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Thermoplastic polymer impregnation of cellulose nanofibre networks: Morphology, mechanical and optical properties

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ABSTRACT

Biobased nanocomposite sheets of cellulose nanofibres (CNF) and cellulose acetate butyrate (CAB) were prepared using resin impregnation. Porous nanofibre networks together with a low viscosity thermoplastic resin were the key elements in the processing. SEM images of the network before the impregnation showed high porosity and after the impregnation indicated impregnated fibre network. A significant improvement in the visible light transmittance was observed for the nanocomposite compared to the nanofibre network, which is explained on the filling of the pores with a transparent matrix. The tensile tests showed an increase of 364% and 145% for stiffness and strength respectively for nanocomposites with 60 wt.% CNF when compared to CAB. Dynamic mechanical properties showed a good interaction between the CAB and cellulose nanofibres. These results show that CAB impregnated cellulose nanofibre networks are promising biocomposite that could be used in applications where transparency and good mechanical properties are of interest.

1. Introduction

Cellulose nanofibres have great potential as reinforcements in polymers, offering a biobased alternative to glass fibre reinforced materials. Several stiff, strong composites based on cellulose nanofibres with high volume fractions have been produced over the last decade [1–3]. Due to the size of the nanofibres in a number of these materials the optical transparency is high, despite the high fibre volume fraction. The composites used in these studies [1–3], however, use low viscosity thermoset polymers such as epoxy, acrylic and polyurethane as well as melamine or phenol formaldehyde. The aim of this study is to produce a cellulose nanocomposite with good mechanical and optical properties based on a biobased thermoplastic. In recent studies CAB has shown to have a good reinforcing effect with cellulose nanocrystals (CNC) at low volume fraction using different manufacturing processes. Examples of these processes are a sol–gel based method [4] and extrusion [5]. CAB has also been used with cellulose nanofibres from bacteria (BC) to produce high volume fraction composites with high strength and stiffness [6] using an impregnation method where the dry network is impregnated with a dilute CAB–acetone solution. CAB is a thermoplastic polymer produced through esterification and plasticization of highly purified cellulose and has a biobased content of 60%. It has been found to have excellent optical clarity, moderate heat and impact resistance as well as high moisture vapour transmission and is being used in several applications, such as coatings, films, and in medical applications [7].

The nanocellulose used in the CAB nanocellulose composite discussed has been from either cellulose nanocrystals or bacterial cellulose. However, of particular interest to the pulp industry and to biorefineries is the exploitation of cellulose side streams. Earlier work has shown that mechanical grinding of dissolving cellulose side-streams produces cellulose nanofibres and that networks formed from these fibres have good strength (96 MPa) and stiffness (8 GPa) [8]. This study also showed that the use of this raw material allows the isolation of cellulose nanofibres without any pre-treatments, thus increasing the efficiency of the nanocellulose production. Of interest is therefore the use of these CNF as reinforcing elements in CAB, with the aim of producing a composite with a high biobased content, good mechanical and optical properties from waste cellulose side streams. Since the stiffness and strength of the composite comes from the fibres, a high fibre volume fraction is required.

The challenge is therefore to produce a nanocomposite from CNF with high volume fraction, which typically has a very low porosity, as shown by the air permeance values [8], and impregnate this with a thermoplastic matrix, in this case CAB. The approach taken here was to create a more porous network by drying the network from acetone and to use a very dilute, low viscosity CAB solution to impregnate this porous network. Porous CNF networks with 40% porosity have earlier been produced by Henriksson et al. [9]. Consolidation of the composite by compression

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molding was then carried out to increase the volume fraction of the composite as well as to increase its transparency. This cellulose nanocomposite was then evaluated by mechanical and light transmittance testing and the underlying morphology studied. DMTA testing was carried out to evaluate the molecular interaction between the CAB and the CNF as well as the thermal stability of the nanocomposite.

2. Experimental

2.1. Materials

Reinforcement: Never-dried cellulose residue from dissolving cellulose was obtained from Domsjö Fabriker AB, Örnsköldsvik Mill, Sweden. The residue is a solid waste product from the industrial wastewater from a dissolving cellulose mill. Earlier work on this residue has shown it to have a high cellulose content (95%) and very low lignin content [8].

Cellulose nanofibres were isolated from this residue using the method reported by Jonoobi et al. [8]. Thus a suspension was made of 3 wt.% fibres dispersed in water using a mechanical blender (Silverson L4RT, England) at 3000 rpm for 10 min. Afterwards, the suspension was ground using a ultra-fine grinder, MKCA 6–3 from Masuko (Japan) at 1440 rpm in contact mode to obtain nanofibres. The nanofibres were then diluted to a concentration of 0.1% for nanofibre network preparation.

Matrix: Cellulose acetate butyrate (CAB-553-0.4) was selected as the polymer resin and was supplied by Eastman Chemical Company (Kingsport, USA). This CAB has an acetyl content of 2.0 wt.%, butyryl 46 wt.% and hydroxyl content of 4.8 wt.%. The high hydroxyl content contributes to its solubility in both ethanol and acetone. It has a melting point in the range of 150–160 °C, as reported by the material supplier. Acetone (VWR International, USA, purity ⩾99%) was used as a solvent for the polymer and also as a medium to create the porous nanofibre network.

Plasticizer: Cellulose acetate butyrate is a brittle polymer, therefore the plasticizer, triethyl citrate (TEC) C12H20O7 (VWR International, USA, purity 98%) was added. Triethyl citrate is environmentally friendly and is compatible with all cellulose esters.

2.2. Processing of CAB/CNF nanocomposite

Fig. 1 shows the schematic of the nanocomposite preparation process including the nanofibre network and impregnation. First, to form the network, the water was removed from the nanofibre suspension (0.1% by weight) through filtration with a Buchner funnel fitted with Whatman filter paper (diameter 125 mm), which

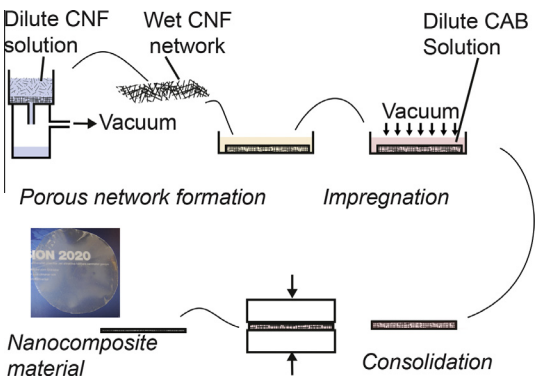

Fig. 1. Schematic diagram of the nanocomposite preparation process, showing the network and impregnation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was connected to a Buchner flask and a vacuum pump. The filtration was continued until the wet network of nanofibres was formed. This wet network was immediately immersed in acetone, covered and left at room temperature for 24 h, in a similar way to the method reported by Henriksson et al. [9]. After immersion in acetone, the network was placed between two filter papers. This stack was then placed between two metal plates and weighted with a mass of 12.5 kg. This assembly was dried at room temperature overnight followed by oven vacuum drying at 55 °C for 8 h at 0.2 mPa. The porosity, P, of the network, was calculated from the bulk volume of the network, V_N. V_N was measured from the mass of mercury displaced when samples of the network were immersed in mercury, M_{Hg}, following a similar system to that used by the measurement of porosity in cellulose fibre paper [10]. Knowing the mass of the immersed samples, M_f, assuming the density of fibres, ρ_f, is 1.5 g cm^{-3} [11] and the density of mercury, ρ_{Hg}, is 13.5 g cm^{-3} the porosity was calculated from

$$P = (M_f \rho_{Hg})/(M_{Hg\rho_f}) \quad (1)$$

The dried cellulose nanofibre network was then impregnated by submerging the network in a diluted solution of 1.75 wt.% CAB and 0.25 wt.% TEC dissolved in a solvent of acetone. The viscosity of this solution was 20 mPas at 20 °C measured using a SV-10 viscometer (Malvern, UK). The impregnation was carried out under vacuum conditions (0.2 MPa) for approximately 12 h, after which the acetone had evaporated. These vacuum conditions were obtained by containing the submersed network in a glass jar, evacuating the air from the jar until the pressure required was reached, and then sealing it. With the acetone evaporated and the network impregnated, the composite was compression molded using a temperature controlled Fontijne Grotnes press LP-300 (Vlaardingen, Netherlands) by preheating the material under contact mode at 150 °C for 2 min to melt the polymer followed by compression under a load of 100 kN for 2 min. The produced composite sheet had a thickness of 0.2 mm and the final nanocomposite had a composition of 60 wt.% fibre, 35 wt.% CAB and 5 wt.% TEC

2.3. Material characteriation

2.3.1. Microscopy

The morphology of nanofibres was studied using an atomic force microscope Nanoscope V Microscope (Veeco Instrument Inc, Santa Babara, CA, USA). Samples for AFM imaging were prepared by depositing a drop of a diluted suspension of nanofibres onto freshly cleaved mica that was then allowed to dry at room temperature. This sample was then imaged in tapping mode and height and amplitude images were collected. The morphology of the nanofibre networks as well as the fractured surface of CAB and its nanocomposite was investigated at room temperature using a high-resolution scanning electron microscope (XHR-SEM FEI Magellan TM 400 L, Brno, Czech Republic) with an acceleration voltage of 5 kV. The samples were sputter coated with gold to avoid charging.

2.3.2. UV–Vis spectroscopy

A Perkin Elmer UV–Vis spectrophotometer Lambda 2 S (Uberlingen, Germany) was employed to measure the light transmittance of the samples in the wavelength range of 300–900 nm. Three samples of each material were studied.

2.3.3. Tensile testing

The tensile tests of the CAB, the CNF network and CAB/CNF composite were performed using a universal testing machine (Shimadzu Autograph AG-X, Japan) with a load cell of 1 kN. The testing was performed at a constant crosshead speed of 2 mm/min at room