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Nanocomposite film prepared by depositing xylan on cellulose nanowhiskers matrix

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Novel bionanocomposite films have been prepared by depositing xylan onto cellulose nanowhiskers through a pH adjustment. Analysis of strength properties, water vapour transmission, transparency, surface morphology and thermal decomposition showed the enhancement of film performance. This provides a new green route to the utilization of biomass for sustainable biomaterials production.

Due to the ever-increasing global demand for materials, international dependence on conventional petroleum resources and environmental concerns, there is considerable interest in the development of alternative and sustainable products, manufactured by green technologies. In an effort to address these challenges, cellulose, the most globally abundant naturally occurring polymer has attracted significant attention for the development of novel biobased materials that are renewable, sustainable and biocompatible.[1,2] Among the proposed applications is the utilization of cellulose nanowhiskers (CNW) as reinforcement or nanofillers for the manufacture of degradable engineered biocomposites with unique properties, including high mechanical strength, low thermal expansion and density, unique morphology, self-assembly and optical properties.[3–6] CNW from biomass are a class of rod-like crystals with dimensions of 100 nm to microns in length and 5–50 nm in diameter. These are mostly obtained by controlled acid hydrolysis of cellulose fibers that selectively hydrolyzes the amorphous regions, leaving behind the less reactive crystalline regions.[7] Several recent studies on CNW and their derivatives indicate the potential biofilm applications of CNW. For example, Goetz *et al.* prepared nanocomposite films from CNW, poly(methyl vinyl ether-*co*-maleic acid) and poly(ethylene glycol) with improved crosslinking density, water sorption properties.[8] Peng *et al.* prepared films based on hemicelluloses and cellulose nanofibers with enhanced mechanical properties.[9]

Xylan from wood with a β-(1–4)-D-xylopyranosyl backbone to which arabinopyranosyl, glucuronic acid and acetyl substituents are attached, constituting 25–35% of dry biomass, represents another abundant biopolymer.[10,11] Xylan can be used to form films, which in combination with biodegradability make it another interesting alternative to the petroleum-based materials for biorefinery products.[12,13] Xylan based films and coatings show low oxygen and grease permeability with relatively improved properties in tensile strength.[9,14,15] The natural association of xylan with cellulose through interactions between substituted, linear regions of the chains[16] has been studied extensively in the pulp paper industry to improve processing and mechanical properties of the pulp.[17] Based on such interactions, the current work will not only examine the potential for depositing xylan on a CNW matrix to prepare novel films under mild conditions, but also to understand how expected improvements depend on the dispersion and distribution of xylan in CNW matrix as well as the interaction between the matrix and the reinforcing phase.

Bionanocomposite films were successfully prepared through a simple and green route by an adjustment of pH to deposit birch wood xylan onto poplar CNW matrix followed by a dialysis, sorbitol addition and solution casting with compositions as described in Table 1. In an effort to study the effect of deposition process on film physicochemical properties, control group films were prepared following exactly the same procedures, except for pH adjustment and dialysis.

Films were conditioned at 50% relative humidity and 23 °C for 24 h and characterized for tensile strength and strain, as summarized in Fig. 1. The tensile strength of pH adjusted films increased from 24.5 MPa to a maximum of 46.3 MPa with 6.3% xylan deposition amount, while there was a decrease in strain, ranging from 8.6 to 7.2%. When the xylan deposition was greater than 6.3%, there was a decrease in tensile strength with a leveling-off in the strain, which could be due to lower film density (Table 2). Films that were pH adjusted and

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Table 1 Composition of xylan modified CNW films

No.	Sample code	Mass weight (g)
1	CNW + S[a]	CNW 0.4, sorbitol 0.2
2	X2.8%[b]	CNW 0.4, sorbitol 0.2; xylan 0.008
3	X3.8%	CNW 0.4, sorbitol 0.2; xylan 0.016
4	X4.6%	CNW 0.4, sorbitol 0.2; xylan 0.024
5	X6.3%	CNW 0.4, sorbitol 0.2; xylan 0.032
6	X7.5%	CNW 0.4, sorbitol 0.2; xylan 0.04
7	X11.2%	CNW 0.4, sorbitol 0.2; xylan 0.08
8	X13.2%	CNW 0.4, sorbitol 0.2; xylan 0.12

[a] CNW: poplar cellulose nanowhiskers; S: sorbitol. [b] Xylan percentage is the actual xylan deposition content of the pH adjusted films after 24 hour water extraction.

Table 2 Density of xylan modified CNW films

Sample code	Film density without pH adjustment (g cm^{-3})	Film density with pH adjustment (g cm^{-3})
CNW + S	1.1333	
X2.8%	1.0872	1.2292
X3.8%	1.2519	1.2667
X4.6%	1.2734	1.2846
X6.3%	1.1818	1.3194
X7.5%	1.1573	1.2650
X11.2%	1.1333	1.2334
X13.2%	1.1389	1.2390

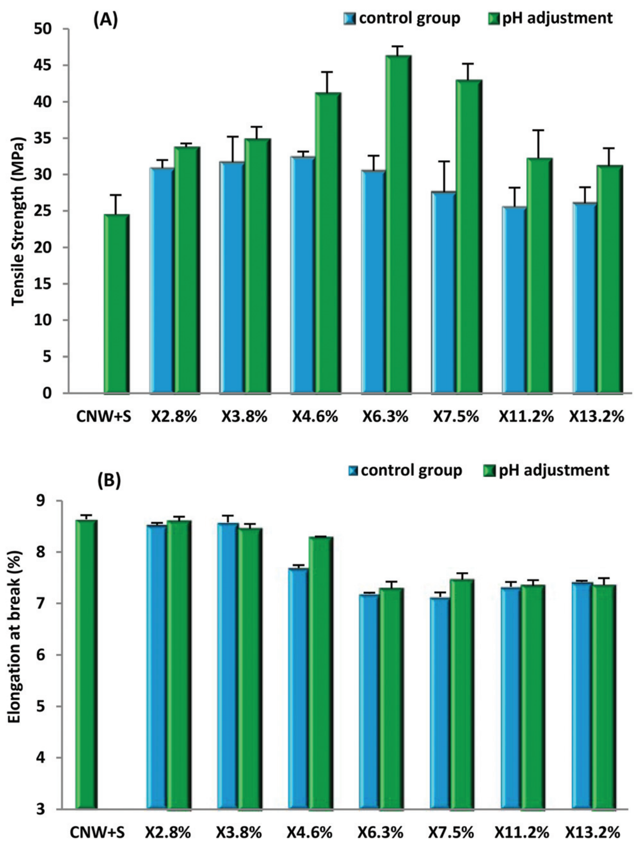

Fig. 1 Effect of xylan on tensile strength (A) and strain (B) of CNW films (control group: films without pH adjustment and dialysis).

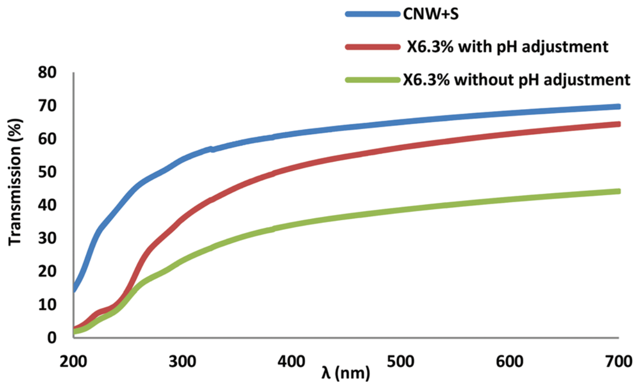

Fig. 2 Transparency measurements of selected films by ultraviolet-visible spectroscopy.

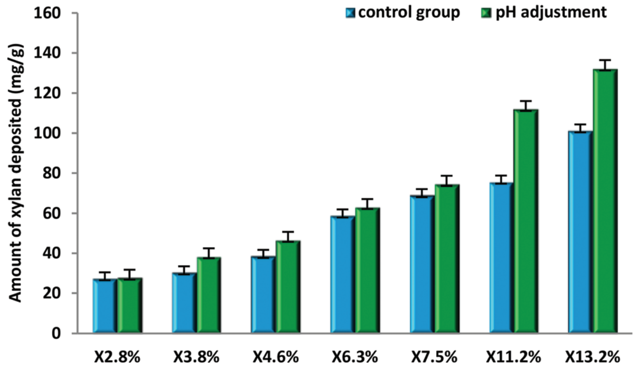

Fig. 3 Deposited amounts of xylan on the CNW films after 24 h Soxhlet extraction with water.

dialyzed exhibited better tensile strength and higher light transmittance (Fig. 2) than control group films, which could result from the higher adsorption of xylan (Fig. 3), better dispersion and mixing uniformity between xylan and CNW. The adjustment of pH from 10 to 4.5, including initial dissolution of xylan and re-deposition of xylan on the CNW surface, played an important role in retaining the xylan on CNW by co-crystallization of xylan segments with CNW and by the formation of strong xylan–CNW hydrogen bonds.[18] Compared to CNW reinforced xylan films and cross-linked hydrogels,[14,19] the superior strength properties of xylan modified CNW matrix films could be attributed to the formation of a rigid hydrogen-bonded network, which resulted from the natural affinity of xylan to CNW in the polymeric matrix yielding an irreversible adsorption. This further affected the film density (Table 2) and acted as a physical barrier to the transport of the diffusing water molecules. Increased xylan deposition from 2.8 to 6.3% yielded denser films with relatively lower water vapour transmission rate (WVTR, Fig. 4) in comparison with those control films. However, the higher WVTR in film X11.2% and X13.2% with pH adjustment may be due to their relatively higher xylan adsorption levels that cause less tortuous paths for water molecules to follow.[15] Furthermore, the introduction of functional

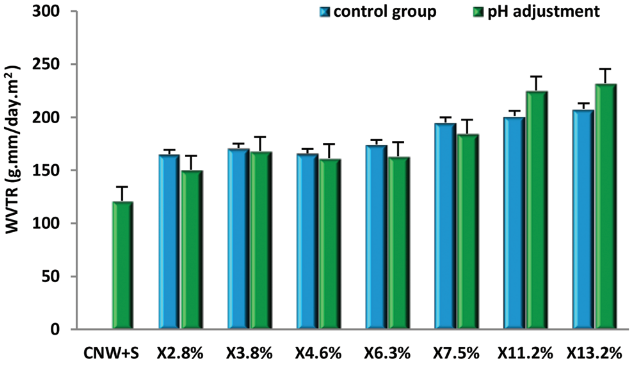

Fig. 4 Specific water vapour transmission rate of films.

groups has been proved to facilitate the properties improvement of xylan based film.[20] Uronic acid existed in the birch wood xylan could also contribute to the association with CNW through hydrogen bonding and/or the formation of esters *via* condensation reaction between carboxylic acids and hydroxyl groups, which further influence the change of film properties.

Molecular structure of the xylan, solubility, aggregation, conformation in solution and interaction with cellulose and plasticizer significantly influence the properties of the biocomposite.[21] Therefore, it is plausible to assume that changes in the physical properties of the films may be affected by the adsorption levels, fine structure and functional groups of xylan. To further characterize these changes in film properties, 3D microscopy images and atomic force microscopy (AFM) were used to analyze the morphology of the films and interaction among materials, as shown in Fig. 5 and 6 with average surface roughness presented in Fig. 7. Isolated poplar CNW were found to be needle-shaped crystals with 4.54 ± 1.55 nm in width and 675 ± 156 nm in length. The images from optical microscopy and the AFM showed obvious differences between the surfaces of unmodified and xylan modified films as well as surfaces of pH adjusted and unadjusted films. Films made from CNW with plasticiser sorbitol had a smooth surface consisting of microfibrils. However, xylan addition resulted in a re-organization of the surface of the bionanocomposite films.

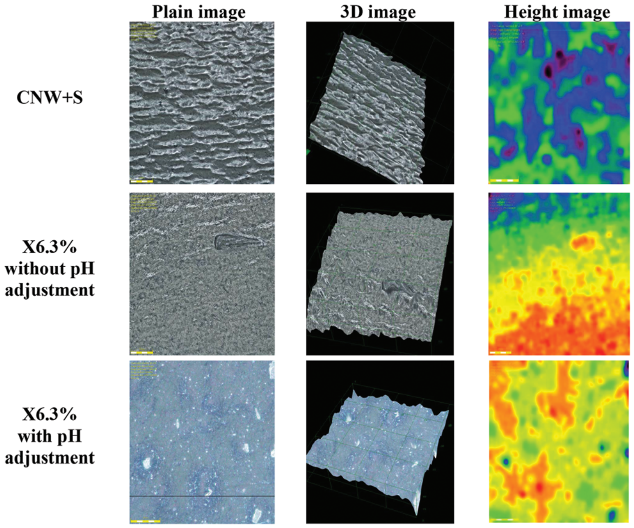

Fig. 5 Plain, 3D and height images of selected xylan modified CNW films rough surface (499 × 499 μm) by DSX500 Olympus Opto-Digital microscope. (In height images different colours represent various heights: red area indicates higher heights and blue area indicates lower heights.)

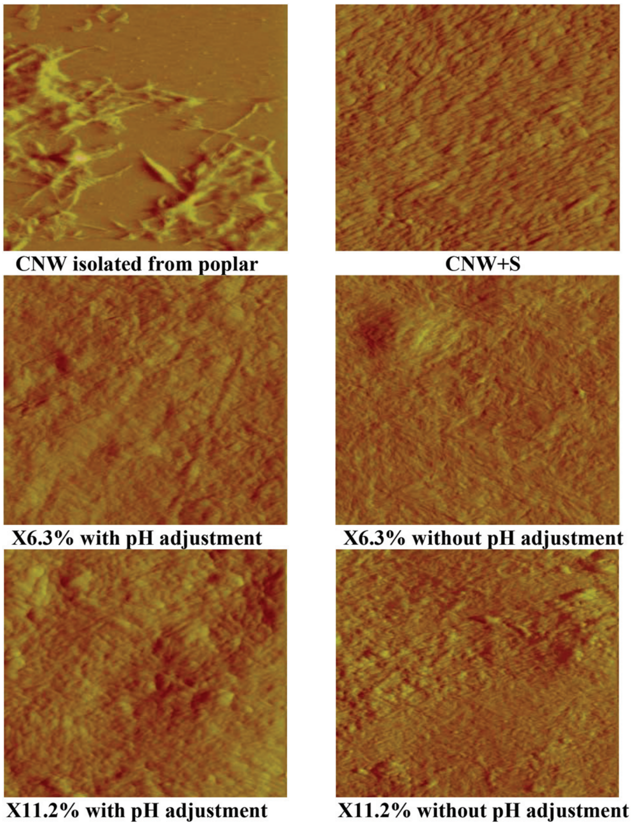

Fig. 6 AFM amplitude images of CNW and selected xylan modified CNW films rough surface (5 × 5 μm).

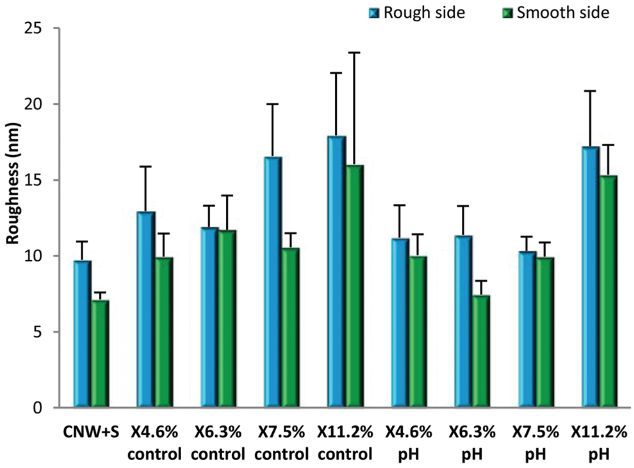

Fig. 7 Average roughness of selected xylan modified CNW films measured by AFM.

In aqueous solutions xylans exist as both dissolved single molecules and aggregated structures in the colloidal size range but with main part in aggregate form, which therefore resulted in the main part of adsorbed xylan in aggregates.[18] Adjustment of pH followed by dialysis against water to remove salt and excess acid can improve the dispersion, distribution and adsorption of xylan on CNW that thereby generated films with relatively lower roughness but rigid networks. In contrast, control films without pH adjustment and dialysis exhibited a surface of significant uneven structure and agglomeration with granules impregnated into the CNW–sorbitol matrix, which resulted in poor tensile strength, poor transparency and higher WVTR.

Thermal stability and decomposition properties of films were also examined by thermal gravimetric analysis (TGA) as shown in Fig. 8. There are three main steps of degradation in CNW + S control film, which included an initial moisture loss (7.68%) at 125 °C, an intermediate loss (47.96%) at temperatures ranging from 175 to 285 °C due to depolymerization, dehydration, and decomposition of glycosyl units followed by the formation of a char,[22] and a final weight loss (24.32%) between 300 and 500 °C ascribed to the oxidation and breakdown of the char to lower molecular weight gaseous products.[22] The onset of thermal degradation occurred at 213 °C, with a maximum rate of mass loss at 235 °C and second-maximum at 355 °C. The sulfate groups introduced to the CNW caused the thermal instability as manifested by multiple peaks on derivative thermogravimetry (DTG).[23] X6.3% film with pH adjustment also exhibited similar three main degradation steps with mass loss 3.29, 55.36 and 19.77%, respectively, but generated a higher onset of degradation at 224 °C, a maximum rate of mass loss at 252 °C and a second-maximum at 360 °C. This enhancement of thermal resistance by the addition of xylan could be attributed to the formation of a confined structure in the CNW nanocomposites film. Interestingly in control X6.3% film without pH adjustment, there is one significant degradation step from 175 to 330 °C with mass loss 76.90% and a small intermediate loss from 330 to 500 °C with weight loss 7.33%, accompanied by a higher onset of degradation at 235 °C and a maximal rate of mass loss at 300 °C. This could be due to the aggregation of xylan on CNW affecting sulfate groups and unreacted crystal interior.

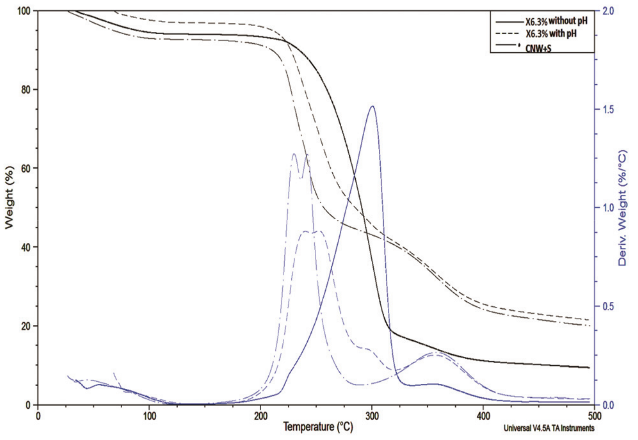

Fig. 8 TG-DTG curves of selected xylan modified CNW films (X6.3% with/without pH adjustment).

Conclusions

The potential property improvement of bionanocomposite films depends on the degree of dispersion and the bonding ability between matrix and modifying phase. Adjustment of pH followed by dialysis was carried out to better disperse and deposit xylan on CNW and sorbitol matrix, resulting in xylan modified CNW films having enhanced performance in mechanical properties and thermal stability.

Materials and methods

CNW were isolated from poplar followed by delignification, hemicellulose removal[24] and 64% sulfuric acid hydrolysis.[5,25] Birch wood xylan was obtained from Sigma-Aldrich and was determined to contain 283.12 μmol g^{-1} uronic acid[26] with weight average molecular weight (M_w) 15 524 g mol^{-1}, number average molecular weight (M_n) 11 385 g mol^{-1} and polydispersity index (PDI) 1.36. Xylan solution was prepared by adding birch xylan to water with adjustment of pH to 11.0 using 2.50 N NaOH under vigorously mixing at 70 °C for 30 min.

Films were formed by mixing CNW, xylan solution and sorbitol with pH adjustment followed by dialysis and solution casting process. At first CNW was added into xylan solution with adjustment of pH to 10.0 under stirring at 70 °C for 30 min. The pH of xylan–CNW solution was adjusted to 4.5 with the addition of 2.0 N H_2SO_4. After cooling the solution to RT, the xylan modified NCW solution was dialyzed (Spectra/Por® Biotech Cellulose Ester Dialysis membranes; MWCO: 100–500 Da) against water until the pH of the solution became neutral. After that, sorbitol was added to the mixture with stirring for 30 min. The solution was then poured into polystyrene petri dishes and allowed to dry at RT for three days.

Mechanical testing, water vapour transmission rate measurement, optical microscopy and AFM analysis, xylan adsorption determination and UV-visible transparency testing procedures followed related literatures.[17,20,27–29] Thermogravimetric analysis was conducted using a Q5000 TA instrument with samples weighing 10–15 mg from RT to 500 °C at 10 °C min^{-1} rate under nitrogen atmosphere.

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Notes and references

1 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak and C. L. Liotta, *Science*, 2006, **311**, 484–489.

2 K. G. Satyanarayana, G. G. Arizaga and F. Wypych, *Prog. Polym. Sci.*, 2009, **34**, 982–1021.

3 S. J. Eichhorn, *Soft Matter*, 2011, **7**, 303–315.

4 L. Heath and W. Thielemans, *Green Chem.*, 2010, **12**, 1448–1453.

5 T. Kohnke, A. Lin, T. Elder, H. Theliander and A. J. Ragauskas, *Green Chem.*, 2012, **14**, 1864–1869.

6 Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, 2010, **110**, 3479–3500.

7 G. Siqueira, J. Bras and A. Dufresne, *Biomacromolecules*, 2009, **10**, 425–432.

8 L. Goetz, A. Mathew, K. Oksman, P. Gatenholm and A. J. Ragauskas, *Carbohydr. Polym.*, 2009, **75**, 85–89.

9 X.-W. Peng, J.-L. Ren, L.-X. Zhong and R.-C. Sun, *Biomacromolecules*, 2011, **12**, 3321–3329.

10 A. Henriksson and P. Gatenhalm, *Cellulose*, 2002, **9**, 55–64.

11 I. Gabrielii, P. Gatenholm, W. Glasser, R. Jain and L. Kenne, *Carbohydr. Polym.*, 2000, **43**, 367–374.

12 K. S. Mikkonen and M. Tenkanen, *Trends Food Sci. Technol.*, 2012, **28**, 90–102.

13 N. M. L. Hansen and D. Plackett, *Biomacromolecules*, 2008, **9**, 1493–1505.

14 A. Saxena, T. J. Elder, S. Pan and A. J. Ragauskas, *Compos. Pt. B-Eng.*, 2009, **40**, 727–730.

15 A. Saxena, T. J. Elder and A. J. Ragauskas, *Carbohydr. Polym.*, 2011, **84**, 1371–1377.

16 A. Linder, R. Bergman, A. Bodin and P. Gatenholm, *Langmuir*, 2003, **19**, 5072–5077.

17 W. Han, C. Zhao, T. Elder, K. Chen, R. Yang, D. Kim, Y. Pu, J. Hsieh and A. J. Ragauskas, *Carbohydr. Polym.*, 2012, **88**, 719–725.

18 A. Linder, R. Bergman, A. Bodin and P. Gatenholm, *Langmuir*, 2003, **19**, 5072–5077.

19 L. Goetz, M. Foston, A. P. Mathew, K. Oksman and A. J. Ragauskas, *Biomacromolecules*, 2010, **11**, 2660–2666.

20 I. Šimkovic, I. Kelnar, I. Uhliariková, R. Mendichi, A. Mandalika and T. Elder, *Carbohydr. Polym.*, 2014, **110**, 464–471.

21 T. Kohnke, A. Ostlund and H. Brelid, *Biomacromolecules*, 2011, **12**, 2633–2641.

22 X. Cao, Y. Habibi and L. A. Lucia, *J. Mater. Chem.*, 2009, **19**, 7137–7145.

23 M. Roman and W. T. Winter, *Biomacromolecules*, 2004, **5**, 1671–1677.

24 M. Foston and A. J. Ragauskas, *Biomass Bioenergy*, 2010, **34**, 1885–1895.

25 D. Bondeson, A. Mathew and K. Oksman, *Cellulose*, 2006, **13**, 171–180.

26 J. Li, K. Kisara, S. Danielsson, M. E. Lindström and G. Gellerstedt, *Carbohydr. Res.*, 2007, **342**, 1442–1449.

27 A. Saxena and A. J. Ragauskas, *Carbohydr. Polym.*, 2009, **78**, 357–360.

28 Y. Q. Pu, J. G. Zhang, T. Elder, Y. L. Deng, P. Gatenholm and A. J. Ragauskas, *Compos. Pt. B-Eng.*, 2007, **38**, 360–366.

29 S. Iwamoto, A. Nakagaito, H. Yano and M. Nogi, *Appl. Phys. A: Mater. Sci. Process.*, 2005, **81**, 1109–1112.