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Wet-spinnning of Cellulose Acetate Reinforced with Acetylated Nano-crystalline Cellulose as Carbon Fibre Precursors

Mahyuni Harahap¹, Bongkot Hararak¹, Inam Khan¹, Surya Pandita¹, Saharman Gea²
¹ School of Metallurgy and Materials, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom.
² Department of Chemistry, Faculty of Mathematic and Natural Science, Universitas Sumatera Utara, Jl. Bioteknologi No.1 Medan 20155, Indonesia.
s.gea@usu.ac.id

Abstract. The search precursors that are bio-based, renewable and biodegradable has attracted significant attention due to increased environmental awareness. Recently, nano-crystalline cellulose (NCC) has been considered as a potential precursor to produce carbon fibre owing to its high crystallinity and excellent mechanical properties. However, its crystallinity prevents it from being dissolved in common solvents. The main aims of this study were: (i) to acetylate NCC to improve its compatibility with cellulose acetate and (ii) to produce wet-spun cellulose acetate fibres reinforced acetylated and unacetylated NCC. In this study, rod-like particles of NCC with diameters in the range 2.0-4.8 nm and lengths of 46-114 nm were characterised using a Transmission Electron Microscope (TEM). The carbonyl (C=O) group of the acetyl group was confirmed using Fourier Transmission Infrared (FTIR), and the crystallinity of NCC was characterised using X-Ray Diffraction (XRD). The crystallinity indicates of the NCC before and after acetylation were 78% and 68% respectively. The morphology of wet-spun cellulose acetate reinforced acetylated NCC was smoother than reinforced NCC. The acetylation on NCC increased its compatibility with the polymer matrix.

Keywords : Nano-crystalline cellulose, Acetylation, Wet-spinning, Carbon Fibre.

1. Introduction
Cellulose is the biggest biopolymer extracted from plants and is also found in micro-organism such as fungi, bacteria, algae and tunicate [1]. Cellulose is a non-aromatic, organic compound with chemical formula (C₆H₁₀O₅)ₙ connected by β-1-4 linkages and composed of D-anhydroglucopyranose units [2]. Cellulose is a semi-crystalline structure which is bonded with lignin, hemicellulose and other compounds as the matrix. A higher crystalline content can be found in nano-crystalline cellulose (NCC) and nano-fibril cellulose (NFC), which can be extracted by acid hydrolysis [3] and steam explosion [4] respectively.

Its nano-crystalline has several benefits in use for polymeric materials such as enhancing abrasion resistance, chemical resistance, hardness, glass transition temperature (Tg) and tensile
strength. Similarly, NCC has a property of polyelectrolyte due to charge sulphate ester introduced on the surface of NCC during acid hydrolysis [5], high specific strength (7.5 GPa) [6] and high modulus (138 GPa) [7].

The utilisation of NCC as a functional material increase significantly over the past 20 years due to these properties [8]. Some examples are, (i) biomedical applications [9], printed electronics [10], fillers in nano-composites [11] and food packaging [12]. The fabrication of nano-fibres from NCC continues to attract significant attention including wet-spinning. For example, Jinfeng W et al., [13] spun NCC-silver to produce highly conductive fibres. Torres-Rendon J et al., [14] produced NCC-based fibre with high mechanical properties (33 GPa). In addition, Lundahl M et al., [15] investigated the effect of hydrogel viscosity and spinnability of NCC wet-spinning.

In this project, cellulose acetate was investigated as a carbon fibre precursor. Modifying NCC through acetylation will improve its dispersibility with the polymer matrix to produce circular and smooth wet-spun fibres. During the carbonisation process, filaments of cellulose acetate will be subjected to thermo-mechanical loading. Adding NCC to cellulose acetate is expected to increase the thermo-mechanical properties of cellulose acetate filaments.

2. Experimental method

2.1 Materials
NCC with molecular weight (M_w) of 14,700 - 27,850, a density of 1.50 g/cm³ and a sulphate content of 246 - 261 mmol/kg was purchased from Celluforce, Canada. Cellulose acetate (M_w of 30,000 g/mol), dimethylsulfoxide (DMSO), pyridine and acetic anhydride were purchased from Sigma-Aldrich, UK.

2.2 Acetylation of NCC
The acetylation process was carried out in a gel form by dispersing a 1.5% (w/v) of NCC in deionised (DI) water in a 30 ml of pyridine using sonication for 10 minutes at 20 ºC - 30 ºC. The suspension was transferred to a 250 ml three-necked bottom-flask. The acetylation was commenced by adding 15 ml of acetic anhydride under reflux in a nitrogen atmosphere at 80 ºC for five hour. After that, the product was precipitated using DI water and acetone (1:1) several times until pH was close to 7. The product was evaporated using a Vacuum brand CVC 3000. Finally, the solid was dried in a vacuum oven at 80 ºC for five hours and coded as Ac-NCC.

2.3 Wet-spinning of cellulose acetate reinforced with NCC and Ac-NCC
A 20% (w/v) cellulose acetate in DMSO introduced to a 6% (w/v) NCC and Ac-NCC solution in DMSO. The concentration of NCC and Ac-NCC in cellulose acetate was 5%. NCC and Ac-NCC were dispersed in cellulose acetate using sonication at 24 kHz at 20 ºC - 30 ºC for 5 minutes. The polymer solutions were spun with condition as following: needle diameter of 0.25 mm, feed rate of 0.004 g/minute and winding speed of 0.44 m/minute. The fibre was precipitated using DI water in a coagulating bath.

2.4 Characterization

2.4.1. Transmission electron microscope. The as-received NCC was characterised using a LoJeol 1200EX transmission electron microscope (TEM). A 1% (w/v) of NCC suspension was dropped on a copper grid (200 mesh) using a pipette, and then it was stained with a drop of 2% uranyl acetate. The excess solution was absorbed with the tip of filter paper. Finally, the nano-particle of NCC was observed using an accelerating voltage of 80 kV.

2.4.2. FTIR spectroscopy. The functional group present in the NCC before and after acetylation was characterised using an FTIR Spectrometer (Nicolet 8700, Thermo Scientific). The disks were prepared by grinding potassium bromide (KBr) with NCC and Ac-NCC with a ratio of 200 mg and 2 mg
respectively. The instrument was operated in a transmission-mode in the range 400 - 4000 cm\(^{-1}\), along with a resolution of 4 cm\(^{-1}\) and 100 scans.

2.4.3. Environmental scanning electron microscope. The morphology of NCC and Ac-NCC was studied using a Philips XL-30 FEG Environmental SEM. It was operated with an accelerating voltage of 10 kV. Before investigated, the sample was sputter-coated (SC 500 emscope) with a thin layer of gold alloy to reduce charging during analysis.

2.4.4. X-ray diffraction. X-Ray diffraction (Equinox 3000) was used to calculate the crystallinity of NCC and Ac-NCC. The instrument was performed over 2 Theta ranging from 0 to 100º with a scan rate of 0.02º sec\(^{-1}\) at 35 kV and 25 mA. The index crystallinity of samples was calculated based on the Segal method \[16\].

\[
\%\text{Crl} = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%
\]  

(1)

3. Results and discussion

3.1. Transmission electron microscope

The TEM micrographs of the as-received NCC dried at 80 ºC for 5 hours are presented in the Figure 1. The length and diameter distribution of NCC was obtained by calculating 115 NCC particles using image J software analysis. Selected particles were dragged and clicked ‘Analyse — Measure’. Once the data were acquired and saved, the dimensions of the particles were imported for statically analysis. The NCC resembles needle-like particles with a length 46-114 nm and diameter 2.0-4.8 nm. The AFM data reported was similar to the average length and diameter distribution by the supplier which was 44-108 nm and 2.3-4.5 nm respectively. The slight different might be caused by differences of instrument used and the sample preparation.

Figure 1. TEM micrograph of as-received NCC.

3.2. Acetylation of NCC

3.2.1. FTIR spectroscopy analysis. Figure 2 presents the FTIR spectra of NCC and Ac-NCC. The hydrogen bonding (O-H) in both of NCC and Ac-NCC appeared at around 3350 cm\(^{-1}\) was associated with the structure of cellulose-I \[17\]. The intensity of the O-H group after acetylation decreased because the hydroxyl groups in NCC were partially substituted by acetyl groups during the acetylation reaction \[18\]. There is a peak of C-H stretching at 2900 cm\(^{-1}\) for NCC before and after acetylation. After acetylation, a new low-intensity peak appeared around 1730 cm\(^{-1}\) which was attributed to the carbonyl (C=O) stretching vibration introduced with the acetate groups on the surface \[19\]. It did not appear for as-received NCC. Similarly, unreacted acetic anhydride and by-products of acetic acid in the sample was not seen. It was confirmed by the absence of a peak at 1700 cm\(^{-1}\) and between 1760
and $1840 \text{ cm}^{-1}$ [20].

![FTIR spectra of NCC before and after acetylation](image)

**Figure 2.** FTIR spectra of NCC before and after acetylation.

### 3.2.2. The morphology of NCC before and after acetylation

The morphology of NCC before and after acetylation dried at 80 °C for 5 hours are presented in Figure 3. The surface of as-received NCC was smooth, and it changed to be rough and flake-like after acetylation. The same behaviour was also observed from another literature [21]. In addition, Ac-NCC appeared in the form of iridescent films instead powder form. This is due to the rod-like particle of NCC has a behaviour of a chiral nematic at critical concentrations. Hence, it produces iridescent film upon drying [21].

![ESEM micrograph for (a) as-received NCC and (b) Ac-NCC](image)

**Figure 3.** ESEM micrograph for (a) as-received NCC and (b) Ac-NCC.

### 3.2.3. X-ray diffraction of NCC

Figure 4 shows the XRD pattern of NCC before and after acetylation. From the result, it shows that NCC has 2 Theta angles at around 14.5, 16.3, 23.5 and 34.5° assigned to the typical reflection planes of 101, 101, 002 and 040 respectively which was presented as cellulose-I [22], the same result as FTIR spectra. The crystallinity of NCC after acetylation decreased from 72% to 68%. The intra- and inter-molecular hydrogen bonds was disrupted by introducing an acetyl group on the surface NCC which in turn disrupts the crystal structure of NCC [23]. Table 1 summarises the decreasing of the crystallinity of NCC after acetylation. The Table shows that there are differences of the crystallinity of NCC from once source to another. It is caused the raw material used for acid hydrolysis of NCC not the same. In addition, the method for the acetylation of NCC being different.
Figure 4. XRD pattern before and after acetylation.

Table 1. The crystallinity of NCC before and after acetylation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallinity (%)</th>
<th>Acetylating agent</th>
<th>Before acetylation</th>
<th>After acetylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCC</td>
<td></td>
<td>Acetic anhydride</td>
<td>72</td>
<td>68</td>
</tr>
<tr>
<td>NCC (24)</td>
<td></td>
<td>Acetic anhydride</td>
<td>81</td>
<td>74</td>
</tr>
<tr>
<td>NCC (25)</td>
<td></td>
<td>Acetic anhydride</td>
<td>77</td>
<td>68</td>
</tr>
</tbody>
</table>

*Data obtained from reference.

3.2.4. Thermogravimetric analysis. Figure 5 represents the TGA traces for NCC before and after acetylation which show three distinct regions. The first stage is dehydration of the sample from room temperature to 100 °C which was assumed to be prominent feature [26].

Figure 5. TGA trades for NCC and Ac-NCC with a heating rate of 10 C.minute\(^{-1}\) in argon.

The second step region in the TGA trace is the decomposition of NCC to the monomer of D-glucopyranose which is seen to be between 270 °C and 400 °C [27]. However, Ac-NCC degraded at a
lower temperature between 210 °C and 400 °C. The decrease in the onset thermal degradation temperature for NCC after acetylation can be rationalised through degree of the crystallinity. It was confirmed from the XRD result. The final step region for both as-received and Ac-NCC was observed to commence around 400 °C attributing to the completing decomposition. The carbon yield of Ac-NCC is approximately 10% higher than as-received NCC.

3.3. The morphology of wet-spun fibres

The morphology and the cross-section of wet-spun cellulose acetate reinforced NCC and Ac-NCC are presented in Figure 6. Longitudinal lines are observed for both polymer fibres which might be coming from inner bone of the needle. The fibre reinforced NCC has lower compatibility with the polymer solution compared to Ac-NCC. It can be seen pores or void appeared at the cross-section of the fibres. In addition, the grooves with some particles are also seen on the surface of wet-spun cellulose acetate. On the other hand, the morphology of cellulose acetate reinforced Ac-NCC is smoother and has fewer particles. It has been reported that the presence of NCC in a polymer matrix leaded to the formation “bead fibres” and the morphology was rough due to poor compatibility [28]. The acetylation on NCC increases its compatibility with the polymer matrix. It assumes that it improves the mechanical properties of the fibre.

![Figure 6. SEM micrographs and cross-section area of wet-spun (a-b) cellulose acetate reinforced 5% NCC and (c-d) cellulose acetate reinforced 5% Ac-NCC.](image)

4. Conclusion

Surface acetylation of NCC in a gel-form has been achieved by introducing acetyl group on the surface of NCC using acetic anhydride as the acetylating agent and pyridine as the catalyst. The porosity of wet-spun fibres decreases and it produces circular as well as continuous fibre. The morphology of cellulose acetate reinforced Ac-NCC is smoother than those reinforced NCC. The particles are also found on the surface of the wet-spun fibre reinforced NCC. It indicates that the acetylation on NCC has improved its compatibility with cellulose acetate. The heat treatment of cellulose acetate reinforced NCC is still on-progress.

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