

Single step functionalisation of celluloses with differing degrees of reactivity as a route for in-situ production of all-cellulose nanocomposites

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Abstract

A method of manufacturing all-cellulose nanocomposites using a single step functionalisation of two different celluloses with differing reactivities is presented. All-cellulose nanocomposites are produced by esterification of microcrystalline cellulose (MCC) in pyridine with hexanoic acid in the presence of bacterial cellulose (BC) followed by solvent removal. Neat MCC is more susceptible to esterification. As a result, neat MCC undergoes severe bulk modification, turning into a toluene-soluble cellulose hexanoate (C₆-MCC) whilst BC undergoes surface-only modification. The solution casted C₆-MCC films have a tensile modulus and strength of 0.99 GPa and 23.1 MPa, respectively. The presence of 5 wt.-% BC in C₆-MCC leads to an increase in tensile modulus and strength of the resulting nanocomposites to 1.42 GPa and 28.4 MPa, respectively.

Keywords

Bacterial cellulose, esterification, mechanical properties, all cellulose composites, solution casting, nanocomposites

Introduction

Cellulose is a linear polymer consisting of two D-anhydroglucose rings linked by $\beta(1\rightarrow4)$ glycosidic bonds. The concept of all-polymer composites was also applied to cellulose to produce renewable all-cellulose composites [1]. However, different manufacturing approaches had to be used because cellulose cannot be heat processed; currently two methods are used to produce all-cellulose composites [2] (i) impregnation of cellulose fibres with a solution containing dissolved cellulose, followed by subsequent regeneration of the dissolved cellulose or (ii) selective dissolution of the surface of cellulose fibres followed by regeneration of cellulose to bond the (loose) fibres together. The first approach was demonstrated by Nishino et al. [3]. They dissolved kraft pulp in 8 wt.-% LiCl in dimethylacetamide (DMAc) solution, which was subsequently infused into a ramie fibre preform. LiCl/DMAc was then removed by a solvent exchange step with methanol, followed by air-drying at room temperature. This essentially creates a composite in which both the reinforcing

fibres and the matrix are cellulose. In a separate study by Nishino et al. [4], filter papers were first activated by immersing them in to distilled water, followed by acetone and DMAc, respectively and then in 8 wt.-% LiCl/DMAc to selectively dissolve only the surface of the fibres. Methanol was once again used to extract the solvent and subsequently air-dried. This manufacturing concept closely resembles that of the manufacturing process of all-thermoplastic polymer composites. The selective dissolution of cellulose on the fibre surface produces the composite matrix after regeneration whilst the fibre core retains its original structure and acts as reinforcement for the regenerated cellulose matrix. This method has also been used to produce all-cellulose composites from microcrystalline cellulose [5] and synthetic cellulose (Cordenka) fibres [6].

In addition to micrometre-scale cellulosic fibres, nanocellulose fibrils can also be used as reinforcement to produce all-cellulose nanocomposites [7, 8]. In this context, bacterial cellulose (BC) serves as an excellent nano-reinforcement [9, 10] for regenerated cellulose. BC is essentially pure cellulose synthesised by bacteria typically from the *Acetobacter* species [11] and is inherently nano-sized as well as highly crystalline in nature, with a fibril diameter of ~50 nm and degree of crystallinity of ~90%, respectively [12]. The tensile modulus of individual BC nanofibres to be approximately 114 GPa [13]. To produce all-cellulose nanocomposites, Soykeabkaew et al. [8] impregnated BC sheets (or nanopapers) with 8 wt.-% LiCl/DMAc solution to selectively dissolve the surface of BC nanofibres, followed by subsequent cellulose regeneration in methanol. The authors reported a tensile modulus and strength of up to 20 ± 1.7 GPa and 395 ± 19 MPa.

In a previous study [14], we showed that freeze-dried BC will undergo severe bulk esterification, leading to the production of cellulose esters but when never-dried BC was used as starting material and solvent exchanged into the same reaction medium, surface-only esterification occurred. Therefore in this study, we further expand upon the original work by Matsumura et al.[15] to produce derivatised all-cellulose nanocomposites in a single step containing *surface-modified* BC-reinforced, cellulose crystallite-reinforced cellulose hexanoate. The concept is based on the esterification of microcrystalline cellulose (MCC) and of BC with hexanoic acid in the same reaction medium (into which BC was solvent exchanged).

Experimental

Materials

Microcrystalline cellulose (MCC) (Celphere[®] SCP-100) was purchased from Asahi Kasei Chemicals Co, pyridine (analaR NORAMPUR, purity $\geq 99.7\%$) and ethanol (GPR, purity $\geq 99\%$) from VWR, hexanoic acid (purity $\geq 99.5\%$), toluene (analaR NORMAPUR, purity $\geq 99.8\%$) and *p*-toluenesulfonyl chloride (purity $\geq 99\%$) from Sigma-Aldrich and sodium hydroxide (purum grade, pellets) from Acros Organics. All the materials were used as received without further purification. Bacterial cellulose (BC) was extracted from commercially available *nata de coco* (CHAOKOH gel in syrup, Ampol Food Processing Ltd, Nakorn Pathom, Thailand) [12, 16].

Esterification of MCC and BC with hexanoic acid

2 g of MCC was added into a 1 L 3-neck round bottom flask containing 400 mL of pyridine and stirred using a magnetic stirrer. To produce derivatised all-cellulose nanocomposites consisting of surface-modified BC-reinforced, cellulose crystallite-reinforced cellulose hexanoate, 100 mg of the extracted and purified neat BC (corresponding to 5 wt.-% BC in derivatised all-cellulose nanocomposites) were solvent exchanged from water through methanol ($3 \times 50 \text{ dm}^3$) into pyridine ($2 \times 50 \text{ dm}^3$) using a homogenisation-centrifugation step as described in our earlier work [12, 16]. The total volume of pyridine was adjusted to 400 mL in the final step prior to the addition of 1.9 g of MCC (to make up a total mass of 2 g cellulose). 92 g (0.48 mol) of *p*-toluenesulfonyl chloride was added into the reaction vessel followed by an equimolar amount of hexanoic acid. The esterification reaction was carried out at 50 °C for 2 h in nitrogen. Afterwards, the reaction medium was subsequently quenched by addition of 600 mL ethanol. The reaction mixture was washed with ethanol ($3 \times 400 \text{ dm}^3$) using a homogenisation-centrifugation step to remove any unreacted reactants. The reaction product was further washed with water ($3 \times 400 \text{ dm}^3$) to remove any ethanol residue, flash frozen in liquid nitrogen and subsequently freeze-dried (Heto PowerDry LL1500 Freeze Dryer, Thermo Scientific, UK). The hexanoic acid-modified MCC and hexanoic acid-modified MCC containing 5 wt.-% BC were termed C₆-MCC and 5 wt.-% BC-C₆-MCC, respectively.

Manufacturing derivatised all-cellulose nanocomposites

Derivatised all-cellulose nanocomposites were produced by solvent casting, instead of thermal consolidation. Solvent casting was chosen as no first or second order transition temperatures were observed. Freeze-dried C₆-MCC and 5 wt.-% BC-C₆-MCC were first dissolved/dispersed in toluene at a concentration of 0.05 g mL⁻¹ overnight. The C₆-MCC solution or C₆-MCC solution containing surface functionalised BC was then poured into a polytetrafluoroethylene mould (20 × 20 × 0.35 mm) and the toluene evaporated overnight at room temperature.

Characterisations of MCC/BC and their derivatised all-cellulose nanocomposites

Attenuated total reflection infrared spectroscopy (ATR-IR) of neat MCC/BC and the derivatised all-cellulose nanocomposites

ATR-IR spectra were recorded using Spectrum One FTIR-spectrometer (Perkin Elmer, MA, USA). The spectra were collected in the range from 4000 to 600 cm⁻¹ at a resolution of 2 cm⁻¹. A total of 16 scans were used for each spectrum.

Tensile properties of derivatised all-cellulose nanocomposite films

The derivatised all-cellulose nanocomposite films were first cut into dog-bone shaped specimens using a Zwick cutter. These specimens had a thickness of 75 μm, an overall length of 35 mm and the narrowest part of the specimen it was 2 mm. Prior to tensile testing, the test specimens were secured onto testing cards using a two-part cold curing epoxy resin (Araldite 2011, Huntsman, Advanced Materials, Cambridge, UK). Tensile tests were conducted using a micro-tensile tester (TST350, Linkam Scientific Instruments, Surrey, UK) equipped with a 200 N load cell. The crosshead speed used was 1 mm min⁻¹. A total of 5 specimens were tested. The compliance of the micro-tensile tester was determined to be $6.38 \times 10^{-3} \text{ mm N}^{-1}$.

Results and discussion

ATR-IR spectra of (derivatised) MCC and BC

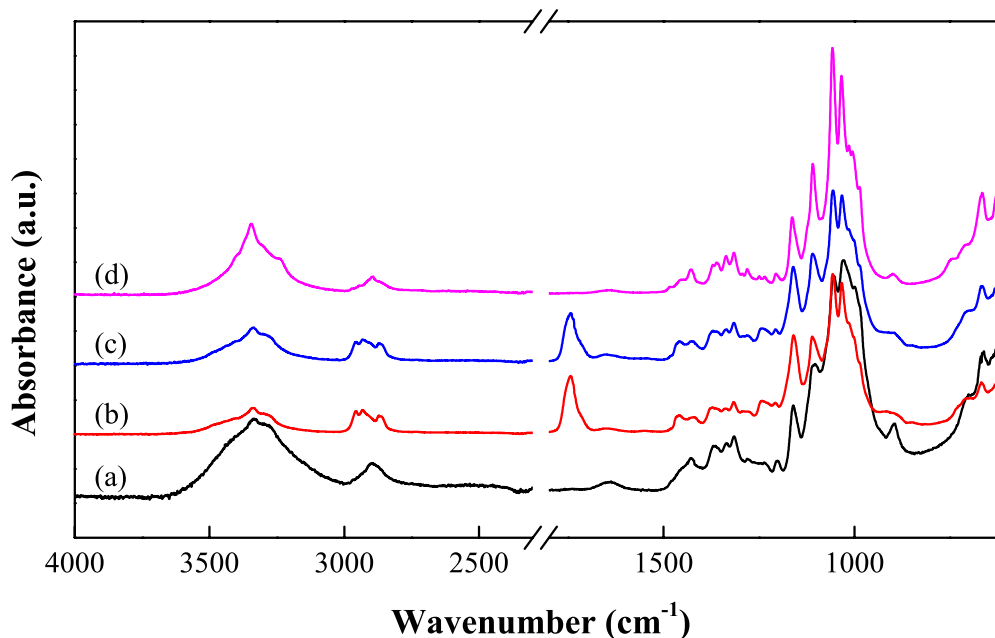


Figure 1: FTIR spectra of (a) neat MCC, (b) C₆-MCC, (c) 5 wt.-% BC-C₆-MCC and (d) neat BC, respectively.

The ATR-IR spectra of C₆-MCC and 5 wt.-% BC-C₆-MCC, along with neat MCC and BC are shown in Figure 1. All spectra were normalised against the intensity of the C-O-C absorption band at around 1158 cm⁻¹ [17]. The appearance of a new carbonyl (C=O) absorption band at 1750 cm⁻¹ can be seen in C₆-MCC and 5 wt.-% BC-C₆-MCC, respectively, which is a direct result of the introduction of hexanonyl groups into cellulose via esterification. A DS of 0.78 was obtained for C₆-MCC based on Figure 1. When 5 wt.-% BC is present in derivatised all-cellulose nanocomposites the overall DS is 0.70. This implies that the amount of ester bonds relative to the amount of C-O-C bonds is reduced, suggesting difficulty in esterifying BC with hexanoic acid compared to neat MCC. This is consistent with our previous study [14], in which we showed that never-dried BC underwent surface-only (instead of bulk) modification. As a result, fewer ester bonds formed within the derivatised all-cellulose nanocomposites when BC is present.

Tensile properties of derivatised all-cellulose nanocomposites

The tensile properties of derivatised all-cellulose nanocomposites are shown in table 1. C₆-MCC possesses a tensile modulus and strength of 0.99 GPa and 23.1 MPa, respectively. These values are comparable to the esterified wood pulp-based thermoformable all-cellulose nanocomposites manufactured by Matsumura et al. [15] with a similar DS. When C₆-MCC is reinforced with 5 wt.-% esterified BC, the tensile modulus and strength increased to 1.42 GPa and 28.4 MPa, respectively. The

marginal improvements of E and σ upon the addition of 5 wt.-% modified BC to C₆-MCC compared to C₆-MCC are postulated to be due to the low loading fraction of BC within the composites. To produce composites with performance that exceed polylactide, a BC loading of >30 vol.-% should be used [10]. Attempts were made to produce all-cellulose nanocomposites with higher BC loading. However, during the evaporation of toluene, the all-cellulose nanocomposites shrunk and cracked severely, indicating the limitation of this technique to produce high loading fraction BC-reinforced, cellulose crystallite-reinforced all-cellulose nanocomposites. This is due to the formation of irreversible hydrogen bonds between the remaining accessible –OH groups of (modified) BC within the C₆-MCC matrix. If this (modified) BC network is not activated (i.e. not prevented from shrinking, typically by hot pressing), the BC network will shrink, causing the severe shrinkage of the high BC loading-reinforced derivatised all-cellulose nanocomposites.

Table 1: Tensile properties of derivatised all-cellulose nanocomposites. E , σ and ε denote tensile modulus, tensile strength and engineering strain-to-failure, respectively.

Sample	E (GPa)	σ (MPa)	ε (%)
C ₆ -MCC	0.99 ± 0.06	23.1 ± 2.5	4.3 ± 0.4
5 wt.-% BC-C ₆ -MCC	1.42 ± 0.04	28.4 ± 2.7	4.9 ± 0.4

Conclusions

A novel method of producing derivatised all-cellulose nanocomposites is presented in this work. By modifying MCC in presence of never-dried BC by esterification with hexanoic acid in the same reaction medium, BC-reinforced derivatised all-cellulose nanocomposites can be produced in a single step. Whilst such (BC-reinforced) derivatised all-cellulose nanocomposites do not possess glass transition or melting temperatures, these nanocomposites can be readily dissolved/dispersed in toluene and solution casted, thereby avoiding the laborious solvent exchange or dissolution steps to manufacture conventional all-cellulose (nano)composites. ATR-IR spectra showed that neat MCC can be severely esterified with hexanoic acid, even in the presence of 5 wt.-% BC. Tensile tests showed that the presence of 5 wt.-% BC in C₆-MCC led to 43% increase in tensile modulus and 22% increase in tensile strength over C₆-MCC. This showed the reinforcing potential of surface-modified BC in derivatised all-cellulose nanocomposites.

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