

Cite this: *Green Chem.*, 2011, **13**, 1158

www.rsc.org/greenchem

## COMMUNICATION

## Composite fibers spun directly from solutions of raw lignocellulosic biomass dissolved in ionic liquids†

Ning Sun,‡<sup>a</sup> Weiyang Li,‡<sup>a,b</sup> Breena Stoner,§<sup>a</sup> Xinyu Jiang,¶<sup>a</sup> Xingmei Lu||<sup>a</sup> and Robin D. Rogers\*<sup>a</sup>

Received 10th January 2011, Accepted 2nd March 2011

DOI: 10.1039/c1gc15033b

Lignocellulosic biomass composite fibers (southern yellow pine and bagasse) were successfully prepared directly from the ionic liquid, 1-ethyl-3-methylimidazolium acetate ([C<sub>2</sub>mim]OAc) with a dry-jet wet spinning process using short dissolution times (10–30 min) and temperatures above the glass transition temperature of lignin. Fibers could not be spun at all from solutions of pine dissolved using previously reported dissolution methods (110 °C, 16 h), while bagasse fibers spun using the higher temperature/shorter time method were stronger than those obtained using the lower temperature/longer time method.

The viscose process is still the most popular technique for making cellulose fibers using cellulose pulp as starting material, despite the environmental and chemical demands of a process using caustic alkali and carbon disulfide, and releasing toxic gaseous hydrogen sulfide.<sup>1,2</sup> We<sup>3</sup> and others<sup>4,5</sup> successfully demonstrated that cellulose pulps can be dissolved using ionic liquids (ILs) as solvent and spun into fibers with and without functional additives. While an advance in terms of lower chemical demand than the viscose process, both processes rely on a cellulose pulp; typically prepared by the kraft process.<sup>6</sup>

We have since turned our attention to direct dissolution of raw lignocellulosic biomass in another form of ‘pulping’.<sup>7</sup> We were curious whether raw biomass rather than pure cellulose or cellulose pulp could also be used to spin fibers and how the method of dissolution and resulting concentration of lignin and hemicellulose might affect the mechanical properties. Such

a one-pot process might eliminate all pulping or pretreatment steps.

To our knowledge, there have been no reports of making such composite fibers directly from raw biomass solution, although composite films have been made from the dissolution of a mixture of free cellulose, starch, and lignin.<sup>8</sup> Raw biomass, such as bagasse, bamboo or rice straw, have been used as the starting materials to prepare regenerated fibers using, *N*-methylmorpholine-*N*-oxide (NMMO),<sup>9–11</sup> however, a pretreatment step was needed to remove lignin and hemicellulose such that the pulp actually dissolved and had a high cellulose content (> 90%).

The direct dissolution and extrusion of biomass composite fibers without any pulping or pretreatment step might provide a simple and efficient route to many novel biodegradable materials. Here we report our initial attempts to prepare such materials and the importance of the biomass type and dissolution methods in obtaining reasonable results.

Twelve different spinning solutions were prepared (Table 1) under different dissolution conditions utilizing: a) pine, b) oak, c) bagasse, d) NaOH pretreated pine (as described in ref. 12), e) the cellulose rich material (CRM) obtained from the dissolution of pine at 175 °C for 30 min and regenerated in acetone/water as in ref. 7a, f) cellulose pulp (DP = 1056), and g) a mixture of cellulose (DP = 1056), xylan, and indulin AT lignin in proportions representing the composition of pine. Generally, 0.5 g of the biomass source was dissolved in 10 g 1-ethyl-3-methylimidazolium acetate ([C<sub>2</sub>mim]OAc) using either an optimized higher temperature method<sup>12</sup> (175 °C 30 min for wood, Table 1 trial 1, 2, 7, 9–12, 185 °C 10 min for bagasse, Table 1 trial 3), or our previously reported lower temperature method for dissolution of lignocellulosic biomass<sup>7a</sup> (110 °C, 16 h bagasse, Table 1 trial 4) to prepare the spinning dope.

For oak, a lower concentration was also used (trial 1) since the solution at 5 wt% (trial 2) prepared with heating at 175 °C for 30 min, was too viscous resulting in inefficient dissolution. The solutions of the CRM, of the cellulose pulp (DP = 1056), and of the cellulose/xylan/indulin AT mixture were prepared by heating at 90 °C for 2 h (CRM, trial 8) or 30 min (pulp, trial 5; standard mixture, trial 6) because they were relatively easy to dissolve.

Fibers were prepared where possible using dry-jet spinning of each of the 12 spinning dopes described above by extrusion into a water bath and collection onto a spool as described in ref. 3.

<sup>a</sup>Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA.  
E-mail: rdrogers@as.ua.edu

<sup>b</sup>State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China

† Electronic supplementary information (ESI) available: Details on the materials, preparation procedures and characterisation of the fibers. See DOI: 10.1039/c1gc15033b

‡ N. Sun and W. Li made equal contributions to this paper.

§ Current address: Department of Chemistry, University of Central Florida, Orlando, FL 32816, USA.

¶ Current address: School of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China.

|| Current address: Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100080, China.

**Table 1** Sources and dissolution conditions of biomass and composition and mechanical properties of the resulting fibers<sup>a</sup>

Trial	Biomass	[Cellulose] <sup>b</sup> (%Biomass)	[Lignin] <sup>b</sup> (%Biomass)	Dissolution conditions	Thickness/ mm	Ultimate stress (MPa)	Max. Strain (%)	[Cellulose] <sup>c</sup> (%Fiber)	[Lignin] <sup>c</sup> (%Fiber)
1	Oak	49.0 <sup>d</sup>	23.8	175 °C, 30 min	0.10(0)	102(5)	4(0)	—	—
2 <sup>e</sup>	Oak	49.0 <sup>d</sup>	23.8	175 °C, 30 min	0.22(1)	36(17)	2(0)	—	—
3	Bagasse	57.8	22.7	185 °C, 10 min	0.11(0)	125(2)	6(2)	63.6	25.3
4	Bagasse	57.8	22.7	110 °C, 16 h	0.09(1)	86(4)	8(3)	57.3	22.3
5	Pulp DP 1056 <sup>f</sup>	100.0	0	90 °C, 30 min	0.06(1)	220(16)	10(0)	—	—
6	Mixture <sup>g</sup>	44.2	31.8	90 °C, 30 min	0.08(0)	126(1)	1(0)	—	—
7	Pine	44.2	31.8	175 °C, 30 min	0.13(0)	49(6)	2(0)	55.9	32.4
8	CRM from Pine <sup>h,i</sup>	—	16.1	90 °C, 2 h	0.06(1)	142(9)	5(0)	—	—
9	Pretreated Pine <sup>j</sup> 10%/2 h	55.2	35.4	175 °C, 30 min	0.09(1)	142(34)	12(4)	—	—
10	Pretreated Pine <sup>j</sup> 10%/4 h	56.9	30.3	175 °C, 30 min	0.08(1)	222(27)	13(2)	63.2	30.6
11	Pretreated Pine <sup>j</sup> 10%/6 h	59.1	29.4	175 °C, 30 min	0.10(0)	206(3)	5(2)	—	—
12	Pretreated Pine <sup>j</sup> 15%/4 h	60.8	31.9	175 °C, 30 min	0.05(0)	336(15)	14(0)	—	—

<sup>a</sup> Weight percentage of the biomass to the mass of IL is 5% for all the trials except for trial 1 which is 3.3%. <sup>b</sup> Lignin and cellulose content (wt %) of original or treated biomass before dissolution. <sup>c</sup> Lignin and cellulose content of the composite fibers. <sup>d</sup> Data from ref. 13. <sup>e</sup> Incomplete dissolution. <sup>f</sup> Fibers made from pulp (DP = 1056) only. <sup>g</sup> Fibers made from a mixture of standards: pulp (DP = 1056) for cellulose, xylan for hemicellulose, and indulin AT for lignin with the weight ratio the same as pine: 44.2/25.0/31.8. <sup>h</sup> CRM was obtained by dissolving 0.5 g pine in 10 g [C<sub>2</sub>mim]OAc at 175 °C for 30 min and regenerated in acetone/water (1 : 1, v/v) as described in ref. 12. <sup>i</sup> Although cellulose and hemicellulose content were not determined here for the CRM due to minimal sample size, previous results have shown the CRM to have a significant hemicellulose content. <sup>j</sup> Pine was pretreated using aqueous NaOH: trial 9, 10% NaOH 2 h; trial 10, 10% NaOH 4 h; trial 11, 10% NaOH 6 h; trial 12, 15% NaOH 4 h.

After spinning, the fibers were soaked in de-ionised (DI) water overnight and air dried.

While bagasse fibers could be prepared using either higher (trial 3, 185 °C 10 min) or lower (trial 4, 110 °C 16 h) temperature heating methods, *wood fibers could only be made using the higher temperature, shorter time method* (trial 7, 175 °C 30 min). This may indicate that there is less polymer degradation (which would lower the DP) with the higher temperature method, and we do note that the cellulose content is higher in the fibers prepared by the higher temperature/shorter time heating methods (trial 3, 64% vs. trial 4, 57%), while the lignin contents for the two fibers are similar (trial 3, 25% vs. Trial 4, 22%).

The biomass composite fibers were brown in color and the surface roughness varied for the different biomass sources. SEM images for fibers prepared from pretreated pine (trial 12) and raw bagasse (trial 3) are shown in Fig. 1. A wrinkled surface texture was observed for these composite fibers. The fibers prepared from pine after NaOH (aq) pretreatment (trial 12, 15% NaOH 4 h), tended to be smoother, perhaps reflecting the higher cellulose content and lower hemicellulose and lignin content.

Fibers from each prepared batch were prescreened to select test fibers of uniform thickness for tensile strength analysis (described in the ESI†). Table 1 compares the biopolymer compositions of the biomass before dissolution and of the resulting fiber with the mechanical properties of the fibers. The stress/strain curves for the fibers are plotted in Fig. 2.

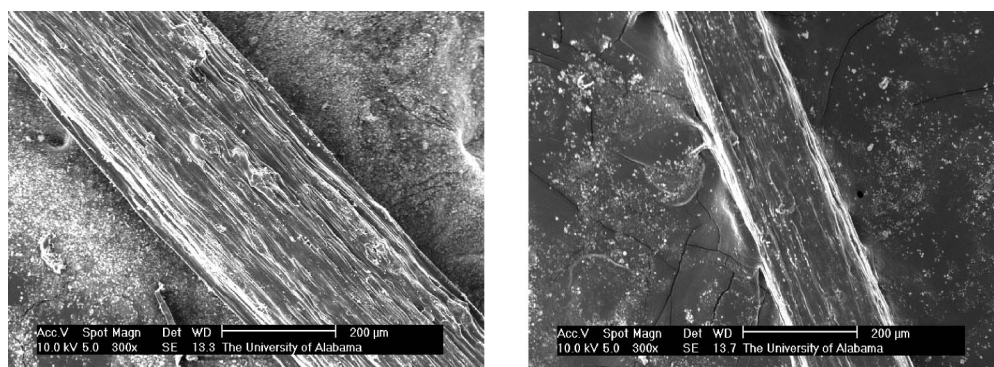
The average thickness of the regenerated fibers varied from one source to another (Table 1), although the same concentration of total biomass was used except for one trial with oak (trial 1). Generally, the fibers prepared from dissolution of untreated biomass (e.g., pine, trial 7, 0.13 mm) were thicker than those prepared from dissolution of pretreated biomass (e.g., pretreated pine, trials 9–12, 0.05–0.10 mm). When the dissolution was

incomplete (oak, trial 2), the fiber was much thicker than that from complete dissolution (0.22 mm vs. 0.10 mm).

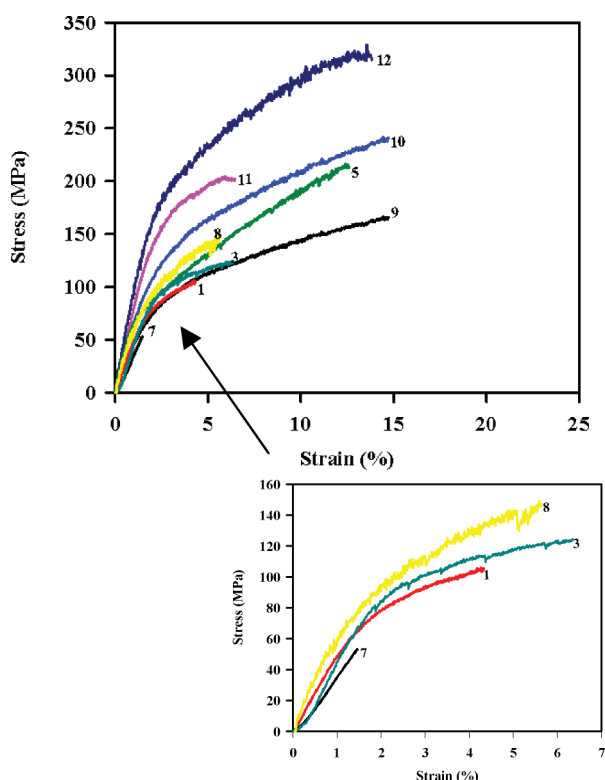
It should be noted that the compositions of the fibers are different from the raw biomass from which they are prepared (trials 3, 4, 7, 10) since the dissolution process followed by fiber coagulation in a water bath removes some water soluble lignin and hemicellulose fractions.<sup>7a,12</sup> The cellulose contents of the resulting fibers are usually higher than that in the starting biomass (trial 3: 64% vs. 58%; trial 7: 56% vs. 44%; trial 10: 63% vs. 57%), while the lignin contents are similar (trial 3: 25% vs. 23%; trial 7: 32% vs. 32%; trial 10: 31% vs. 30%).

The bagasse fibers made with the higher temperature method are stronger with higher stress, compared to the fibers made with the lower temperature method (125 MPa for fibers from trial 3, 185 °C 10 min vs. 86 MPa for fibers from trial 4, 110 °C 16 h). This is consistent with the observation that fibers could not be spun at all using the spinning dope prepared from dissolution of wood at the lower temperature, but fibers could be prepared when the dissolution was carried out at a higher temperature for a shorter period of time.

One factor in the ability to spin fibers, as well as the resulting strength of the fibers is related to the compositional differences which result from the different heating methods (*vide supra*). As shown in Table 1 in trials 3 and 4, fibers prepared from solutions of bagasse dissolved at 185 °C for 10 min have a higher cellulose content compared to those spun from solutions prepared using the lower temperature heating method (64% vs. 57%), although the lignin content of the two fibers are similar (25% vs. 22%). These results are consistent with the previous observation that the higher temperature method facilitates the separation of the major components from biomass, even if pure DI water is used for coagulation instead of the 1 : 1 acetone : water mixture described earlier.<sup>7a,12,14</sup>



**Fig. 1** SEM images at 300× for fibers made from a) bagasse dissolved in  $[C_2mim]OAc$  at 185 °C for 10 min (trial 3), and b) pine pretreated with 15% NaOH for 4 h then dissolved in  $[C_2mim]OAc$  at 175 °C for 30 min (trial 12).



**Fig. 2** Stress strain curves for fibers made from original biomass resources with the higher temperature shorter time dissolution method. The numbers correspond to the trial numbers in Table 1: 1) 3.33% oak dissolved at 175 °C for 30 min, 3) 5% bagasse dissolved at 185 °C for 10 min, 5) 3% pulp DP 1056 dissolved at 90 °C for 30 min, 7) 5% pine dissolved in at 175 °C for 30 min, 8) 5% CRM from pine (Trial 3) dissolved at 90 °C for 2 h, 9) 5% pretreated pine (10% NaOH for 2 h) dissolved at 175 °C for 30 min, 10) 5% pretreated pine (10% NaOH for 4 h) dissolved at 175 °C for 30 min, 11) 5% pretreated pine (10% NaOH for 6 h) dissolved at 175 °C for 30 min, 12) 5% pretreated pine (15% NaOH for 4 h) dissolved at 175 °C for 30 min.

Generally, stronger fibers were obtained by using biomass sources with higher cellulose contents which resulted in fibers correspondingly higher in cellulose. As shown in Fig. 2, the fibers made from bagasse and oak are much stronger than pine and the cellulose contents decrease in the order bagasse-based fibers 58% > oak-based fibers 49% > pine-based fibers 44%.

Fibers were also spun from solutions prepared by redissolving the CRM obtained from pine dissolved at 175 °C 30 min in fresh  $[C_2mim]OAc$ . As expected, these fibers exhibit better mechanical properties compared to those prepared by directly dissolving pine (stress: 142 MPa vs. 49 MPa; strain: 5% vs. 2%). This is most likely due to the removal of free lignin and hemicellulose in the first coagulation step.

In an attempt to learn more about the role of the individual biopolymers in the resulting fiber strength, a spinning solution was prepared by dissolving 0.5 g total mass of a mixture of 44% cellulose pulp (DP = 1056), 24% xylan, and 32% indulin AT (to simulate the approximate composition of the pine samples we studied) in 10 g of the IL (Table 1, trial 6). We have previously shown<sup>15</sup> the ready separation of unbound lignin and hemicellulose from cellulose using such artificial mixtures and indeed the results here suggest significantly more lignin and hemicellulose loss in trial 6. Thus, the resulting fibers from trial 6 should contain more cellulose compared to trial 7 and result in significantly stronger fibers. Indeed, while the composite fibers prepared from this solution exhibited lower stress compared to fibers made from 100% cellulose pulp (126 MPa vs. 220 MPa, trial 5), they are still stronger compared to those made from the original pine (126 MPa vs. 49 MPa, trial 7).

The fibers prepared by dissolution of cellulose pulp (trial 5) have similar mechanical properties to the those prepared using this same pulp dissolved in  $[C_2mim]Cl$  (stress: 220 vs. 217 MPa, strain: 10% vs. 13%), although different extrusion conditions were used.<sup>3</sup>

By far, the greatest effect on the strength of the prepared fibers arises from NaOH pretreatment before dissolution, where the pretreatment results in higher cellulose content of the recovered wood (pretreated pine, 55–61% vs. original pine, 44%). Both stress and strain are dramatically higher and these fibers are even stronger than those prepared using 100% cellulose pulp with DP 1056. For example, fibers made from pine pretreated with 15% NaOH for 4 h (cellulose content = 61%) exhibit an ultimate stress value of 336 MPa, while those made from the pine after pretreatment with 10% NaOH for 4 h (cellulose content = 57%) exhibit ultimate stress of 222 MPa. As discussed above, 15% NaOH treatment for 4 h seems to be most efficient in hemicellulose/lignin removal and results in the highest cellulose content in the pretreated pine. Although the recovered pine after pretreatment with 10% NaOH for 6 h has a slightly higher

cellulose content than that pretreated with 10% NaOH for 4 h (59% vs. 57%), the resulting fibers have decreased strength (stress: 206 MPa vs. 222 MPa; strain: 5% vs. 13%). This may be due to degradation of the cellulose with the longer treatment time.

In conclusion, biomass composite fibers can be prepared directly from solutions of raw biomass dissolved in the IL with stronger fibers resulting from the dissolution at higher temperatures for shorter times. While fibers can be prepared from bagasse using either higher or lower temperature methods, continuous fibers from dissolved wood can only be prepared when using the higher temperature, shorter time method. Stronger fibers can be obtained by using a biomass source with a higher cellulose content or by pretreating the biomass to remove some hemicellulose and lignin prior to dissolution in the IL, although the latter somewhat defeats the purpose of the one-pot dissolution and spinning strategy.

We thank Ms. Tere Pi Johnson of the Sugar Cane Growers Cooperative of Florida for bagasse samples. W. Li thanks the China Scholarships Council (No. 2008615051) for support.

## Notes and references

- 1 A. G. Wilkes, in *Regenerated Cellulose Fibers*, ed. C. Woodings, CRC Press, New York, 2000, pp. 37–61.
- 2 T. Heinze and T. Liebert, *Prog. Polym. Sci.*, 2001, **26**, 1689–1762.
- 3 N. Sun, R. P. Swatloski, M. L. Maxim, M. Rahman, A. G. Harland, A. Haque, S. K. Spear, D. T. Daly and R. D. Rogers, *J. Mater. Chem.*, 2008, **18**, 283–290.
- 4 H. Zhang, Z. Wang, Z. Zhang, J. Wu, J. Zhang and J. He, *Adv. Mater.*, 2007, **19**, 698–704.
- 5 G. Viswanathan, S. Murugesan, V. Pushparaj, O. Nalamasu, P. M. Ajayan and R. J. Linhardt, *Biomacromolecules*, 2006, **7**, 415–418.
- 6 G. Gellerstedt, “Pulping chemistry”, in *Wood and Cellulosic Chemistry*, ed. D. N.-S. Hon and N. Shiraishi, Marcel Dekker, New York, 2001, pp. 859–905.
- 7 (a) N. Sun, M. Rahman, Y. Qin, M. L. Maxim, H. Rodríguez and R. D. Rogers, *Green Chem.*, 2009, **11**, 646–65; (b) I. Kilpeläinen, H. B. Xie, A. King, M. Granstrom, S. Heikkinen and D. S. Argyropoulos, *J. Agric. Food Chem.*, 2007, **55**, 9142–9148; (c) M. Zavrel, D. Bross, M. Funke, J. Buchs and A. C. Spiess, *Bioresour. Technol.*, 2009, **100**, 2580–2587; (d) A. Brandt, J. P. Hallett, D. J. Leak, R. J. Murphy and T. Welton, *Green Chem.*, 2010, **12**, 672–679; (e) D. A. Fort, R. C. Remsing, R. P. Swatloski, P. Moyna, G. Moyna and R. D. Rogers, *Green Chem.*, 2007, **9**, 63–69.
- 8 R. Wu, X. Wang, F. Li, H. Li and Y. Wang, *Bioresour. Technol.*, 2009, **100**, 2569–2574.
- 9 A. J. Uddin, A. Yamamoto, Y. Gotoh and M. Nagura, *Text. Res. J.*, 2010, **80**, 1846–1858.
- 10 G. Yang, Y. Zhang, H. Shao and X. Hu, *Holzforschung*, 2009, **63**, 18–22.
- 11 S. K. Lim, T. W. Son, D. W. Lee, B. K. Park and K. M. Cho, *J. Appl. Polym. Sci.*, 2001, **82**, 1097–4628.
- 12 W. Li, N. Sun, B. Stoner, X. Jiang, X. Lu and R. D. Rogers, unpublished results.
- 13 G. Gellerstedt, “Pulping chemistry”, in *Wood and Cellulosic Chemistry*, ed. D. N.-S. Hon and N. Shiraishi, Marcel Dekker, New York, 2001, pp. 859–905.
- 14 N. Sun, X. Jiang, M. L. Maxim, A. Metlen and R. D. Rogers, *ChemSusChem*, 2011, **4**, 65–73.
- 15 N. Sun, H. Rodríguez, M. Rahman and R. D. Rogers, *Chem. Commun.*, 2011, **47**, 1405–1421.