to flow induced orientation. This was demonstrated by Stråååt et al.[3] for melt spun fibers comparing CB and MWCNT.[3] CB may thus be preferable over both GNP and MWCNT in both solution spun and melt spun fibers where flow induced orientation always will play an important role.

Even though the conductivity of the produced fibers was disappointingly low with regard to the high content of filler it should be remarked that a fiber with a conductivity of 0.6 S/cm, as in the case of 50 wt % CB in cellulose, would hardly be possible to produce in a conventional melt spinning process.[3] In this sense the results presented are of technological significance. We further believe that higher conductivities can be achieved by optimizing the type of CB, its degree of dispersion and the spinning conditions.

Mechanical Properties

When measuring textile strength, the tenacity of the fiber is the most common way of expressing the fiber strength. Tenacity is defined as the breaking force (or the maximum force) of a fiber divided by its linear density which is expressed in units of tex (g/1,000 meter). The result from the mechanical testing of the fibers is reproduced graphically in Figures 8–10.

Figure 8 shows that for fibers containing CB the tenacity declines from about 14 cN/tex for the reference sample (0 wt % filler) to approximately 8 cN/tex for the fibers with high loading of filler. For fibers containing GNP the tenacity declines to about 10–11 cN/tex. The weakening effect is probably because of low adhesion between cellulose and filler particles in
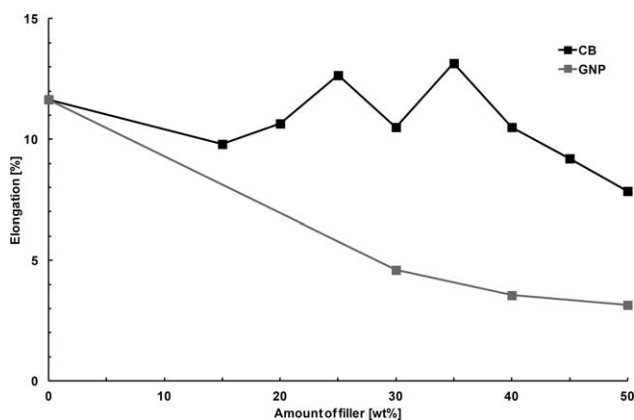
combination with the microporosity developed with increasing amount of filler. The precipitation of cellulose during exchange of EmimAc and water resulted, as already pointed out, in a swollen fiber structure holding a lot of water. We have not studied the interaction between cellulose and filler in detail but it seems reasonable to assume, that any interactions formed during consolidation of the fiber structure upon drying must be low. Hydrogen bonds may develop between cellulose aggregates upon drying. No corresponding interactions will develop between cellulose and carbon particles.

The tenacity of the pure cellulose fiber (0 wt % filler) is similar to that reported by Olsson and Westman,[22] who measured 14–16 cN/tex for fibers wet spun in hot water (80°C) from a 10 wt % solution of a dissolving pulp in EmimAc.

The elongation of a fiber is defined as the strain at maximum force during the tensile test. From Figure 9 it can be concluded that for fibers containing CB the elongation is pretty much unaffected by the addition of filler.

For fibers containing GNP the elongation is clearly lower and declines to about 3%. GNP oriented along the fiber has no inherent elongation (stiff compared to the cellulose matrix) and, presumably, act as stress concentrators lowering the elongation significantly.
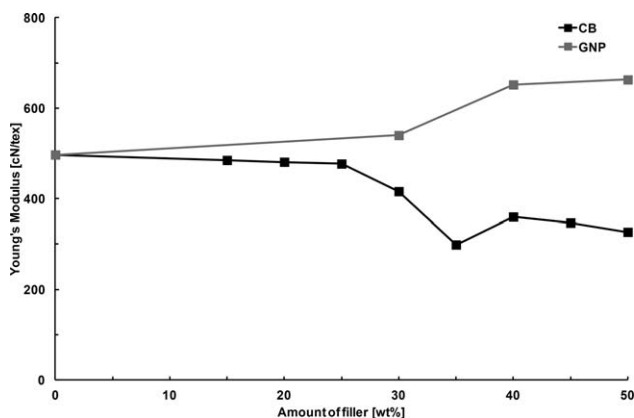

Figure 10. Young's Modulus of wet spun cellulose fibers with different amount of filler (CB or GNP). The standard deviation was 8%.

Finally, Figure 10 presents Young's Modulus of the wet spun cellulose fibers measured as the secant modulus at 1% strain. Young's Modulus is a measure of stiffness in the fiber direction. Fibers with CB are almost unaffected up to 25 wt % filler and then from 30 wt % filler the curve recedes from around 500 cN/tex to about 350 cN/tex. The decreasing stiffness may be a result of increasing porosity and the low aspect ratio of the carbon aggregates. For fibers with GNP the opposite trend can be seen; stiffness increases with added amount of GNP. This can be related to the high aspect ratio of GNP and its high inherent stiffness, and the fact that the GNPs are oriented along the fiber direction.

Finally we note that the strength of the produced fibers is lower compared to standard wet spun cellulose fibers of the cuprammonium and viscose type showing tenacities in the range 15–25 cN/tex.[27,28] To be technically useful fiber strength thus need to be improved.

CONCLUSIONS

Spin dopes based on the ionic liquid EmimAc with dissolved cellulose and suspended carbon fillers can be wet spun into fibers with high carbon loadings (up to 50 wt %). The carbon fillers, carbon black (CB) and graphene nanoplatelets (GNP), are possible to disperse well in an ionic liquid based cellulose solution by simple shear mixing. However, the addition of CB and GNP particles to the spin dope results in formation of micropores in the fiber.

The electrical conductivity of wet spun cellulose/CB and cellulose/GNP fibers is low despite high carbon loadings because of the coagulation and drying process of the fibers, preventing the formation of a conductive network of carbon particles. Still, the highest conductivity obtained (0.6 S/cm) would not be possible to achieve by conventional melt spinning of a CB filled thermoplastic material. CB is preferred over GNP for electrical conductivity. The mechanical properties of the carbon-filled fibers were found to be similar or lower compared to the pure cellulose fibers because of low interfacial interactions and formation of microporosity.

ACKNOWLEDGMENTS

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