Carbohydrate Polymers 152 (2016) 361–369

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Strong and electrically conductive nanopaper from cellulose nanofibers and polypyrrole

Makara Lay[a,b], J. Alberto Méndez[a], Marc Delgado-Aguilar[a], Kim Ngun Bun[b], Fabiola Vilaseca[a,*]

[a] LEPAMAP Group, Dept. of Chemical Engineering, Agricultural and Food Technology, University of Girona, C/Maria Aurèlia Capmany 61, 17071 Girona, Spain

[b] Dept. of Geo-resources and Geotechnical Engineering, Institute of Technology of Cambodia, PP Box 86, Russian Conf. Blvd. Phnom Penh, Cambodia

ARTICLE INFO

Article history:
Received 17 May 2016
Accepted 27 June 2016
Available online 11 July 2016

Keywords:
Cellulose nanofibers
Polypyrrole
Conductive nanopaper
Mechanical properties
Electrical conductivity

ABSTRACT

In this work, we prepare cellulose nanopapers of high mechanical performance and with the electrical conductivity of a semiconductor. Cellulose nanofibers (CNF) from bleached softwood pulp were coated with polypyrrole (PPy) via in situ chemical polymerization, in presence of iron chloride (III) as oxidant agent. The structure and morphology of nanopapers were studied, as well as their thermal, mechanical and conductive properties. Nanopaper from pure CNF exhibited a very high tensile response (224 MPa tensile strength and 14.5 GPa elastic modulus). The addition of up to maximum 20% of polypyrrole gave CNF/PPy nanopapers of high flexibility and still good mechanical properties (94 MPa strength and 8.8 GPa modulus). The electrical conductivity of the resulting CNF/PPy nanopaper was of 5.2 10^{-2} S cm^{-1}, with a specific capacitance of 7.4 F g^{-1}. The final materials are strong and conductive nanopapers that can find application as biodegradable flexible thin-film transistor (TFT) or as flexible biosensor.

1. Introduction

The recent development of nanotechnology, together with the global concern for environment, is focusing on the use of bio-resources as alternative to mineral or non-renewable ones (Thakur, 2015). Nowadays, one exciting research area is the isolation and use of nanocelluloses. Cellulose is the most abundant biological raw material that can self-assemble into well-defined architectures at micro and nano scale. Therefore, from their origin, cellulose nanofibers are renewable, inexpensive, and non-toxic. In addition, and due to their chemical structure and high crystallinity, nanocelluloses have and remarkable physical, thermal, and mechanical properties, such as high specific surface area and high elastic modulus (Lavoine, Desloges, Dufresne, & Bras, 2012; Siró & Plackett, 2010). Among the different nanocelluloses, cellulose nanofibers (CNFs) consist of a long web-like structure with micrometer length and 10–100 nm in diameter that imparts unique properties. The isolation of CNFs can be performed by a wide variety of mechanical techniques such as refining, grinding, high pressure homogenization or cryocrushing (Wang, Sain, & Oksman, 2007). Different pre-treatments can also be applied to reduce the energy consumption as well as to modify the surface energy of CNFs (Jonoobi et al., 2015).

In combination with a suitable polymer matrix, cellulose nanofibers networks show considerable potential as effective reinforcement for high-quality bio-based composites. Likewise, their flexibility and high aspect ratio make CNFs outstanding materials for wide range of applications. The last decade, CNFs have been used as nanofillers to reinforce nanocomposites (Miao & Hamad, 2013; Saba, Tahir, & Jawaid, 2014) with thermoplastic and thermoset polymers for packaging products, construction materials, automobiles, furniture, and pharmaceuticals (Hoenich, 2006; Ioelovich, 2008; Jeon, Yang, & Kim, 2012; Kalia et al., 2011; Zhang, Nypelö et al., 2013; Zhang, Zhang et al., 2013). More recently, CNFs have gained much attention for its use as biomedical material because of their exceptional surface chemistry and excellent biological properties (biocompatibility and biodegradability) (Lin & Dufresne, 2014).

Due to their benign nature, high available surface area, smoothness, and reduced porosity, CNF films have been reported as potential substrates for biosensors (Salas, Nypelö, Rodriguez-Abreu, Carrillo, & Rojas, 2014). However, and because of the intrinsic insulating characteristics, specific strategies need to be developed to impart electrical activity to CNF. In this sense, the combination of CNFs with conductive polymers (CPs) allows to extend the functionality of CNFs in energy storage devices, solar

* Corresponding author.
E-mail address: fabiola.vilaseca@udg.edu (F. Vilaseca).

http://dx.doi.org/10.1016/j.carbpol.2016.06.102
0144-8617/

cells or electronic applications (Huang et al., 2013; Koga et al., 2014; Luo, Zhang, Li, Liao, & Li, 2014; Nyholm, Nyström, Mihranyan, & Strømme, 2011; Tammela et al., 2015; Wang et al., 2015; Zheng et al., 2013).

Conducting polymers are attractive candidates because they have good intrinsic conductivity, from a few to 500 S cm^{-1}. CPs are rendered conductive through a conjugated bond system along the polymer backbone. They are typically formed either through chemical oxidation or electrochemical oxidation of the monomer (Snook, Kao, & Best, 2011). In the chemical oxidation process, for example with iron chloride, the molecular weight and structural features of the resulting polymer are feasible to control. Among conducting polymers, polypyrrole (PPy) has an appreciable environmental stability (Buitrago-Sierra, García-Fernández, Pastor-Blas, & Sepúlveda-Escribano, 2013) and is easy to synthesize (Ansari, 2006; Eisazadeh, Engineering, & Box, 2007; Huang, Kang, & Ni, 2006; Trchova & Kova, 2003; Wang, Li, & Yang, 2001). PPy offers a greater degree of flexibility in electrochemical processing than most conducting polymers, and consequently the material has been the subject of much research as a supercapacitor or battery electrode (Snook et al., 2011). In 2006, Huang et al. investigated the in-situ polymerization of pyrrole on different pulp systems demonstrating the good adhesion between the conductive polymer and the fibers (Huang et al., 2006). The specific parameters and the sequence for the polymerization reaction, and their effect on the fiber degradation have also been studied (Beneventi, Alila, Boufi, Chaussy, & Nortier, 2006). Other authors have performed a soaking-polymerization procedure on printing paper (Yuan et al., 2013). In this case, the conductive polymer remained mainly at the surface of the printing paper showing high value of surface electrical conductivity. The viability of coating PPy on CNF was demonstrated by Nyström et al. (2010). They verified the conductivity and the ion-charge capacity of a cellulose nanocomposite with high amount of PPy conductive polymer. In a further work, the authors investigated the mechanical properties of PPy-cellulose nancomposites of different porosity (Carlsson et al., 2012). In a different study (Nyström, Strømme, Sjödin, & Nyholm, 2012), they improved the capacitance of this type of cellulose nanocomposites. Later, Wang et al. (2015) performed surface modification of cellulose nanofibers to produce cellulose-based supercapacitors. The coating of PPy on CNF substrate has reduced moisture content of CNF in nature and also protected against degradation, as PPy is known to be insoluble in most solutions and solvents (Sasso et al., 2010). Carlsson, Mihranyan, Strømme, and Nyholm (2014) found that the individual nanocellulose fibrils should be coated by a thin layer of PPy less than 50 nm of thickness to avoid the problems associated with the low redox reaction rates and poor mechanical properties of nanocomposites.

In the present work, cellulose nanofibers are coated with polypyrrole using $FeCl_3$ as oxidant agent. In previous studies, large amounts of polypyrrole were used to obtain a substantial increase of the electrical activity of cellulose nanofibers. However, as consequence, brittle cellulose-nanocomposites were obtained. In this study, pyrrole was polymerized on cellulose nanofiber surface at certain reaction times to obtain very flexible and strong structures with electrical conductive capacity. The obtained CNF/PPy nanopapers were characterized considering their morphology and their mechanical, thermal and electrical response.

2. Materials and methods

2.1. Materials

Bleached pine pulp from Arauco (Chile) was used as cellulose raw material. The cellulose content of the pulp was 95%. Pyrrole was supplied by Sigma Aldrich and used as received for the chemical synthesis of polypyrrole. The rest of materials, $FeCl_3$, Tween-80, 2,2,6,6-tetramethyl-1-1-piperidinyloxy (TEMPO), sodium bromide (NaBr), sodium hypochlorite (NaOCl), HCl, NaOH, and NaCl were also supplied by Sigma Aldrich and used without further purification. Silver coating 3850 was supplied by Holland shielding system BV, Holland.

2.2. Preparation of CNF suspension

The bleached pine pulp (30 g dry weight) was dispersed in 2 L of distilled water and disintegrated at 6000 rpm for 30 min in a pulper (PAPEL QUIMIA, S.A, SPAIN). From this suspension, CNFs were extracted by means of a TEMPO-mediated oxidation followed by a mechanical homogenization (homogenizer NS1001L PANDA 2K-GEA, Italy). The TEMPO-mediated oxidation was performed at pH 10 (Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009) and the obtained cellulose suspension was diluted to 1 wt% and passed through a high-pressure homogenizer, one time at 300 bar and three times at 600 bar of pressure. As a result, a transparent gel of cellulose nanofibers (CNF) at 1% concentration was obtained and stored at 4 °C prior use.

2.3. Preparation of CNF and CNF/PPy nanopapers

CNF gel was first diluted to 0.2% with distilled water and dispersed by using a sonicator Q700 for 10 min (5 min pulse on, 2 min pulse off, and 5 min pulse on) at 60% of amplitude. Afterwards, the CNF suspension was filtered overnight using a glass filter funnel with a nitrocellulose membrane GSWP29325 (hydrophilic) of 0.22 μm pore-size. After filtering, the nitrocellulose membrane was peeled off and the CNF cake was placed between two pieces of immobile transfer membranes of polyvinylidene fluoride (PVDF) (hydrophobic) of 0.45 μm pore-size to prevent adhesion between sample and membrane. Finally, the samples were dried using a laboratory sheet dryer at a vacuum pressure of −0.6 bar at 92 ± 3 °C for 20 min.

For the preparation of CNF/PPy nanopapers the same filtering procedure was used. Firstly, a dilute suspension of CNF (0.1%, 400 mg of dry weight) was sonicated for 10 min under the same setting conditions described above. This CNF suspension will be later mixed with a solution of pyrrole. For the preparation of the pyrrole solution, 0.1 mL of pyrrole was dissolved in 15 mL of 0.5 M HCl. After stirring the mixture for 3 min using magnetic stirrer, one drop (0.05 mL) of Tween-80 was added and stirred until completely homogenous. Afterwards, the solution of pyrrole was introduced into the above CNF suspension, and the mixture was stirred for 5 min. In order to initiate the polymerization, 0.578 g of $FeCl_3$ in 15 mL of HCl 0.5 M was added drop wise into the suspension. The final mixture was stirred at room temperature for 20, 40, 60, 120, and 180 min, in independent experiments, to get the different conductive nanopapers named as CNF/PPy20, CNF/PPy40, CNF/PPy60, CNF/PPy120, and CNF/PPy180, respectively. At the end, the mixture (CNF and PPy) was filtered using a glass filter and washed subsequently with 500 mL of 0.5 M HCl, 500 mL of 0.1 M NaCl, and 500 mL of distilled water. During the last washing with distilled water, the suspension was sonicated for 2 min to remove any small gas bubbles and to allow a better organization of CNF/PPy nanostructures without undesired side effects, such as crystal structure damage (Ali et al., 2014). Thereafter, the filtration was continued for 3 more hours until there is no residual water. The obtained CNF/PPy was finally dried in sheet dryer for 20 min.