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Surface grafting of cellulose nanocrystals with natural antimicrobial rosin mixture using a green process

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ABSTRACT

Surface functionalization of cellulose nanocrystals (CNCs) aims to improve their properties. The main objective of this study was the esterification of the surface of CNCs using nontoxic resin acids, rosin. The structural and morphological modifications of CNC nanorods were characterized by ^{13}C NMR and Fourier transform infrared spectroscopy, atomic force microscopy, and X-ray diffraction analyses. The properties of functionalized CNCs were evaluated by thermogravimetric analysis and contact-angle measurements. The results indicate that the esterification proceeded from the surface of the CNC. The antimicrobial activities of the modified and neat CNC were investigated; the rosin-grafted CNC exhibited a strong antibacterial activity against Gram-negative bacteria and a modest antibacterial activity against Gram-positive bacteria.

1. Introduction

As viable alternatives to existing fossil resources, sustainable, green, and environmentally friendly materials are in demand for several applications. Ecofriendly processes are required for an entirely sustainable approach in terms of worldwide activities involving both academic and industrial sectors.

In the last couple of decades, cellulose-based nanomaterials have attracted much interest owing to their low density, renewability, biodegradability, sustainability, a high aspect ratio, a high tensile strength, lower production cost than glass and carbon nanofibers, and wide applicability (Abdul Khalil et al., 2014; Mariano, El Kissi, & Dufresne, 2014). In 2014, one patent per week and two scientific papers per day on nanocellulose were published. Some of them involved cellulose nanocrystals (CNCs) obtained by acid hydrolysis (Mei-Chun, Qinglin, Kunlin, Sunyoung, et al., 2015; Mei-Chun, Qinglin, Kunlin, Yan, & Yiqiang, 2015), and others involved microfibrillated cellulose processed by mechanical treatment (Lavoine, Desloges, Dufresne, & Bras, 2012; Saini, Belgacem, Mendes, Elegir, & Bras, 2015). In these studies, the surface of CNCs was modified to benefit from their large specific area. Because of the presence of reactive surface OH groups, various molecules can be grafted on the CNC surfaces. Indeed, the surface of CNCs has been functionalized with various chemicals, thus extending their diverse specific applications (Habibi, 2014; Siqueira, Bras, & Dufresne, 2010a). Their surfaces have been modified by various methods such as adsorption of molecules (cationic interactions) (Heux, Chauve, & Bonini, 2000), covalent grafting of single molecules (acetylation) (Çetin et al., 2009), coupling with isocyanate derivatives (Siqueira, Bras, & Dufresne, 2010b), silylation (Goussé, Chanzy, Excoffier, Soubeyrand, & Fleury, 2002), acetylation with acetic anhydride (Missoum, Belgacem, Barnes, Brochier-Salon, & Bras, 2012), covalent grafting of polymer chains by free-radical initiation (Kan, Li, Wijesekera, & Cranston, 2013), and ring-opening polymerization (Carlmark, Larsson, & Malmström, 2012). However, most of these methods require the use of different solvents and/or reagents from fossil resources, thus strongly limiting the environmental advantage of the use of CNCs.

Rosin is a natural product of pine resins. The production of rosin has crossed one million metric tons per year. Rosin is a mixture of abietic- and pimaric-type acids with characteristic hydrophenanthrene structures; five of them are shown in Fig. 1. Rosin is an abundant and inexpensive hydrocarbon biomass. Rosin and its derivatives have been used as paper-sizing agents, emulsifiers, surface coatings, chewing gums, tackifiers in adhesives, insulating materials, and additives for printing inks. They have also been evaluated in the pharmaceutical field as microencapsulating materials (Lee & Hong, 2002; Mandaogade, Satturwar, Fulzele, Gogte, & Dorle, 2002; Wilbon, Chu, & Tang, 2013). Rosins have been chemically modified in a diverse manner such as oxidation, hydrogenation, dehydrogenation, isomerization, Diels–Alder reactions, and

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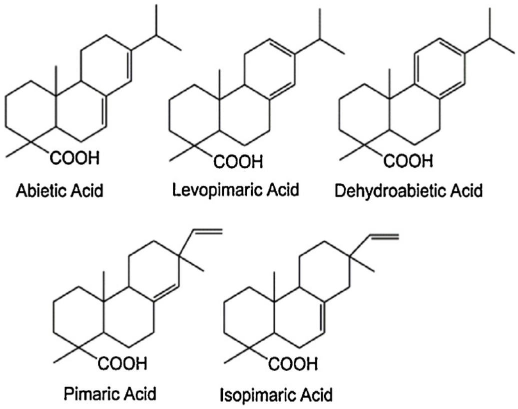

Fig. 1. The most representative structures found in rosin.

reactions with formaldehyde and phenol, affording new monomers or molecules. The reactions of the carboxylic functions include the preparation of salts with diverse cations, esterification, and alkoxylation (Gandini & Lacerda, 2015).

In this study, CNCs were functionalized with rosin, a bio-based mixture of molecules, without using hazardous solvents to develop novel applications of CNCs. Some studies have attempted to graft rosin onto bio-based polymers; however, to the best of our knowledge, rosin has not been grafted to CNCs. For example, Duan, Chen, Jiang, and Li (2008) reported the microwave-assisted graft copolymerization of rosin-(2-acryloyloxy)ethyl ester with chitosan using potassium persulfate as the initiator. The resulting copolymer was used as a carrier of fenoprofen calcium for the controlled release of drugs in artificial intestinal juice. Wang et al. (2011) prepared rosin polymer-grafted lignin composites in “grafting from” by atom transfer radical polymerization using 2-bromoisobutyryl ester-modified lignin, as the macroinitiator. Espino-Pérez, Domenek, Belgacem, Sillard, and Bras (2014) developed a solvent-free esterification of CNC surface using phenylacetic acid and hydrocinnamic acid. In this process, the two carboxylic acids acted both as a grafting agent and as a solvent above their melting point. Therefore, we decided to use the rosin mixture (melting point = 93.5 °C) and not pure molecules such as abietic acid (mp = 155 °C), levopimaric acid (mp = 147 °C), dehydroabietic acid (mp = 172 °C), pimaric acid (mp = 217 °C), and isopimaric acid (mp = 132 °C).

The development of materials based on CNCs with antimicrobial properties and their potential numerous applications have attracted much interest in recent years. Diverse techniques have been reported for the modification of the surface of CNCs with antimicrobial activities (Azizi, Ahmad, Hussein, & Ibrahim, 2013; Yu, Qin, Sun, Yan, & Yao, 2014). A typical example is the modification of CNCs with silver, as reported by Fortunati et al. (2014). Ternary nanobiocomposite films from poly(lactic acid) (PLA), modified CNCs (s-CNC), and silver nanoparticles (Ag) have also been prepared and characterized. The PLA nanobiocomposites showed a significant antibacterial activity due to the Ag content. However, these approaches require the use of heavy metals. Herein, we demonstrate an environmentally friendly approach for the production of modified CNC with bactericidal activity.

In this study, we developed an environmentally friendly and simple chemical modification for the solvent-free esterification of CNC surface using nontoxic renewable rosin acids at 130 °C. The rosin-grafted CNC was characterized by Fourier transform infrared (FT-IR) spectroscopy, ^{13}C NMR, contact-angle measurements, atomic force microscopy (AFM), thermogravimetric analysis (TGA), and X-ray diffraction (XRD). Finally, the antimicrobial properties of the grafted building blocks were assessed.

2. Experimental

2.1. Materials

CNCs were obtained from the University of Maine (USA). Rosin was a commercial chemical-grade product supplied from Aldrich Chemicals (Saint Quentin Fallavier, France); it was in fact a mixture of abietic, levopimaric, dehydroabietic, pimaric, and isopimaric acids with a molecular weight of 302 g mol^{-1}, and was used as received without further purification.

Bacillus subtilis spores were provided by Humeau, France and *Escherichia coli* ATCC 8739 were purchased from Microbiologics, Collection of Microorganisms and Cell Cultures.

2.2. Chemical modification of CNCs

The grafting procedure was adapted from the recently published SolReact process (Espino-Pérez et al., 2014). A closed distillation system equipped with a condenser held at 5 °C was used for water evaporation. An aqueous CNC suspension (6.2 wt%) was first ultrasonicated for 3 min using a Branson sonicator. The pH was adjusted to 4 with HCl (0.1 mol L^{-1}). A flask with the CNC dispersion was attached to the distillation system and placed in an oil bath at 130 °C. After 10 min, an excess of rosin (10 equiv based on the CNC dry weight) was added slowly to ensure the melting of the rosin. After water evaporation, the mixture was stirred at 130 °C (higher than the melting point of the rosin) for 10 h. The rosin mixture was used as both solvent and grafting agent for the esterification of CNC surface. After the reaction, the rosin-grafted CNC was purified from the unreacted rosin by six-time dispersion–centrifugation with a large excess of ethanol at room temperature (10,000 rpm at 4 °C for 10 min). Therefore, the characterized rosin-grafted CNC corresponds to the grafted rosin on CNC (Fig. 2).

2.3. Characterization

2.3.1. AFM

AFM was used to ascertain and compare the morphology of the CNC and rosin-grafted CNC. The AFM measurements were performed using a Multimodal AFM (DI, Veeco, Instrumentation Group) working on the tapping mode. Approximately 0.01 wt% suspensions were first dispersed in water with ultrasonic stirring for 2 min and then deposited on a mica substrate and dried at room temperature. The geometrical aspects of the CNCs were measured using digital image analysis (ImageJ software). At least five measurements were performed with several AFM images, and the average value was calculated.

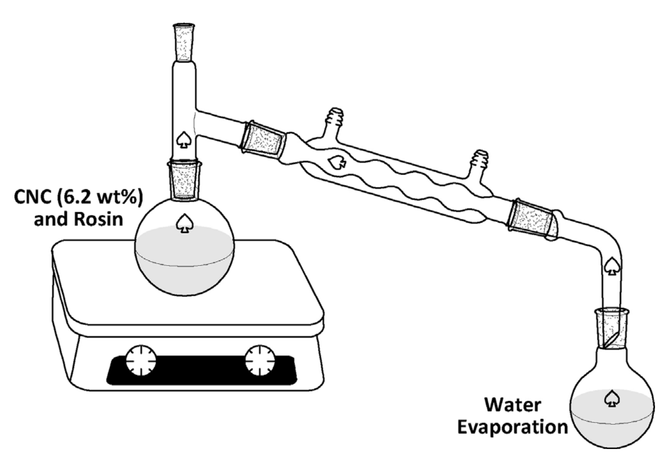

Fig. 2. Chemical reaction for the functionalization of CNCs.