Generation of Spherical Cellulose Nanoparticles from Ionic Liquid Processing via Novel Nonsolvent Addition and Drying

Jafar Al Hakkak,1 Warren J. Grigsby2, Kalyani Kathirgamanathan,3 and Neil R. Edmonds3

1Plant & Food Research Ltd., Mt. Albert Road, Auckland, New Zealand
2Scion, Rotorua, New Zealand
3School of Chemical Sciences, University of Auckland, Auckland, New Zealand

Correspondence should be addressed to Warren J. Grigsby; warren.grigsby@scionresearch.com

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A novel method to prepare spherical cellulose nanoparticles has been developed using imidazolium ionic liquid processing and regeneration from controlled acetonitrile nonsolvent addition and drying. Nanoparticles ranging from 100 to 400 nm have been prepared with high uniformity. Minimisation of moisture via solvent exchange drying led to discrete nanoparticles, whereas the presence of ambient moisture during regeneration contributed to aggregated morphologies. Chemical analyses of the spherical cellulose nanoparticles reveal a high-amorphous cellulose content. Furthermore, the range of particle sizes achieved with acetonitrile nonsolvent fractionation and solvent exchange drying suggest the size and uniformity of nanoparticle distributions reflect the fractionated cellulose weight fractions. This ionic liquid method is simple, energy efficient, and likely to have wide applicability across other biopolymers as well as potential to prepare surface functionalized spherical cellulose nanoparticles.

1. Introduction

Cellulose is a highly abundant natural polymer. Of the 40 billion tons renewed annually, some 200 million tons are used as raw materials in industrial processing [1, 2]. The use of cellulose as a starting material for product development is a viable approach from both an environmental and economical perspective. Native cellulose is strongly resistant to breakdown due to a highly crystalline network structure and, due to its fibrous nature, is found in many applications ranging from textiles and films through to paper products. Over the past two decades, nanocellulose has gained high interest as a potential biomaterial within the industrial and scientific communities. Potential applications of this material range from new kinds of composite materials to uses in medical technology and the food and pharma industries. However, for some nanocellulose products, a high-energy input can be required for the initial defibrillation of the starting materials [1]. Alternative methods which are less energy-intensive to produce nanoscale materials would open up greater utility for nanocellulose materials.
modification [9]. Generation of uniform spherical nanoparticles is difficult via mechanical, chemical, or ionic liquid approaches [10–12]. In the current paper, we report a new, facile method to create and isolate spherical cellulose nanoparticles from ionic liquid using acetonitrile nonsolvent addition. This novel regeneration of spherical nanoparticles is a simple process, producing spherical cellulose particles in the range of 100–400 nm. The potential applications of these materials include use in polymer composites, bioplastics, films and foams, implant materials, and biodegradable tissue scaffolds through to drug delivery and membrane preparation via surface modifications.

2. Experimental

2.1. Materials. 1-Ethyl-3-methylimidazolium acetate (EMIMAc) and microcrystalline cellulose were purchased from Sigma Aldrich. EMIMAc was vacuum-dried at 68°C for 24 hours before use. A stock solution of cellulose in EMIMAc solution was first prepared by heating EMIMAc (94 g) in a round bottom flask under a nitrogen atmosphere maintained at 80°C with magnetic stirring. Cellulose (e.g., 1.8 g, 2% w/v) was added and dissolved for over 16 hours maintaining a nitrogen atmosphere.

2.2. Regeneration of Cellulose from EMIMAc. For the regeneration method, a 2–8% cellulose solution (30 g) was transferred to a flask, and heat was maintained at 55°C. A nonsolvent (100 mL), either water or acetonitrile, was added to the cellulose solution with stirring. The samples were then centrifuged to recover the precipitate. The precipitates were separated from the filtrate and further washed with the respective nonsolvent up to four times. The recovered precipitates were then washed with water prior to freeze drying.

2.3. Preparation of Cellulose Nanoparticles by Solvent Drying. For the solvent drying method, the above fractionation procedure was followed by adding acetonitrile (100 mL) to a 2% cellulose EMIMAc solution (30 g) with stirring. The precipitated fraction was first washed with acetonitrile by centrifugation, decanted, and then suspended in ethanol and washed four times. After this, the precipitate was then repeatedly washed with acetone and finally washed with diethyl ether three times. In between the washings, sonication was used to suspend the sample in the solvent. After washing with diethyl ether, the gentle abrasion of the isolated material in a dry atmosphere was required to prevent the cellulose molecules from aggregating and bonding.

2.4. Characterisation. Scanning electron microscopy (SEM) images were acquired using a Philips XL30S field emission scanning electron microscope, operating at an acceleration voltage of 5.0 kV. The samples were mounted on aluminum studs using adhesive tape and sputter coated with platinum under vacuum using a standard technique.

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet FTIR 8700 spectrometer in the transmission mode. Powdered cellulose samples were mixed with dried KBr and then pellets formed by compressing into discs. FTIR spectra were acquired between 4000 and 400 cm$^{-1}$ using 64 to 128 scans for each sample.

Solid state $^{13}$C NMR spectra were obtained on a Bruker Avance DRX 200 instrument with a 7 mm doubly tuned 1H/13C MAS probe (Bruker) at a frequency of 50.32 MHz. Hartmann–Hahn matching was conducted using glycine. Samples were packed into a zirconia rotor fitted with a Kel-F cap and spun at 5 kHz. A standard cross polarisation-magic angle spinning (CP-MAS) pulse program was used with a 1H preparation pulse of 5.56 $\mu$s, 1H decoupling field of 47 kHz, and an acquisition time of 20 ms.

X-ray diffraction was undertaken on a Bruker AXS D8 advance diffractometer at 25°C using Cu-Kα ($\lambda$ = 1.5418 Å) radiation in the 2θ range 5 to 35°. Acquisitions were taken at 0.01° steps using intervals of 0.5 s per step.

3. Results and Discussion

Using either water or acetonitrile as a nonsolvent, each one was added to a cellulose solution in EMIMAc, an imidazolium-based ionic liquid. Nonsolvent was added to regenerate cellulose into fractions which were dried, either by freeze-drying or solvent exchange methodology. Quantitative precipitation was achieved when water was used as a nonsolvent, whereas two fractions were obtained using acetonitrile. The SEM micrographs of the freeze-dried acetonitrile and water fractions are illustrated in (Figure 1). The cellulose regenerated with water was not of particle morphology being film-like in appearance. The fraction regenerated with acetonitrile had a particle morphology, with spherical micron-sized particles embedded in a gel matrix. Moreover, when a small region of a spherical particle was magnified, SEM revealed this to be aggregated nanoparticles with diameters less than 100 nm (as shown by arrow in Figure 1(b)). This aggregated nanoparticle morphology is comparable to that produced by enzymatic hydrolysis and ultrasonic [13] or homogenization [10] processing of cotton fibre.

Recovered fractionated samples were initially analysed to provide a qualitative assessment including chemical characterisation with FTIR (Figure 2). A comparison of the original cellulose and spherical cellulose particles spectra reveals an absence of new bands confirming no chemical modification to cellulose. However, the symmetric CH$_2$ bending absorption at 1430 cm$^{-1}$ was observed to decrease, suggestive of a reduction in the degree of crystallinity of this sample. The C–O–C stretching band at 898 cm$^{-1}$ was evident for the amorphous component [14] was more intense in the particles than the original cellulose. The greater intensity of this β-(1→4)-glycosidic linkage absorption suggests the spherical cellulose particles had more amorphous cellulose content than the starting material which was further confirmed by $^{13}$C NMR and XRD measurements.

Results of $^{13}$C NMR and XRD analyses (Figure 3) suggest the fractionated material regenerated with both water and
acetonitrile may also retain proportions of ordered cellulose. X-Ray diffractogram intensities indicate that the original cellulose crystallinity was lost during dissolution and regeneration. However, in applying the sensitivity of the C4 (81–93 ppm) and C6 (60–70 ppm) regions to order/disorder in cellulose samples [15], solid state $^{13}$C NMR results reveal the cellulose regenerated with water to have a C4 peak at 87 ppm, whereas the spherical particles have this peak at 83 ppm. Furthermore, in using the comparative assessments of CP/MAS $^{13}$C NMR and XRD by Isogai et al. for cellulose polymorphs [16], C4 signals for cellulose II and cellulose IV II are between 87.8–88.8 ppm and 83.5–84.6 ppm, respectively. Therefore, the NMR results and associated XRD patterns confirm that the cellulose regenerated with water had cellulose II crystalline character and the coalesced spherical particles obtained on acetonitrile nonsolvent addition have

Figure 1: SEM images of fraction 1 regenerated with acetonitrile (a, b) and cellulose regenerated with water (c, d).

Figure 2: FTIR spectra of original cellulose (b) and the spherical particles fractionated from acetonitrile (a).
some cellulose IV\textsubscript{II} crystalline character likely induced by their agglomeration.

In comparing the regenerated cellulose morphologies achieved with water and acetonitrile, it was evident the relative polarity of these nonsolvents was a factor in particle generation. In the solid phase, imaging of individual natural cellulose molecules by AFM has revealed differing conformations due to surface polarity [17]. Wan et al. report that individual cellulose chains adopt an extended conformation on a positively charged surface, whereas on a negatively charged surface, a compact globule conformation is adopted [17]. By analogy, in EMIMAC solution, the ionic liquid provides a negatively charged surface for cellulose molecules to adopt a globular confirmation. When regenerated with the aprotic nonsolvent acetonitrile, this produces the observed particles as solvation is decreased. Conversely, when regenerated with water or with excess moisture, hydrogen bonding by the imidazolium ion is affected [18] which impacts cellulose solvation and may bring cellulose molecules together increasing chain entanglement, reforming of hydrogen bonds and inducing cellulose precipitation.

The above results using acetonitrile nonsolvent addition demonstrate that preparation of spherical cellulose nanoparticles is possible from ionic liquid. To further improve particle separation, cellulose was regenerated using acetonitrile addition to give two fractions [7], and the fractionated samples then dried by solvent exchange to reduce moisture influences on particle morphology (Figure 1). In this process, each regenerated fraction was first washed with acetonitrile to remove the residual ionic liquid, then with ethanol to remove any acetonitrile, and later with acetone to remove any residual ethanol and finally with ether to dry the sample. This method of drying eliminated the absorption of moisture to a reasonable extent, minimizing any moisture-induced agglomeration and coalescence of particles observed above (Figure 1). The SEM images of regenerated fractions dried by the solvent exchange method reveal visible improvement in the appearance and individuality of cellulose nanoparticles (Figure 4). This attempt to minimize the influence of moisture has led to fraction 1 exhibiting particles in an aggregated state with sizes ranging from 120 to 350 nm. The nanoparticles formed were of different sizes and state, being comparable to those isolated on acid hydrolysis.

![Image](https://via.placeholder.com/150)

**Figure 3:** $^{13}$C NMR spectra (a, c) and XRD diffractograms of fraction 1 regenerated with acetonitrile (a, b) and cellulose regenerated with water (c, d).
and ultrasonication [11]. In fraction 2, the particles were smaller and more uniform than observed in fraction 1. Moreover, with prior analyses revealing fractionation by molecular weight on nonsolvent addition [6, 7], the range and uniformity of nanoparticle sizes evident in (Figure 4) may suggest these particle distributions reflect fractionated cellulose molecular weights which can be achieved on acetonitrile nonsolvent addition [7].

4. Conclusion

This study has revealed cellulose dissolution in EMIMAC solvent and selection of acetonitrile as a nonsolvent for cellulose regeneration creates new potential for the production of spherical nano- and submicron-sized cellulose particles. The amount of moisture present when regenerating cellulose has a great influence on the resulting morphology of the material regenerated. Evident in (Figure 1) was a high rate of nanoparticle agglomeration likely promoted by a relatively high absorbed moisture content compared to nanoparticles produced using a solvent drying regime (Figure 4). Furthermore, we believe that nanoparticle aggregation can be avoided by working in isolation of any ambient moisture and results further improved by using more dilute cellulose solutions and performing both dissolution and regeneration under a strict anhydrous environment. In developing this new method to generate cellulose nanoparticles, it will be scalable and applicable to other plant polysaccharides or biopolymer systems also. Moreover, as the surface properties of nanocellulose affect its processability [19], these results offer the potential for differing types of modifications resulting in surface-functionalized cellulose nanoparticles which may be advantageous in different types of applications.

Data Availability

The data provided in this manuscript are freely available through a PhD thesis at the University of Auckland (URL: https://researchspace.auckland.ac.nz/handle/2292/5949).

Disclosure

Aspects of this article were highlighted at the BIOPOL 2013 conference in honour of the late Prof. Allan Easteal who was a colleague, supervisor, and contributor to this study.

Conflicts of Interest

The authors declare no conflicts of interest in publication of this study.

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References


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