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Rice straw nanofibrillated cellulose films with antimicrobial properties via supramolecular route

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ABSTRACT

Novel antimicrobial nanofibrillated cellulose (NFC) with new optical and good tensile strength properties was prepared through supramolecular modification of TEMPO-oxidized NFC by Cu-, Zn-, and Fe–terpyridine metal complexes (M–Tpy). The prepared terpyridine-modified NFC (NFC–M–Tpy) derivatives were characterized using transmission electron microscopy (TEM), Fourier transform infrared (FTIR), and elemental analysis. Films casted from aqueous suspensions of NFC–M–Tpy plasticized by glycerol were made and characterized using X-ray diffraction (XRD), tensile strength, porosity, water vapor permeability, and antimicrobial properties testing. Attaching the different M–Tpy moieties to NFC resulted in increasing tensile strength and Young's modulus, decreasing porosity and water vapor permeability (WVP), and imparted NFC antimicrobial properties against Gram-positive bacteria (*Staphylococcus aureus*), Gram-negative bacteria (*Escherichia coli*), as well as yeast (*Saccharomyces cervisiae*). NFC–Cu–Tpy film showed higher antimicrobial properties than NFC–Zn–Tpy and NFC–Fe–Tpy films while the other properties tested showed independence on the type of metal center in the terpyridine complex. The NFC–Cu–Tpy was used for coating bagasse paper sheets and tensile strength, burst strength, water vapor permeability, porosity, and water sorption of coated paper sheets were tested. NFC–Cu–Tpy coating improved tensile strength properties and reduced porosity, WVP, and water absorption of coated paper sheets more than in case of using NFC. The prepared nanocellulosic materials can find potential applications in active packaging and healthcare paper products.

1. Introduction

Nanofibrillated cellulose (NFC) consists of cellulose fibrils with few nanometers width and up to several microns in length. It can be produced by different technologies; one of the convenient technologies is through high shear action or ultrasonic treatment of cellulose fibers oxidized using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)/NaOCl system (Saito et al., 2007; Abdul Khalil et al., 2016). NFC has the advantages of cellulosic materials such as biodegradability, non-toxicity, wide availability of starting lignocellulosic materials, possibility of chemical modification, low density, and good strength properties. In addition, NFC has the unique properties of nanomaterials such as high volume to area ratio, transparency, stronger interaction with surrounding matrices, and pronounced effect at low concentrations. The presence of carboxylic groups at the surface of TEMPO-oxidized NFC as a result of oxidation of primary hydroxyl groups adds new functionality to this material and allows selective chemical modification utilizing reactivity of carboxylic groups. Different reactions have been used for chemical modification of NFC such as esterification, etherification, amidation, and grafting (for examples, Siró and Plackett, 2010; Habibi, 2014; Abdul Khalil et al., 2016; Li et al., 2013a; Maatar et al., 2013; Mashkour et al., 2015; Missoum et al., 2014; Sirviö et al., 2014; Wan et al., 2015). These reactions are based on covalent bonding between hydroxyl and carboxylic functional groups at surface of NFC and the introduced moieties. In contrast to molecular chemistry used in these reactions, use of supramolecular routes for synthesis of new derivatives involve use of different non-covalent intermolecular bonds between reactants such as hydrogen bonding, charge transfer, π-stacking, and chelation of metal cations (Lehn, 1995). Chemical synthesis through supramolecular routes has the advantages of much higher selectivity, less side reactions, and easier purification of products than in case of using molec-

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ular chemistry. In addition, the supramolecular bonds could be reversible ones and thus can be used for preparation of smart materials. Large and complicated structures can be easily prepared from small molecules using supramolecular routes.

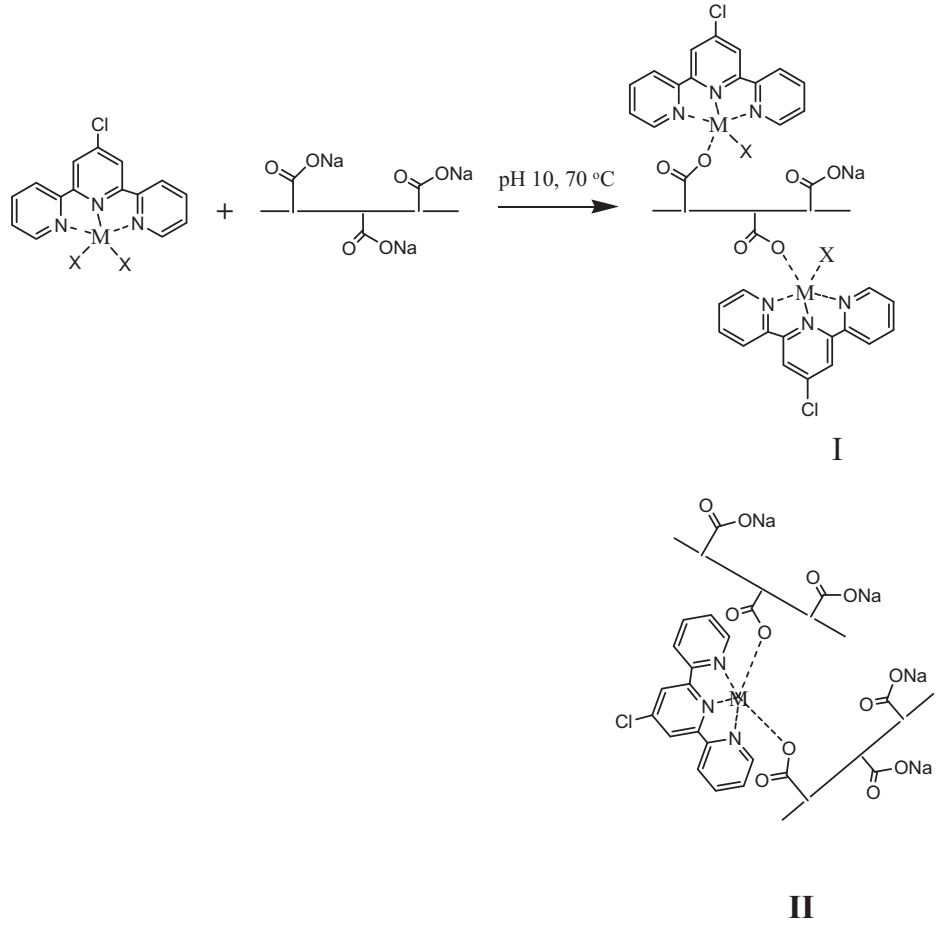
Use of supramolecular routes for preparation of cellulose derivatives or chemical modification of nanocelluloses in particular is rare. Preparation of new carboxymethyl cellulose derivative with antimicrobial properties via supramolecular route using a terpyridine–copper complex was recently reported (Hassan et al., 2015a). Another example for supramolecular modification of cellulose fibers was through covalently attaching β-cyclodextrin onto the fiber surface followed by immobilization of poly(ε-caprolactone) oligomers having both ends capped with adamantane motifs through the host/guest inclusion complexation between β-cyclodextrin and adamantine (Zhao et al., 2010).

Regarding supramolecular chemical modification of nanocelluloses, little work is published so far. For example, cellulose nanocrystals were grafted with β-cyclodextrin then pluronic polymer was introduced on the surface by means of inclusion interaction between β-cyclodextrin and hydrophobic segment of the polymer; the modified nancrystals can be used in drug delivery applications (Lin and Dufresne, 2013).

The other published work on modification of nanocelluloses' surfaces through supramolecular route depended on adsorption of surfactants with long hydrophobic chain or polyelectrolytes by electrostatic force to modify surface properties rather than to prepare new derivatives (for examples, Salajková et al., 2012; Syverud et al., 2011; Xhanari et al., 2011; Zhou et al., 2009).

Terpyridines are *N*-heterocycles compounds which exhibit high binding affinity toward transition metal ions. This property has been utilized in preparation of simple terpyridine complexes of one or two terpyridine units as well as different assemblies having large molecular weight structures with several terpyridine units. The terpyridine metal complexes have distinct photo-physical, electrochemical, and magnetic properties. They have been widely investigated for different applications such as catalysis, nano-electronics, and dye sensitized solar cells (Schubert, Winter, & Newkome, 2011). In addition, antimicrobial properties of some copper, zinc, ruthenium, silver, and iridium terpyridine metal complexes have been reported (Alghool et al., 2015; Fik et al., 2014; Frei et al., 2014; Kharadi, 2014; Kharat et al., 2012; Pandrala et al., 2013; Patel et al., 2006; Patel et al., 2010; Patel et al., 2012a,b).). Simple terpyridines like that used in the current work could be prepared easily from relatively simple chemicals and following convenient chemical methods. Preparation of 4′-chloro-2,2′:6′,2″-terpyridine used in our work at large scale has been reported (Schubert et al., 2002).

Due to the distinct properties of terpyridines, they have been attached to polymers to generate new materials with pendent terpyridine units which can be further transformed into metallo-supramolecular assemblies (Breul et al., 2013; Köytepe et al., 2013; Li et al., 2013b; Maeda et al., 2013; Muronoi et al., 2013; Schubert et al., 2011; Yang et al., 2013). Preparation of terpyridine-modified cellulose nanocrystals via etherification their surfaces with 4′-chloro[2,2′:6′,2″] terpyridine and their ability to further assemble metallo-supramolecular derivatives with optical and electrical



Scheme 1. Possible reactions between TEMPO-oxidized NFC and terpyridine metal complexes (solid line depicts NFC).