



# Nanocomposites with functionalised polysaccharide nanocrystals through aqueous free radical polymerisation promoted by ozonolysis



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## ABSTRACT

Cellulose nanocrystals (CNC) and starch nanocrystals (SNC) were grafted by ozone-initiated free-radical polymerisation of styrene in a heterogeneous medium. Surface functionalisation was confirmed by infrared spectroscopy, contact angle measurements, and thermogravimetric and elemental analysis. X-ray diffraction and scanning electron microscopy showed that there was no significant change in the morphology or crystallinity of the nanoparticles following ozonolysis. The grafting efficiency, quantified by <sup>13</sup>C NMR, was greater for SNC, with a styrene/anhydroglucose ratio of 1.56 compared to 0.25 for CNC. The thermal stability improved by 100 °C. The contact angles were 97° and 78° following the SNC and CNC grafting, respectively, demonstrating the efficiency of the grafting in changing the surface properties even at low levels of surface substitution. The grafting increased the compatibility with the polylactide, and produced nanocomposites with improved water vapour barrier properties. Ozone-mediated grafting is thus a promising approach for surface functionalisation of polysaccharide nanocrystals.

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## 1. Introduction

Nanopolysaccharide materials, such as cellulose nanocrystals (CNC) or starch nanocrystals (SNC), exhibit unique features, such as excellent mechanical properties, availability, renewability, tunable morphologies and shapes, and high aspect ratios. These features

*Abbreviations:* AFM, atomic force microscopy; AGU, anhydroglucose monomer unit; CCD, charge-coupled device; CNC, cellulose nanocrystals; CNC–OOH, CNC hydroperoxide; CP/MAS, cross-polarisation/magic angle spinning; FEG-SEM, field-emission gun scanning electron microscopy;  $I_c$ , crystallinity index;  $I_1$ ,  $I_2$ , two X-ray intensities; IR, infrared spectroscopy;  $l$ , film thickness; MCC, microcrystalline cellulose; NMR, nuclear magnetic resonance;  $P$ , permeability; PLA, poly(lactic acid); PSty, polystyrene; RH, relative humidity;  $S$ , exchange surface area; SNC, starch nanocrystals; SNC–OOH, SNC hydroperoxide; Sty, styrene monomer unit; TGA, thermogravimetric analysis; TMS, tetramethylsilane;  $W_{sl}$ , work of adhesion; WVTR, water vapour transmission rate; XRD, X-ray diffraction;  $\gamma_{lv}$ , liquid–vapour surface tension;  $\gamma_{sl}$ , solid–liquid surface tension;  $\gamma_{sv}$ , solid–vapour surface tension;  $\Delta P$ , gradient for partial pressure of water;  $\theta_y$ , contact angle;  $\chi_c$ , crystallinity index.

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have attracted significant academic interest, resulting in several reviews and books on bio-based nanomaterials (Dufresne, 2012; Habibi, Lucia, & Rojas, 2010; Le Corre, Bras, & Dufresne, 2010). In particular, nanopolysaccharides are used in composite materials as reinforcing agents (Siqueira, Bras, & Dufresne, 2010) and as novel functional materials (Habibi et al., 2010), or can be chemically functionalised because of the hydroxyl groups at their surface (Angellier, Molina-Boisseau, Belgacem, & Dufresne, 2005; Lam, Male, Chong, Leung, & Luong, 2012; Tomasik & Schilling, 2004). The functionalities arising from the grafting on the surface of the polysaccharide nanoparticles produce materials with mechanical adaptability (Capadona, Shanmuganathan, Tyler, Rowan, & Weder, 2008), pH responsiveness (Way, Hsu, Shanmuganathan, Weder, & Rowan, 2012), support for enzyme immobilisation (Mahmoud, Male, Hrapovic, & Luong, 2009), induction of electron conduction in bacterial cellulose (Yoon, Jin, Kook, & Pyun, 2006), antimicrobial properties (Drogat et al., 2011), the creation of hybrid CNC–DNA complexes (Mangalam, Simonsen & Benight, 2009; Moss, Moore, & Chan, 1981), bioimaging fluorescent properties (Dong & Roman, 2007), and that can be used for drug delivery (Román-Aguirre,

Dong, Hirani, & Lee, 2010). Functionalised SNCs have also been used in the development of hydrogels (Zhang et al., 2010) and aerogels (García-Gonzalez, Alnaief, & Smirnova, 2011).

There has been considerable effort devoted to the functionalisation of polysaccharide nanoparticles with polymers to develop hydrophobic polysaccharides. This should enhance their compatibility with hydrophobic polymer matrices to improve the mechanical, thermal, and/or barrier properties of the nanocomposites. For example, polymers such as polylactides (Braun, Dorgan, & Hollingsworth, 2012; Goffin et al., 2011; Peltzer, Pei, Zhou, Berglund, & Jimenez, 2014), polycaprolactone (Goffin, Habibi, Raquez, & Dubois, 2012; Tian, Fu, Chen, Meng, & Lucia, 2014), poly(hydroxybutyrate) (Wei, McDonald & Stark, 2015), polypropylene (Ljungberg, Bonini, Bortolussi, Boisson, Heux, & Cavaillé, 2005), poly(ethylene oxide) (Kloser & Gray, 2010), poly(2-ethyl-2-oxazoline) (Tehrani & Neysi, 2013), polyurethane (Cao, Habibi, & Lucia, 2009) and polystyrene (Yi, Xu, Zhang, & Zhang, 2008) have been grafted onto CNC. Furthermore, other grafting techniques, such as click chemistry (Chen, Lin, Huang, & Dufresne, 2015) and single-electron transfer living radical polymerisation (Wu, Xu, Zhuang, & Zhu, 2015) have been used. Despite the low degradation temperature of the SNC, some success has also been reported for the grafting of polylactide (García, Lamanna, D'Accorso, Dufresne, Aranguren, & Goyanes, 2012), polycaprolactone (Labet, Thielemans, & Dufresne, 2007; Yu, Ai, Dufresne, Gao, Huang, & Chang, 2008), polytetrahydrofuran, and poly(ethylene glycol) (Labet, Thielemans, & Dufresne, 2007).

Surface chemical modification using polymers can be implemented by using either a “grafting-to” or “grafting-from” method. The first method involves the direct grafting of organic molecules via a reaction with the available hydroxyl groups on the surface of the polysaccharide nanoparticles. The main disadvantage of this method is that the grafting of large molecules, such as polymers, rapidly results in the steric hindrance of reactive sites, and consequently produces a very low yield. For this reason, the “grafting-from” approach has been widely used. Here, the first stage involves the grafting of the monomer onto the polysaccharide surface and the second stage involves its polymerisation. This method achieves a greater grafting density and improved control of the reaction (O'dian, 2004). However, most of the published “grafting-from” techniques employ organic solvents and harsh energy-intensive conditions, such as high temperatures or pressures (Roy, Guthrie, & Perrier, 2005). This topic has been reviewed for cellulose (Roy, Semsarilar, Guthrie, & Perrier, 2009), starch (Athawale & Rath, 1999), and for nanoscale cellulose (Lin, Huang, & Dufresne, 2012; Missoum, Belgacem, & Bras, 2013).

To develop reactions that comply with the principles of green chemistry (Anastas & Kirchhoff, 2002), grafting should be performed in an aqueous medium, with the efficient activation of substrates generating few, if any, residues. The use of ozone as an activator to graft polysaccharides was first reported in the 1950s (Borunsky, 1957; Kargin, Koslov, Plate, & Konoreva, 1959). Ozone is cheap, used industrially, can be used in aqueous solvents, and leaves no residues. Furthermore, the oxygen-containing radicals produced by ozone react with a large variety of monomers. There are a few reports on the production of cellulose and starch grafted copolymers using ozone activation (Bataille, Dufourd, & Sapieha, 1994; De Bruyn, Sprong, Gaborieau, Roper, & Gilbert, 2007; Morandi, Heath, & Thielemans, 2009; Song, Wang, Pan, & Wang, 2008). De Bruyn et al. (De Bruyn, Sprong, Gaborieau, David, Roper, & Gilbert, 2006) used this method to graft highly branched starch with various synthetic polymers, such as polystyrene, using free-radical polymerisation where the ozone-activated amylopectin chains functioned as macro-initiators. Their optimised method yielded a latex where the starch was completely encapsulated by the hydrophobic synthetic polymer.

Researchers recently demonstrated that poly(lactic acid) (PLA) exhibits affinity for aromatic structures (Salazar, Domenek, & Ducruet, 2014). The grafting of styrene moieties to the surface of polysaccharide nanocrystals may therefore yield a compatibilizing effect. The grafting of hydrophobic molecules interferes with hydrogen bonding between the polysaccharide nanocrystals and thus reduces agglomeration. Furthermore, compatibility with hydrophobic polymers can be improved, which aids dispersion. The crystalline structures of cellulose and starch nanoparticles impact on several applications. They provide improved reinforcement or barriers when dispersed in polymer materials. The aim of this study is to functionalise polysaccharide nanocrystals in a heterogeneous system under mild conditions whilst retaining their crystalline structure. The approach uses ozone to add surface peroxide functionality to the CNC and SNC; subsequently, surface-initiated graft polymerisation occurs by thermolysis and redox activation. This is the first time such a strategy has been proposed for SNC and CNC. A comparison between the reactivity of each polysaccharide will be performed. Moreover, both nanocrystals have different shape factors. CNC and SNC exhibit rod-like and platelet-like shapes, respectively; this allows evaluation of the effect of the hydrophobic surface grafting, as well as the effect of the morphological factors on the barrier properties of the nanocomposites.

## 2. Experimental

### 2.1. Materials

Microcrystalline cellulose (MCC) powder was acquired from Sigma–Aldrich (France) and used as a raw material for the production of CNC. For the production of SNC, native waxy maize starch was kindly provided by Cargill (Krefeld, Germany). Sulfuric acid (95%) and styrene were obtained from Sigma–Aldrich. The sodium acetate buffer ( $0.1 \text{ mol L}^{-1}$ ) was prepared from sodium acetate (Sigma–Aldrich) and glacial acetic acid (Merck). Ethanol, acetone, chloroform, and toluene were purchased from Merck and used as supplied. The styrene inhibitors were removed on a basic alumina column ( $\text{Al}_2\text{O}_3$  90 active, Merck); the purified styrene was stored at  $4^\circ\text{C}$  for a maximum of five days before use.

### 2.2. Production of cellulose and starch nanocrystals

The preparation of the CNC followed an adaptation of the optimised method developed by Bondeson, Mathew, and Oksman (2006). MCC at 7.1 wt% was dispersed in water. Sulfuric acid was slowly added to a concentration of 64 wt%. The CNC in the acid suspension was subsequently hydrolysed at  $44^\circ\text{C}$  for 130 min under mechanical stirring. The waxy maize hydrolysis followed the method employed by Angellier, Choisnard, Molina-Boisseau, Ozil, and Dufresne (2004). In this case, acid hydrolysis is gentler but requires a longer period to produce SNC, i.e. 5 days at  $40^\circ\text{C}$ . A solution of 28 wt% sulfuric acid was prepared before the addition of the waxy maize starch to a concentration of 12.8 wt%. In both cases, the excess sulfuric acid was removed by the application of water exchange/centrifugation cycles. Subsequently, the resulting suspensions containing the nanocrystals were dialysed in deionised water over one week for the CNC and two days for the SNC, and homogenised using an Ultra-Turax T25 homogeniser (France). Finally, the samples were subjected to an ultrasound source to achieve satisfactory dispersion of the nanocrystals, and subsequently neutralised and stored at  $4^\circ\text{C}$ . A drop of chloroform was added to prevent microbial development. Considering the SNC, recent studies show the presence of microparticles following the hydrolysis procedure (LeCorre, Bras & Dufresne, 2011). Therefore,

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