Re-dispersible carrot nanofibers with high mechanical properties and reinforcing capacity for use in composite materials

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ABSTRACT

The separation of nanofibers from carrot juice residue and their reinforcing potential is demonstrated. Morphological properties, X-ray diffraction (XRD), and specific surface area (SSA) measurements showed that carrot nanofibers (CNF) have maintained the crystalline structure of native cellulose, while presenting a SSA as high as 246 $m^2.g^{-1}$ and diameters between 3 and 36 nm. CNF could be redispersed in water after drying, giving nanofibers with SSA and diameter comparable to properties of initial never-dried CNF. Finally, we propose possible uses of CNF either as strong nanopaper with excellent mechanical properties, i.e. modulus of 13.3 GPa and strength of 175 MPa, or as reinforcing phase in polymer matrices (CAB). Interesting properties of carrot nanofibers in terms of their possible transport and use from the dry state, as well as their remarkable mechanical properties afforded to nanopaper and nanocomposites may promote their use in environmentally benign constituent in industrial applications.

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1. Introduction

Carrot is an important root vegetable and it is often used for juice production [1]. After juicing, around 30–50% of carrot remained as a juice by-product [2]. Although thousands of tons of carrot residue produced in the process of juice extraction can be utilized for animal feed, this agricultural by-product is usually discarded as waste material. The high organic matter content present in that kind of waste generally causes undesirable environmental problems [1,3]. Carrot residue (dry) has been reported to contain cellulose (81%), hemicelluloses (9%), lignin (2.5%) and pectin (7.5%) [4,5]. The residue also contains small amounts of proteins, lipids and carbohydrates, carotenes and minerals like Ca, P, Fe and Mg [3,5]. The primary walls of plant cells usually consist of rigid cellulosic nanofibers embedded in a hemicellulose and pectin matrix [6,7]. These nanofibers have diameters raging of 3–20 nm and lengths of up to several micrometers depending on their origin [8,9]. Each nanofiber can be considered as a string of cellulose crystals linked along the fiber axis by disordered amorphous domains [10], e.g. twists and kinks [11]. *In vivo*, cellulose nanofibers presents a predicted stiffness of 130 GPa and strength in the range of 7–8 GPa [12]. However the network of cellulose nanofibers has considerably lower elastic modulus. Abe and Yano [13] have compared the mechanical properties of cellulose nanofibers networks from three different sources, namely wood pulp, rice straw and potato tuber. The measured mechanical properties of the networks had similar properties; the E-modulus was about 11 GPa. Henriksson et al. [14] reported that networks made of cellulose nanofibers, pre-treated with enzymes prior to the mechanical separation, can have a modulus of 14.7 GPa and the modulus values decreased with increased porosity. Due to the high mechanical properties of the cellulose nanofibers, many researchers have utilized them as reinforcing phase in polymer nanocomposites [15–19]. Different mechanical processes to separate cellulose nanofibers are reported in the literature. Usually, repeated mechanical treatments using high-pressure homogenizer, microfluidizer, grinders, cryo-crushing, or ultrasonic are required to individualize the nanofibers [18–27]. Nakagaito et al. [19] indirectly evaluated the degree of fibrillation of wood pulp, passing through a high pressure homogenizer from 2 to 30 times. It was observed that the disintegration was improved by increasing the number of passes to 30 times. It is not difficult to conclude that higher number

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of passes results in an increased energy necessary to isolation of nanofibers. Therefore, some pretreatments such as enzymatic acid hydrolysis, and TEMPO-mediated oxidation are being used in order to facilitate the disintegration of cellulose fibers to nanoscale and also to decrease the energy consumption of the process [14,21,27,28]. In general, excessive treatments and passes through grinders and/or homogenizers required to isolate fine cellulose nanofibers can reduce the crystallinity and the degree of polymerization of cellulose chains, leading to degradation of mechanical properties of isolated nanofibers [13,22]. Here, we report the isolation of carrot nanofibers from a residue of carrot juice process. Extensive characterization of the new cellulose nanofibers revealed that carrot nanofibers have unique properties and low energy consumption in the separation process, with potential application in high-performance polymer nanocomposites. Thus, the reinforcing capability of carrot nanofibers in thermoplastic cellulose based polymer (CAB) is demonstrated.

2. Experimental section

2.1. Materials

Carrots, purchased from the local market, were used as raw material for the juicing. Carrot pulps obtained after juicing were washed with distilled water at 85 °C for 2 h. Thereafter the pulp was treated with a 2 wt% NaOH solution at 80 °C for 2 h under mechanical stirring, in order to purify cellulose by removing other constituents present in the pulp. The material was then filtered and washed with distilled water until the alkali was completely eliminated. A subsequent bleaching treatment was carried out to remove non-cellulosic components such as lignin, tannin and beta-carotene. The solution used in this treatment consisted of equal parts of acetate buffer, aqueous chlorite (1.7 wt% in water) and distilled water. The bleaching treatment was performed at 80 °C for 2 h under mechanical stirring. Once again the material was filtered and washed with distilled water.

Cellulose acetate butyrate (CAB-553-0.4), supplied by Eastman Chemical Company (Kingsport, USA) was used as polymer matrix for prepared nanocomposites. The used CAB has a glass transition temperature of 136 °C and a melt temperature around 150 °C, as reported by the supplier. Cellulose acetate butyrate is a thermoplastic polymer, based on cellulose (60%) and it is soluble in ethanol. Further more a good compatibility between the matrix and the cellulose nanofiber is expected.

Ethanol absolute (100%) purchased from VWR, was used as solvent for the CAB and for the solvent exchange of carrot nanofibers.

Bleached carrot pulp was first disintegrated by a high-shear mixing (Silverson L4RT, Silverson Machine Ltd., England), using 2 wt% concentration. The pulp was ground using a supermass colloider (MKCA6-2, Masuko Sangyo, Japan) and passed through the instrument for 20 min. The grinding was done in contact mode and the gap between the discs was adjusted to 10 μm. The ground fibers were homogenized using a two-chamber high-pressure homogenizer (APV-2000, Denmark) after being diluted with water to 0.1% consistency and passed through the instrument up to 5 times. The pressure was kept at 600 bars in both chambers.

Fiber networks (nanopapers) of carrot nanofibers were prepared by vacuum filtration of a diluted suspension (0.5 wt%). The suspension was filtrated on a Büchner funnel using Whatman filter paper number 5. After filtration, the wet films were stacked between filter papers and placed between two metal plates and dried at 90 °C for 2 h, at pressure of 20 bar. The dried nanopapers were cut in small pieces for the redispersion study. The pieces were swollen in water in order to make a 1% wt suspension and mixed with ultra-turrax for 5 min, at room temperature and 10,000 rpm.

For the nanocomposites preparation, carrot nanofibers (CNF) in aqueous medium were solvent exchanged to ethanol by successive centrifuge procedures. Polymer matrix (CAB) was first dissolved in ethanol. The solution 15 wt% was magnetically stirred for 12 h at room temperature. Dissolved CAB suspensions were mixed with the appropriate amount of carrot nanofibers to achieve final nanocomposites concentration of 3, 6, 9 and, 12 wt%. The CAB/CNF suspensions were homogenized by magnetic stirring for 4 h, followed by sonication (UP 400S Hielscher Ultrasonics, Germany) for 3 min, to ensure good dispersion of nanofibers in CAB. The CAB/CNF suspensions were then cast in polystyrene Petri dishes and were left to evaporate for 24 h in a preheated vacuum oven at 60 °C. In the first 3 h, the pressure of the vacuum oven was controlled to 200 mbar in order to avoid formation of air bubbles; thereafter, the pressure was increased to 850 mbar and maintained for 20 h. The neat CAB solution was exposed to the same procedure. The CAB and the nanocomposite films were removed from the Petri dishes using water and were placed into the vacuum oven, at 70 °C and 0 mbar, for one week to remove the remaining solvent.

The volume fractions of carrot nanofibers were calculated using the Eq (1),

$$\emptyset = (w_r/\rho_r) \, / \, ((w_r/\rho_r)+ (1\text{-} \, w_r)/\rho_m) \qquad (1)$$

where, w_r is weight % of reinforcements, ρ_r represent the density of the fibers (1.58 g/cm^3) and ρ_m is the density of the matrix polymer (1.2 g/cm^3). The volume fractions of nanofibers were determined to be 2.4, 5.3, 8.7 and 10 vol%, respectively.

2.2. Characterization

Scanning Electron Microscopy (SEM) images were acquired with a FEI NovaNano SEM (FEI Company, USA), equipped with Schottly field emission gun. An acceleration voltage of 5.0 kV and working distance of 4.6—5.0 mm were used in the experiments. The samples were frozen in liquid nitrogen, fractured, mounted on a sample holder and coated with gold layer of 5 nm.

Atomic Force Microscopy (AFM) was performed on a Multimode Scanning Probe Microscope with a Nanoscope V (Veeco Instruments USA) using an etched silicon tip with a nominal spring constant of 5 N/m and a nominal frequency of 70 kHz. Height, phase and amplitude images were obtained in tapping mode at the resonance frequency of the cantilever with a scan rate of 0.5 line/s. Prior to AFM analysis a drop of a diluted suspension was deposited on a mica surface and allowed to dry at room temperature.

X-ray diffraction (XRD) analyses of prepared nanopapers were recorded on a Philips X'pert Multipurpose X-ray Diffraction System (MPD) at a speed rate of 0.05°/sec and a range from 5 to 45° (2θ). Crystallinity index was calculated from the X-ray diffraction patterns according to the following equation [29]:

$$Cr \, I = \frac{I_{002} - I_{am}}{I_{002}} \qquad (2)$$

where I_{002} and I_{am} are the intensities of the peaks at 2-θ of about 22 and 18, respectively.

Brunauer—Emmett—Teller specific surface area (BET) of CNF was determined by nitrogen physisorption on a surface area and pore size analyzer (Coulter SA3100) by subjecting the CNF suspension beforehand to supercritical drying as reported elsewhere [30].

Mechanical properties of the nanopapers were measured using an Instron 3366 machine equipped with 1 kN load cell. The tensile tests were conducted at constant speed of 2 mm/min, at relative humidity of 35% and room temperature (25 °C). The samples were