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To cite this article: Koon-Yang Lee & Alexander Bismarck (2015) Single step functionalization of cellulosics with differing degrees of reactivity as a route for in situ production of all-cellulose nanocomposites, Nanocomposites, 1:4, 214-222

To link to this article: http://dx.doi.org/10.1080/20550324.2015.1118265

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Published online: 16 Feb 2016.

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Single step functionalization 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 functionalization 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, with an accessible amount of hydroxyl groups of 1.79 compared to BC, with an accessible hydroxyl group content of 0.80. As a result, neat MCC undergoes severe bulk modification, turning into a toluene-soluble cellulose hexanoate (C6-MCC) while BC undergoes surface-only modification. 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

Cite this article K-Y Lee and A. Bismarck: Nanocomposites, 2015, 214–222

Introduction

The concept of ‘self-reinforced polymers,’ also known as ‘all-polymer composites,’ was first introduced and explored by Capiati and Porter.1 They originally used the term ‘one-polymer composites.’ The authors showed that the interfacial shear strength between polyethylene and polyethylene fibers was much greater than between polyester and glass fibers. All-polyethylene composites were subsequently produced by consolidation of highly oriented high-density polyethylene (HDPE) films/fibers with HDPE or low-density polyethylene in a hot press2 or co-extrusion of HDPE.3 Since then, numerous manufacturing methods have been developed to produce all-polymer composites.4–9 The essence of all-polymer composites lies in the compaction processes, whereby only a fraction of the reinforcing fiber surface is melted under low contact pressure and subsequently consolidated at high pressure for a short period of time.10 Once the material is cooled, the reinforcing fibers are bound together, in analogy to conventional fiber-reinforced polymer systems. All-polyethylene4–7 and all-polypropylene8–10 composites have been successfully manufactured and were shown to have significant commercial potential. More recently, all-polylactide composites have also been produced.11–13 For a comprehensive review on the technology and recent development of all-polymer composites, the readers are referred to a recent publication by Alcock and Peijs.14

Cellulose is a linear polymer consisting of two d-anhydroglucose rings linked by β(1 → 4) glycosidic bonds. The concept of all-polymer composites was also applied to cellulose to produce renewable all-cellulose composites.15 However, different manufacturing approaches had to be used because cellulose cannot be heat processed; currently, two methods are used to produce all-cellulose composites:16 (i) impregnation of cellulose fibers with a solution containing dissolved...
cellulose, followed by subsequent regeneration of the dissolved cellulose or (ii) selective dissolution of the surface of cellulose fibers followed by the regeneration of cellulose to bond the (loose) fibers together. The first approach was demonstrated by Nishino et al. They dissolved kraft pulp in 8 wt.% LiCl in dimethylacetamide (DMAc) solution, which was subsequently infused into a ramie fiber 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 fibers and the matrix are cellulose. In a separate study by Nishino et al., 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 fibers. 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 fiber surface produces the composite matrix after regeneration while the fiber 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 (MCC) and synthetic cellulose (Cordenka) fibers.

In addition to micrometer-scale cellulosic fibers, nanocellulose fibrils can also be used as reinforcement to produce all-cellulose nanocomposites. In this context, bacterial cellulose (BC) serves as an excellent nanoreinforcement for regenerated cellulose. BC is essentially pure cellulose synthesized by bacteria typically from the Acetobacter species. It is inherently nano-sized and highly crystalline in nature, with a fibril diameter of ~50 nm and degree of crystallinity of ~90%, respectively. BC can be produced in static or shaken cultures, as well as in various types of bioreactors. Raman spectroscopy was used to estimate tensile modulus of individual BC nanofibers to be approximately 114 GPa. The idea of using BC (or any nanocellulose) in polymers stems from the possibility of exploiting the high stiffness and strength of cellulose crystals in composite applications. To produce all-cellulose nanocomposites, Soykeabkaew et al. impregnated BC sheets (or nanofibers) with 8 wt.% LiCl/DMAc solution to selectively dissolve the surface of BC nanofibers, 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. The manufacturing of all-cellulose (nano)composites requires the dissolution and subsequent regeneration of cellulose. Regeneration of dissolved cellulose is rather laborious as multiple solvent exchange steps are required. While the high vapor pressure of DMAc allows for its simple removal, the gel-like cellulose still needs to be washed with water to fully regenerate the dissolved cellulose. Furthermore, the dissolution time of cellulose in LiCl/DMAc significantly affects the mechanical performance of all-cellulose composites. To avoid these manufacturing issues, Matsumura et al. took a different approach to exploit the properties of cellulose crystals in all-cellulose nanocomposites. This was achieved by the partial derivatization of dissolving wood pulp. The authors managed to partially esterify dissolving wood pulp with hexanonyl groups to produce cellulose crystallite-reinforced cellulose hexanoate, with tensile modulus and strength of up to 1.3 GPa and 25 MPa, respectively. The major advantage of partial derivatization of wood pulp to produce derivatized all-cellulose nanocomposites lies in the fact that these all-cellulose nanocomposites are in principal thermoformable.

In a previous study, 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. to produce derivatized 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 MCC and of BC with hexanoic acid in the same reaction medium (into which BC was solvent exchanged).

**Experimental**

**Materials**

MCC (Celphree® SCP-100, degree of polymerization = ~100–300, bulk density = ~0.5–0.8 g cm⁻³) was purchased from Asahi Kasei Chemicals Co. pyridine (analaR NORAMPUR, purity ≥ 99.7%) and ethanol (GPR, purity ≥ 99%) from VWR, hexanoic acid (purity ≥ 99.5%), toluene (analaR NORMAPUR, purity ≥ 99.8%), deuterium oxide (purity ≥ 99.99 atom% D), and p-toluensulfonic acid (purity ≥ 99%) from Sigma-Aldrich and sodium hydroxide (purum grade, pellets) from Acros Organics. All materials were used as received without further purification. BC was extracted from commercially available nata de coco (CHAOKOH gel in syrup, Ampol Food Processing Ltd, Nakorn Pathom, Thailand). The extraction method of BC from nata de coco is thoroughly described in our earlier work elsewhere.

**Esterification of MCC and BC with hexanoic acid**

Two grams of MCC was added into a 1-L three-neck round bottom flask containing 400 mL of pyridine and stirred using a magnetic stirrer. To produce derivatized 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 derivatized all-cellulose nanocomposites) were solvent exchanged from water through methanol (3 × 50 dm³) into pyridine (2 × 50 dm³) using a homogenization–centrifugation step as described in our earlier work. 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-toluensulfonic acid 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. Afterward, the reaction medium was subsequently quenched by the addition of 600 mL ethanol. The reaction mixture was washed with ethanol (3 × 400 dm³) using a homogenization–centrifugation step to remove any unreacted reactants. The reaction product was further washed...
with water (3 × 400 dm³) 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 derivatized all-cellulose nanocomposites**

derivatized all-cellulose nanocomposites were produced by solvent casting, instead of thermal consolidation. Solvent casting was chosen as no first- or second-order transition temperatures (see results and discussion section) 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-functionalized BC was then poured into a polytetrafluoroethylene mold (20 × 20 × 0.35 mm) and the toluene evaporated overnight at room temperature.

**Characterization of MCC/BC and their derivatized all-cellulose nanocomposites**

Attenuated total reflection infrared spectroscopy (ATR-IR) of neat MCC/BC and the derivatized 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. To further quantify the degree of substitution (DS) of our derivatized all-cellulose nanocomposites, the asymmetric vibration of the C–O–C bond at 1158 cm⁻¹ was chosen as an internal standard. A calibration curve to calculate the DS was created using cellulose acetate and cellulose triacetate with known DS. A relationship is then drawn between DS and the ratio of the 1750 and 1158 cm⁻¹ absorption bands. The DS of our derivatized all-cellulose nanocomposites was then calculated based on their respective 1750–1158 cm⁻¹ absorption band ratios.

**Differential scanning calorimetric (DSC) characterization of modified MCC and derivatized all-cellulose nanocomposites**

Thermal behavior of modified MCC and the derivatized all-cellulose nanocomposites was characterized using DSC (Q2000, TA Instruments, UK). A sample mass of approximately 10 mg was used for each sample. A heat-cool-heat regime was employed: the sample was first heated from room temperature to 200 °C using a heating rate of 10 °C min⁻¹ followed by a cooling step at a rate of 10 °C min⁻¹ to room temperature. The sample was then reheated to 200 °C using a heating rate of 10 °C min⁻¹.

**Accessibility of hydroxyl (–OH) groups of neat MCC and BC**

In order to quantify the availability of –OH groups of neat MCC and BC for the esterification reaction, we adapted and further developed⁵⁸ the hydrogen/deuterium (H/D) exchange method of Frilette et al.⁵⁹ The measurement was conducted using dynamic vapor sorption (DVS-Advantage, Surface Measurement Systems Ltd, Alperton, UK). A sample of 30 mg of neat MCC powder or freeze-dried BC was placed into the sample chamber and pre-conditioned at 0% relative humidity (RH) of deuterium oxide (D₂O) for 10 h at room temperature. The RH of D₂O was then increased to 90% for 48 h to allow for the adsorption of D₂O and hence H/D exchange with accessible –OH groups on neat MCC and BC. The RH was then reduced to 0% for 10 h to remove any adsorbed D₂O molecules. The mass gain due to H/D exchange was recorded in situ. As deuterium is one neutron heavier than hydrogen, the mass increase after D₂O desorption and hence the amount of accessible hydroxyl groups available was back calculated from:

\[
\Delta m = \frac{[\text{OH}] \times m_2 \times N_A \times m_r}{162140}
\]

where \(\Delta m\) is the mass increase after H/D exchange (mg), \([\text{OH}]\) is the concentration of accessible and available hydroxyl groups, \(m_2\) is the initial mass of the sample (mg), \(N_A\) is the Avogadro number, and \(m_r\) is the mass of a neutron (mg). It should be noted that we assumed that cellulose consists only of a single glucose unit with a molecular mass of 162,140 and neglected the slight difference in the molecular structure of the cellulose chain end group containing a reducing group on one end of the molecule and a non-reducing group on the other end.

**X-ray diffraction (XRD) of neat MCC/BC and derivatized all-cellulose nanocomposites**

XRD patterns were obtained using an X-ray diffractometer (PANalytical X’Pert 1, PANalytical Ltd, Cambridge, UK) equipped with Ni-filtered Cu Kα (1.541 Å) X-ray source. Measurements were taken from 2θ = 10° – 45° using a step size of 0.02°. The crystallinity of the samples was calculated based on the area under the XRD peaks using the following equation:

\[
X_c[\%] = \frac{A_c}{A_c + A_a} \times 100
\]

where \(A_c\) and \(A_a\) are the total crystalline and total amorphous areas, respectively, between 10° and 45°. Scherrer’s equation was used to determine the lateral dimensions of crystalline domains of the (1 1 0) and (2 0 0) composite reflections \(L_c\):

\[
L_c = \frac{K \Delta \lambda}{\beta \cos \theta}
\]

where \(\beta\) is the full width at half maximum of the 0 0 2 reflection (in radians), \(\theta\) is the Bragg angle in degrees and \(K = 0.91\).

**Thermal stability of neat MCC/BC and derivatized all-cellulose nanocomposites**

The thermal degradation behavior in nitrogen atmosphere was investigated using thermogravimetric analysis (Q500, TA Instruments, UK). A sample mass of approximately 5 mg was heated from 30 to 600 °C using a heating rate of 10 °C min⁻¹.

**Tensile properties of derivatized all-cellulose nanocomposite films**

The derivatized 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 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 200N load cell. The crosshead speed used was 1 mm min⁻¹. A total of five specimens were tested. The compliance of the micro-tensile tester was determined to be 6.38 x 10⁻³ mm N⁻¹.

**Results and discussion**

As aforementioned, Matsumura et al. introduced hexanonyl groups onto wood pulp. The authors observed that wood pulp could be modified into cellulose hexanoate with DS of up to 2.5 and were able to thermoform the polymer at 150 – 170 °C. C₆-MCC and 5 wt.% BC-C₆-MCC synthesized in this study, on the other hand, did not show any first- and second-order transition temperatures in DSC, indicating that C₆-MCC and 5 wt.% BC-C₆-MCC are not thermoformable. This is attributed to the relatively low DS of the C₆-MCC and 5 wt.% BC-C₆-MCC (see ATR-IR section later). The cellulose is not modified sufficiently to reduce the amount/strength of hydrogen bonds between cellulose molecules to allow for long-range movements of cellulose molecules. Even though the DS of C₆-MCC and 5 wt.% BC-C₆-MCC are low, it is sufficient to reduce its solubility. Pure cellulose can only be dissolved in selected solvents, such as concentrated phosphoric acid, N,N-dimethylmorpholine N-oxide (NMMO) or LiCl/DMAc. The synthesized C₆-MCC dissolved, while 5 wt.% BC-C₆-MCC formed a homogenous suspension in toluene at room temperature (Fig. 1). As control, we also dispersed neat MCC in toluene (Fig. 1, left) but as expected, neat MCC did not dissolve in toluene.

**ATR-IR spectra of (derivatized) MCC and BC**

The ATR-IR spectra of C₆-MCC and 5 wt.% BC-C₆-MCC, along with neat MCC and BC are shown in Fig. 2. All spectra were normalized against the intensity of the C⁻O⁻C absorption band at around 1158 cm⁻¹. 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 (see Table 1). When 5 wt.% BC is present in derivatized 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, confirming the difficulty in esterifying BC with hexanoic acid compared to neat MCC. This is consistent with our previous study, in which we showed that never-dried BC underwent surface-only (instead of bulk) modification (see Fig. 3 for the FTIR spectra of hexanoic acid-modified freeze-dried or never-dried solvent exchanged BC). As a result, fewer ester bonds formed within the derivatized all-cellulose nanocomposites when BC is present.

**Accessibility of hydroxyl groups**

The accessible hydroxyl groups of neat BC and MCC are shown in Table 1. Neat MCC possessed a much higher fraction of accessible –OH groups (1.79 out of 3) compared to neat BC (0.80). As a result, MCC underwent severe bulk esterification, producing toluene-soluble cellulose hexanoate, while solvent exchanged BC underwent surface-only esterification also in the presence of MCC. MCC is typically manufactured by acid hydrolysis of pulp, which is then washed and spray-dried, which might explain the higher reactivity of MCC. This observation is consistent with our previous study, we observed that thorough dehydration processes, such as freeze- or spray-drying, resulted in an increase in the number of accessible –OH groups. Even though neat MCC possesses a high amount of accessible –OH groups, the DS of esterified MCC (C₆-MCC) was limited to 0.78 (see Table 1), instead of DS ≥ 1.79. This could be attributed to: (i) formation of a ‘skin-core’ structure as hypothesized by Asai et al. and/or (ii) the relatively short reaction time of 2 h.

**XRD of (derivatized) MCC and BC**

The XRD patterns of neat MCC and BC, as well as C₆-MCC and 5 wt.% BC-C₆-MCC are shown in Fig. 4. The diffraction peaks
Broadening of the XRD peaks was observed for C6-MCC and 5 wt.% BC-C6-MCC. The crystallinity of all samples was calculated based on the area under the XRD peaks (equation (2)). The crystallinity, d-spacing, and size of the crystalline domains associated with reflection planes of peak 4 (Iα1 1 0 and Iβ2 0 0) are tabulated in Table 1. It can be seen from this table that neat MCC and BC are highly crystalline, with a crystallinity of around 85–90%. The esterification of neat MCC (with and without the presence of BC) with hexanoic acid decreased both the crystallinity of our derivatized all-cellulose nanocomposites to about 50%. Combining this with the low DS of the derivatized all-cellulose nanocomposites, it is hypothesized that neat cellulose crystallites are still present within the derivatized all-cellulose nanocomposites.

Table 1  Degree of substitution (DS), accessible –OH groups ([OH]), crystallinity (χc), d-spacing of the Iα(1 1 0) and Iβ(2 0 0) reflections (d4), crystallite size of the Iα(1 1 0) and Iβ(2 0 0) reflections (L4) and onset thermal degradation temperature (Td) of neat MCC, neat BC and the derivatized all-cellulose nanocomposites

| Sample                  | DS | [OH] | χc (%) | d4 (Å) | L4 (Å) | Td (°C) |
|-------------------------|----|------|--------|--------|--------|---------|
| Neat MCC                | 1.79 | 90 ± 4 | 4.0 ± 0.5 | 6.2 ± 0.9 | 293    |
| C6-MCC                  | 0.78 | 49 ± 2   | 4.0 ± 0.8 | 3.7 ± 0.3 | 240    |
| 5 wt.% BC-C6-MCC        | 0.70 | 43 ± 12  | 4.0 ± 0.1 | 5.0 ± 0.3 | 251    |
| Neat BC                 | 0.80 | 85 ± 13  | 4.0 ± 0.1 | 6.3 ± 0.2 | 294    |

*Maximum of 3.

During the esterification of MCC, which resulted in the incomplete formation of cellulose hexanoate (with and without the presence of BC), the crystalline structure of MCC was not retained. Broadening of the XRD peaks was observed for C6-MCC and 5 wt.% BC-C6-MCC. The crystallinity of all samples was calculated based on the area under the XRD peaks (equation (2)). The crystallinity, d-spacing, and size of the crystalline domains associated with reflection planes of peak 4 (Iα1 1 0 and Iβ2 0 0) are tabulated in Table 1. It can be seen from this table that neat MCC and BC are highly crystalline, with a crystallinity of around 85–90%. The esterification of neat MCC (with and without the presence of BC) with hexanoic acid decreased both the crystallinity of our derivatized all-cellulose nanocomposites to about 50%. Combining this with the low DS of the derivatized all-cellulose nanocomposites, it is hypothesized that neat cellulose crystallites are still present within the derivatized all-cellulose nanocomposites.
The esterification of cellulose is hypothesized to proceed from the disordered (amorphous) to the ordered (crystalline) regions of cellulose.\(^{41, 42}\) A different view was presented by Asai et al.,\(^{38}\) who suggested that the esterification of cellulose should proceed from the surface of cellulose fibers to the core, producing somewhat of ‘skin-core structure.’ The lack of transition temperatures and the much reduced solvent resistivity would suggest that derivatized cellulose crystals could possess the aforementioned ‘skin-core structure.’ The d-spacings of the \(l_1 (1 1 0)\) and \(l_2 (2 0 0)\) reflection planes stayed constant but the crystallite size of the derivatized all-cellulose nanocomposites decreased compared to neat MCC and BC. This decrease in the crystallite size of the derivatized all-cellulose nanocomposites is in good agreement with the formation of a ‘skin-core structure’ of the modified cellulose crystallites.

**Thermal degradation behavior of (derivatized) MCC and BC**

Figure 5 shows the thermal degradation behavior in nitrogen of neat MCC, neat BC, C\(_6\)-MCC, and 5 wt.% BC-C\(_6\)-MCC. All samples underwent single-step degradation. A small mass loss can be observed at around 100 °C for neat MCC and BC. This is attributed to the loss of water from these samples. Hexanonyl esterified cellulose, on the other hand, is hydrophobic\(^{29}\) and, therefore, the initial mass loss due to water loss was not observed for C\(_6\)-MCC and 5 wt.% BC-C\(_6\)-MCC. The onset degradation (defined as the temperature where a sharp change in mass loss occurs) of C\(_6\)-MCC and 5 wt.% BC-C\(_6\)-MCC shifted to lower temperatures (see Table 1). This is thought to be due to the reduced crystallinity of the modified cellulose. Furthermore, the esterification reaction also the reduced number of effective hydrogen bonds between the cellulose fibers/crystals, which further reduces the thermal stability when compared to neat MCC and BC.

**Tensile properties of derivatized all-cellulose nanocomposites**

The tensile properties of derivatized all-cellulose nanocomposites are shown in Table 2. For comparison, we have also included the tensile properties of commercially available cellulose esters in Table 2 and the tensile properties of various all-cellulose (nano)composites in Table 3. C\(_6\)-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.\(^{29}\) with a similar DS. When C\(_6\)-MCC is reinforced with 5 wt.% esterified BC, the tensile modulus and strength increased to 1.42 GPa and 28.4 MPa, respectively. One of the most commonly used micromechanical models for the prediction of tensile moduli of randomly oriented short fiber composites is the Cox-Krenchel model,\(^{43, 44}\) which was developed based on classical shear-lag theory. It has recently been adopted to analyze the reinforcing efficiency of nanocellulose in various polymer matrices.\(^{24}\) The micromechanical model is written as:

\[
E_{\text{composite}} = \eta_i \eta_f v_f E_f + (1 - v_f) E_m
\]

where \(E_{\text{composite}}\) denote the predicted tensile modulus of the composite, fiber orientation factor, fiber volume fraction, tensile modulus of the fiber and matrix, respectively. The limited stress transfer efficiency caused by the fact that the reinforcing fibers have a finite length \(\eta_i\) can be obtained from ‘shear-lag’ model:

\[
\eta_i = 1 - \frac{\tanh(\frac{L}{d})}{\frac{L}{d}}
\]

\[
\beta = \frac{2}{d} \left[ \frac{2 \times G_m}{E_f \ln \left( \frac{r}{r_{\text{m,eff}}} \right)} \right]^{1.5}
\]

where \(L, d, G_m, X_i, \) and \(v\) denote the fiber length, fiber diameter, shear modulus of the matrix, packing of fibers in the composites and Poisson ratio of the matrix, respectively. In the original Cox publication,\(^{41}\) \(X_i = \sqrt{3}/2\) was used, assuming hexagonal packing of fibers with a mean centre-to-centre fibre spacing of \(R\). Previously we showed that the esterification of BC with hexanoic acid does not lead to changes in the morphology of BC.\(^{39}\) Therefore, our input parameters for equations (4)–(7) are \(E_m = 0.99\) GPa, \(d = 50\) nm, for the BC fibril length \(L\) we assume 1 \(\mu\)m and \(v = 0.34\). A predicted composite tensile modulus of 1.46 GPa was obtained, which is in good agreement with our experimental findings.

While both the tensile modulus and strength of the resulting BC-reinforced derivatized all-cellulose nanocomposites improved over C\(_6\)-MCC, the mechanical performance is still lower than that of the highest performing renewable polymer, polylactide (\(E = 4\) GPa, \(\sigma = 50\) MPa). It should be noted that the tensile properties of our composites are still comparable to commercially available cellulose esters (see Table 2). Nevertheless, the marginal improvements of \(E\) and \(\sigma\) upon
Figure 5  Thermal degradation behavior of \(a\) neat MCC, \(b\) C\(_6\)-MCC, \(c\) 5 wt.% BC-C\(_6\)-MCC and \(d\) neat BC, respectively, in nitrogen atmosphere

Table 2  Tensile properties of derivatized all-cellulose nanocomposites

| Sample                  | \(E\) (GPa) | \(\sigma\) (MPa) | \(\varepsilon\) (%) |
|-------------------------|-------------|-----------------|--------------------|
| 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          |
| Cellulose acetate\(^a\) | 1.90        | 38.1            |                    |
| Cellulose acetate propionate\(^a\) | 1.40 | 33.6            |                    |
| Cellulose acetate butyrate\(^a\) | 1.37       | 36.3            |                    |

Note: \(E\), \(\sigma\) and \(\varepsilon\) denote tensile modulus, tensile strength and engineering strain-to-failure, respectively.

\(^a\)Average data obtained from Matweb (http://www.matweb.com) based on molded polymers.

\(^b\)Values estimated from figures published.

Table 3  Tensile properties of all-cellulose nanocomposites manufactured by various authors. \(E\) and \(\sigma\) denote tensile modulus and strength, respectively.

| Source of cellulose | \(E\) (GPa) | \(\sigma\) (MPa) | Solvent used       | Ref |
|---------------------|-------------|-----------------|--------------------|-----|
| Ramie/Kraft pulp\(^a\) | 2.0\(^a\) | 48.0 ± 60       | LiCl/DMAc          |17  |
| Filter paper\(^a\) | 2.0\(^a\) | 40.0            | LiCl/DMAc          |18  |
| Linen flax         | 0.8         | 45              | Ionic liquid       |20  |
| Cordenka fibres    | 2.5         | 50              | Ionic liquid       |19  |
| MCC\(^c\)          | 2.57 ± 0.37 | 35.8 ± 4.4      | LiCl/DMAc          |17  |
|                     | 3.00 ± 0.37 | 49.7 ± 3.4      | LiCl/DMAc          |17  |
|                     | 1.82 ± 0.32 | 24.3 ± 7.5      | LiCl/DMAc          |17  |
|                     | 1.38 ± 0.74 | 15.5 ± 3.0      | LiCl/DMAc          |17  |
|                     | 1.65 ± 0.39 | 29.7 ± 6.2      | LiCl/DMAc          |17  |
|                     | 2.67 ± 0.30 | 62.7 ± 5.4      | LiCl/DMAc          |17  |
|                     | 2.17 ± 0.24 | 25.2 ± 4.0      | LiCl/DMAc          |17  |
|                     | 2.62 ± 0.49 | 10.1 ± 3.5      | LiCl/DMAc          |17  |
|                     | 2.02 ± 0.70 | 28.3 ± 9.4      | LiCl/DMAc          |17  |
|                     | 1.20 ± 0.17 | 20.9 ± 5.3      | LiCl/DMAc          |17  |
|                     | 3.18 ± 0.12 | 58.7 ± 3.9      | LiCl/DMAc          |17  |
|                     | 2.27 ± 0.43 | 22.5 ± 1.4      | LiCl/DMAc          |17  |
|                     | 1.78 ± 0.39 | 29.0 ± 4.9      | LiCl/DMAc          |17  |
|                     | 2.56 ± 0.43 | 48.8 ± 8.0      | LiCl/DMAc          |17  |
|                     | 2.97 ± 0.59 | 58.5 ± 7.9      | LiCl/DMAc          |17  |
|                     | 3.57 ± 1.07 | 21.7 ± 15.2     | LiCl/DMAc          |17  |
|                     | 7.37 ± 1.06 | 102.3 ± 21.6    | LiCl/DMAc          |17  |
|                     | 5.46 ± 0.82 | 105.3 ± 9.9     | LiCl/DMAc          |17  |
|                     | 5.52 ± 0.80 | 85.2 ± 9.0      | LiCl/DMAc          |17  |
|                     | 6.94 ± 0.74 | 105.7 ± 29.8    | LiCl/DMAc          |17  |
| MCC\(^d\)           | 0.8\(^b\)  | 35\(^b\)       | LiCl/DMAc          |21  |
|                     | 0.8\(^a\)  | 40\(^a\)       | LiCl/DMAc          |21  |
|                     | 1.2\(^a\)  | 55\(^a\)       | LiCl/DMAc          |21  |
|                     | 1.6\(^a\)  | 58\(^a\)       | LiCl/DMAc          |21  |
|                     | 1.8\(^a\)  | 60\(^a\)       | LiCl/DMAc          |21  |
| BC\(^e\)            | 16.0 ± 1.0  | 392 ± 23        | LiCl/DMAc          |22  |
|                     | 18.0 ± 0.8  | 411 ± 22        | LiCl/DMAc          |22  |
|                     | 16.0 ± 0.6  | 309 ± 25        | LiCl/DMAc          |22  |
|                     | 11.0 ± 0.6  | 188 ± 19        | LiCl/DMAc          |22  |
|                     | 4.4 ± 0.3   | 97 ± 16         | LiCl/DMAc          |22  |
|                     | 2.0 ± 0.4   | 75 ± 16         | LiCl/DMAc          |22  |
| MCC\(^f\)           | 12.1        | 218.6           | LiCl/DMAc          |24  |
|                     | 13.6        | 242.8           | LiCl/DMAc          |24  |
|                     | 14.9        | 215.1           | LiCl/DMAc          |24  |
| Beech pulp          | 12          | 154             | LiCl/DMAc          |24  |

\(^a\)Average data obtained from Matweb (http://www.matweb.com) based on molded polymers.

\(^b\)Values estimated from figures published.

\(^c\)Values estimated from figures published.

\(^d\)Values estimated from figures published.

\(^e\)Values estimated from figures published.

\(^f\)Values estimated from figures published.
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 to produce with performance that exceed polylactide, a BC loading of >30 vol.% should be used. Attempts were made to produce all-cellulose nanocomposites with higher BC loading. However, during the evaporation of toluene, the all-cellulose nanocomposites shrank and cracked severely, indicating the limitation of this technique to produce high-loading fraction BC-reinforced, cellulose crystal lattice-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 derivatized all-cellulose nanocomposites.

Conclusions

A novel method of producing derivatized all-cellulose nanocomposites is presented in this work. By modifying MCC in the presence of never-dried BC by esterification with hexanoic acid, even in the presence of 5 wt.% BC, the thermal degradation temperatures of C₆-MCC and 0.70, respectively. Such low DS explains the lack of glass shrinkage of the high BC loading-reinforced derivatized all-cellulose nanocomposites.

Acknowledgements

The authors would like to thank the UK Engineering and Physical Science Research Council (EPSRC) for funding this work (grant number EP/F028946/1).

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