Food Hydrocolloids 79 (2018) 30–39

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Improved redispersibility of cellulose nanofibrils in water using maltodextrin as a green, easily removable and non-toxic additive

J. Velásquez-Cock [a], P. Gañán [b], C. Gómez H. [c], P. Posada [c], C. Castro [d], A. Dufresne [e], R. Zuluaga [a, *]

[a] Facultad de Ingeniería Agroindustrial, Universidad Pontificia Bolivariana, Circular 1° N° 70-01, Medellín, Colombia
[b] Facultad de Ingeniería Química, Universidad Pontificia Bolivariana, Circular 1° N° 70-01, Medellín, Colombia
[c] Programa de Ingeniería en Nanotecnología, Universidad Pontificia Bolivariana, Circular 1° N° 70-01, Medellín, Colombia
[d] Facultad de Ingeniería Textil, Universidad Pontificia Bolivariana, Circular 1° N° 70-01, Medellín, Colombia
[e] Université Grenoble Alpes, CNRS, Grenoble INP, LGP2, F-38000 Grenoble, France

ARTICLE INFO

Article history:
Available online 28 December 2017

Keywords:
Cellulose nanofibrils
Redispersion
Hornification
Maltodextrin

ABSTRACT

The irreversible aggregation of cellulose nanofibrils (CNFs) during their dehydration or hornification, increases their commercialization costs, restricting their storage and transportation to cellulosic suspensions. This issue has prompted the development of different alternatives in literature; some of them require energy intensive treatments for their redispersion or the use of additives which are not convenient for food or pharmaceutical related applications. To overcome these problems, the present work evaluates the use of maltodextrin (MDX) as a capping agent to avoid CNFs hornification. Different nanocellulose to MDX (N:M) ratios were evaluated. The physico-chemical, morphological and rheological properties of ensuing samples were analyzed. Infrared spectroscopy and thermal analyses indicate a complete removal of MDX after cellulose isolation. A suspension stability comparable to the never-dried product was achieved when using a N:M ratio beyond 1:1.5, and it was maintained up to a ratio of 1:2.5. Morphological and rheological data agree with these results.

1. Introduction

Cellulose nanofibrils (CNFs) are a nano-sized material obtained from the deconstruction of plant-derived cellulose fibers. It is characterized by lengths from several hundred nanometers to micrometers and diameters between 5 and 100 nm (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). This high aspect ratio is coupled with a rheological storage modulus (G′) in the order of 10^5 Pa for a 5 wt.% aqueous suspension (Pääkkö et al., 2007), and interesting properties for films obtained from CNFs, such as an elastic modulus of 13 GPa (Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008), high light transmittance (Okahisa, Yoshida, Miyaguchi, & Yano, 2009) and low oxygen permeability (Aulin, Gällstedt, & Lindström, 2010).

The broad array of properties of CNFs allows the use of this nanomaterial in a wide range of applications, such as nanocomposites (Lavoine, Desloges, Dufresne, & Bras, 2012), electronic (Okahisa et al., 2009; Zhang et al., 2016) and medical devices (Siró & Plackett, 2010), paper coating (Hamada, Tahara, & Uchida, 2012), paper filler (Shatkin, Wegner, Bilek, & Cowie, 2014), reinforcement in cementitious materials (Peters, Rushing, Landis, & Cummins, 2010), controlled drug release (Ioelovich & Figovsky, 2008), food packaging (Siró & Plackett, 2010) and rheological modifier of food (Gómez H. et al., 2016), among others. Its versatility is coupled with its availability, as it was estimated that plants synthesize nearly 10^{12} t of cellulose annually (Huber et al., 2011; Klemm, Heublein, Fink, & Bohn, 2005).

The aforementioned characteristics prompted the construction of pilot plants in Canada, the United States of America, Japan, Sweden and Finland (Meyer, Tapin-Lingua, Da Silva Perez, Arndt, & Kautto, 2012; Rebouillat & Fernand, 2013), which is the first step in the commercialization of this nanomaterial. It is predicted that by 2024 its demand will be near 33,000 t (Cowie, Bilek, Wegner, & Shatkin, 2014).

In spite of the improvements toward the reduction of production costs and industrial applications of CNFs, there are different challenges that must be solved in order to achieve a successful

* Corresponding author.
E-mail address: robin.zuluaga@upb.edu.co (R. Zuluaga).

https://doi.org/10.1016/j.foodhyd.2017.12.024
0268-005X/

commercialization. Among these issues, the irreversible formation of hydrogen bonds and van der Waals interactions between the fibrils during their dehydration, or hornification (Déléris & Wallecan, 2017), could jeopardize the large-scale distribution of CNFs in the short-term, as the nanomaterial must be shipped as wet suspensions, with high water contents (Eyholzer et al., 2009; Missoum, Bras, & Belgacem, 2012). The wet storage of CNFs increases its transportation cost (Butchosa & Zhou, 2014) and allows the growth of different microorganisms in the suspension (Béguin & Aubert, 1994).

These disadvantages have prompted the study of different alternatives to solve cellulose hornification. Peng et al. (2013) studied various dehydration methods, reporting a decrease in the fibril agglomeration by capillary forces when using freeze-drying compared to oven and spray-drying. These type of agglomerations were absent for supercritical drying. However, none of the studied methods could recover the characteristics of the original suspension after rehydration. On another hand, Jiang and Hsieh (2014) have studied the effect of the freezing temperature in a freeze drying process of cellulose nanocrystals (CNCs) and CNFs obtained by pre-treating the samples with a (2,2,6,6-tetramethylpiperidine-1-oxyl) radical (TEMPO)-mediated oxidation. The authors noted a lower agglomeration when the suspension was frozen at −196 °C before sublimating the water. The effect of *tert*-butanol in the aqueous medium resulted in the presence of a narrower dehydrated product, as water crystallizes in needle shaped rather than hexagonal crystals, diminishing the displacement of the fibrils associated to the formation of ice crystals (Jiang & Hsieh, 2014).

Another alternative, proposed by Eyholzer et al. (2009) consists in the chemical modification of CNFs by carboxymethylation, therefore avoiding the formation of interfibrillar hydrogen bonds, while Yan et al. (Yan et al., 2016) performed a solvent exchange, followed by the addition of alkyl ketene dimer (AKD) in ethyl acetate and 1-methylidazole as catalyst at 60 °C. After oven-drying the samples, the authors reported the formation of a fluffy cake which was composed of highly hydrophobic CNFs, whose contact angle with water was above 100°. The resulting product was useful to incorporate CNFs in polymeric matrix composites (Yan et al., 2016).

Other attempts have tried to incorporate additives to prevent the hornification of CNFs. Missoum et al. (Missoum et al., 2012) used sodium chloride in freeze-dried cellulose at different pHs. It was reported that sodium ions screened the negative charges from oxygen, while chloride screened the positive charges, blocking the hydrogen bonding. Suspensions were redispersed by mechanically stirring the samples at 10,000 rpm in a rotor-stator system for a short time, followed by dialyzing the suspension against deionized water, to remove the residual salt (Missoum et al., 2012).

Another approach was proposed by Butchosa and Zhou (Butchosa & Zhou, 2014), who adsorbed carboxy-methylcellulose (CMC) over CNFs previous to their dehydration. The authors redispersed the dried product by magnetically stirring it overnight and mechanically mixing at 10,000 rpm in a rotor-stator system for 15 min. To achieve a successful redispersion, an adsorption level of 23 mg_{CMC}/g_{CNFs} was required (Butchosa & Zhou, 2014). On another hand, Fairman (Fairman, 2014) evaluated cetyl trimethylammonium bromide (CTAB), as its cationic nature favored its adsorption over the cellulosic surface. A content of 5 wt.% CTAB was required to redisperse the dehydrated CNFs, while lower quantities of the surfactant failed to reconstitute the properties of the original product after rehydrating the samples.

Some of these alternatives show important advances in the redispersion of CNFs. Nevertheless, some of them require energy-intensive methods of redispersion or might use an additive that is inadequate or toxic for food and pharmaceutical-related applications, as is the case for CTAB (Isomaa, 1975), restricting its use in some of the most promising sectors for new developments of CNFs (Gómez H. et al., 2016).

The present work attempts to evaluate the use of a capping agent to avoid hornification of CNFs. Maltodextrin (MDX) was chosen as it is approved by the Food and Drug Administration of the United States of America (FDA) to be used as a food additive, and is generally recognized as a safe (GRAS) material (Castro, Durrieu, Raynaud, & Rouilly, 2016). Also, it has been used in a previous study to control mild hornification in microcrystalline cellulose (MCC) during spray drying (Buliga, Tuason, & Venables, 2002).

To study the influence of MDX in the hornification of oven-dried CNFs, different nanocellulose to maltodextrin (N:M) ratios were evaluated from 1:1 to 1:2.5. These mixtures were oven-dried and redispersed with a mild mechanical treatment, followed by isolating the redispersed CNFs with hot water. The resulting suspensions were analyzed in their stability, physico-chemical, thermal, morphological and rheological properties, to evaluate the changes exerted during drying, redispersion and isolation processes. The analysis was conducted via sedimentation, attenuated total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA), colorimetric and rheological measurements and field-emission scanning electron microscopy (FE-SEM).

2. Materials and methods

2.1. Materials

Ground rachis from banana plants (c.v. *Valery*) harvested in Antioquia, Colombia, was provided by Banacol S.A. Potassium hydroxide and sodium chloride, reagent grade; sodium chlorite, synthesis quality; glacial acetic acid, fuming hydrochloric acid and Congo red were manufactured by Merck and purchased from a local provider.

Maltodextrin, derived from the enzymatic hydrolysis of native cornstarch (Dextrose equivalent: 19), commercial grade was obtained from a local provider, TECNAS S.A.

2.2. Methods

2.2.1. Cellulose nanofibrils isolation

Ground banana rachis was chemically isolated by the treatment KOH-5, described elsewhere (Zuluaga et al., 2009). Briefly, ground banana rachis was subjected to an alkaline hydrolysis with a KOH solution (5 wt.%) at room temperature for 14 h, to remove part of the lignin and hemicelluloses. It was followed by a delignification treatment with acidified sodium chlorite and a second alkaline treatment with a KOH solution (5 wt.%) for 14 h. Finally, a demineralization treatment was performed with HCl (1 wt.%) for 2 h at 80 °C. The cellulose-rich product was mechanically processed according to (Velásquez-Cock et al., 2016), by passing a 2 wt.% cellulosic material 30 times through a grinding equipment (G30).

The cellulosic product was composed of an entangled network of CNFs, CNFs bundles and sub-fibrillated material, with most of the CNF's diameters in the 10–40 nm range, while there were some minor fractions above 100 nm and below 10 nm (Velásquez-Cock et al., 2016). The DPv of CNFs was 742 ± 19 (Velásquez-Cock et al., 2016) and their neutral sugar profile was composed of glucose (73.91 wt.%), xylose (19.11 wt.%) and mannose (5.85 wt.%) (Zuluaga et al., 2009). The pH of the suspension was 6.59 ± 0.26, and the measured pH was not adjusted.