Carbohydrate Polymers 134 (2015) 258–266

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Bark derived submicron-sized and nano-sized cellulose fibers: From industrial waste to high performance materials

Sandeep S. Nair, Ning Yan*

Faculty of Forestry, University of Toronto, 33 Willcocks Street, Toronto, Ontario M5S3B3, Canada

ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form 23 July 2015
Accepted 24 July 2015
Available online 29 July 2015

Keywords:
Cellulose nanofibers
Bark residue
Micro grinder
Mechanical properties
Water vapour permeability

ABSTRACT

In this study, the use of bark as a natural source for the production of cellulose nanofibers has been explored for the first time. The fibrillation using bleached and unbleached cellulose fibers from the bark yielded sub-micron scale (<1 μm) and nanoscale fibers (<100 nm). Previous attempts to break the cross-linked lignin barrier to produce fibrillated submicron sized or nano sized cellulose fibers with high lignin content (>20%) have never been possible from any other sources. The maximum elastic modulus value of 15.6 GPa and tensile strength value of 76 MPa were obtained for the films made from fibrillated bark cellulose fibers. The water vapour barrier efficiency for these films is comparable to nanocellulose films from other studies.

1. Introduction

The plant cell wall is a complex structure in which the cellulose molecules are closely associated with other polysaccharides, lignin and extractives. Around 36 individual cellulose molecules are closely held together by strong hydrogen bonding to form elemental fibrils or microfibrils (Habibi, Lucia, & Rojas, 2010). Cellulose nanofibers (CNFs) can be either a single microfibril or an aggregate of microfibrils. The diameter of CNFs can range from 2 to 100 nm and lengths up to several micrometers depending on their origin (Hoeger et al., 2013; Iwamoto, Nakagaito, Yano, & Nogi, 2005; Stelte & Sanadi, 2009). With a theoretical modulus of 146 GPa (Eichhorn & Young, 2001), smaller dimension, high surface-to-volume ratio, and high abundance, CNFs have been considered a prime candidate for many applications in material science field (Abraham et al., 2011). The ability to form hydrogen bonds resulting in strong network also makes CNFs a strong candidate for packaging application with excellent barrier applications (Nair, Zhu, Deng, & Ragauskas, 2014a). CNFs were first produced by Turbak, Snyder, and Sandberg (1983) from wood pulp using a high pressure homogenizer. Using high pressure drops and mechanical forces, micron- sized cellulose fibers were successfully disintegrated to submicron and nano-sized fibers. Currently, numerous methods of mechanical fibrillation have been used for the production of CNFs such as homogenizers (Chinga-Carrasco & Syverud, 2012), microfluiders (Henriksson, Berglund, Isaksson, Lindstrom, & Nishino, 2008), and grinders (Nair, Zhu, Deng, & Ragauskas, 2014b; Wang et al., 2012). Mechanical fibrillation using a micro grinder has several advantages compared to other means of fibrillation processes. The micro grinder can be used to fibrillate long fibers without any pretreatments (Siro & Plackett, 2010), and also has a great potential for commercial scale-up as it can be used for fibrillating large quantities of fibers. Also, other devices like homogenizer or micro fluidizer are more energy consuming than micro grinder (Spence, Venditti, Rojas, Habibi, & Pawlak, 2011). Chemical (Saito, Kimura, Nishiyama, & Isogai, 2007) and enzymatic pretreatments (Henriksson, Henriksson, Berglund, & Lindstrom, 2007) before mechanical fibrillation can facilitate in the disintegration of cellulose fiber and thereby reduce the energy required for fibrillation. However, most of these methods are more expensive, results in a lower yield of final products compared to mechanical fibrillation, and requires waste stream management.

CNFs are prepared from a variety of cellulose sources. Bleached kraft pulp is the most common raw material used followed by bleached sulphite pulp (Lavoine, Desloges, Dufresne, & Bras, 2012). In the last decade, significant research has been conducted on the production of nanocellulose based materials from agricultural based waste. Agricultural wastes such as soybean stock (Wang & Sain, 2007), pineapple leaf (Cherian et al., 2010), wheat straw and soy hulls (Alemdar & Sain, 2008; Leyva et al., 2011) have also been studied as a source in the production of CNFs. Even though, a variety of sources were investigated in detail, the use of bark as a natural source for the production of CNFs has not been explored yet. Bark

* Corresponding author. Fax: +1 4169783834.
E-mail address: ning.yan@utoronto.ca (N. Yan).

http://dx.doi.org/10.1016/j.carbpol.2015.07.080
0144-8617/

comprises of all the tissues outside of the vascular cambium and represents the outermost layers of the stem and roots of woody plants. It is mainly composed of polysaccharides, lignin and extractives. The amount of bark is so enormous that it has to be continually removed from mill sites and forest operations as waste. While the majority of bark is disposed of by burning, some are used for low grade utilization such as fuel, charcoal, and in mulching and soil amendment (Harkin & Rowe, 1971). In the past few decades, significant research has been ongoing for exploring new ways of using bark residues for value added applications. However, most of them have been limited to the use of extractives from bark residue. Several value added products such as phenol formaldehyde (PF) resins (Zhao, Yan, & Fen, 2013a), polyurethane foams (D'Souza, Camargo, & Yan, 2014), and PF novolac resin (Zhao, Zhang, Yan, & Farnood, 2013b) have been synthesized from bark residue. Even though, bark has got a high amount of extractives compared to wood, it also has significant amounts of holocellulose. Recently, Huang and Yan (2014) have shown that the holocellulose content varies between 29 and 45% among various hardwood and softwood species. No major research have been conducted of extracting value added CNFs from bark.

The objective of this work is to investigate the fibrillation process of cellulose fibers to submicron and nano-sized fibers in the bark residue after the removal of extractives. This includes a fundamental understanding of the morphological development of cellulose fibers in bark residue during various stages of the fibrillation process using micro grinding. Some of the previous research has shown that the presence of cross-linked lignin intimately associated with cellulose and hemicellulose act as a barrier to mechanically produce nanofibers. Therefore, the effect of lignin on the fibrillation process will also be compared.

2. Materials and methods

2.1. Materials

Lodgepole pine bark was supplied by FPInnovations. All other chemicals used were from Caledon labs (Georgetown, ON, Canada).

2.2. Bark extraction

The bark was air dried and was ground using a Wiley mill and then passed through a 10 mesh (2 mm). Ground bark particles were extracted using 1% NaOH solution under extraction temperature of 90 °C, extraction time of 120 min, and liquor:bark ratio of 10:1 conditions. After filtration, alkali treated residues were extensively washed with hot water and stored. The alkali treated residues after washing were termed as unbleached fibers.

2.3. Chlorite treatment of bark residue

Chlorite treatment was used to obtain samples with reduced lignin content (Wise, Murphy, & Daddieco, 1946). Air dry bark residue after extraction (100 g) was weighed and transferred to a flask. Distilled water (3200 mL), glacial acetic acid (10 mL), and reagent grade sodium chlorite (30 g) are added successively. The flask was placed on a steam bath adjusted to a temperature of 70–80 °C. The flask was heated for 1 h at the reaction temperature with occasional stirring. After 1 h, glacial acetic acid (10 mL), and reagent grade sodium chlorite (30 g) were added again and heating continued at a temperature of 70–80 °C again for 1 h. The same process was continued. At the end of the fourth hour of chlorination, the flask was placed in an ice bath until the contents were cooled below 10 °C. The filtered bleached fibers were washed a number of times to remove the color and odour of chlorine dioxide. The fibers obtained after chlorination were termed as bleached fibers.

2.4. Chemical composition analysis

2.4.1. Holocellulose and α-cellulose determination

Holocellulose and α-cellulose contents in extracted bark (unbleached fibers) were determined following a procedure developed by Browning (1967). A total of 0.5 g of oven-dried unbleached fibers was weighed and 16 mL of sodium acetate buffer solution was added. The mixture was placed in a water bath at 70 °C and 1 mL of 27% (w/v) $NaClO_2$ was added every 30 min for 4 h continuously. The filtered holocellulose was separated in two sets of experiments. The first set was oven-dried at 65 °C and weighed to determine the holocellulose content. The second set of filtered holocellulose was kept in the desiccator for 24 h and then transferred into beakers for the α-cellulose determination. Three milliliter of 17.5% NaOH solution was added to the prepared holocellulose and incubated at 20 °C, followed by another 6 mL after 5 min. The total treatment lasted 45 min. Then distilled water was added, and the mixture was allowed to stand for 1 h. The solution was filtered under vacuum into 40–60 grade crucibles and washed with 30 mL of distilled water. Crucibles and samples were then oven-dried to determine the α-cellulose. Holocellulose and α-cellulose in bleached fibers was determined in the same way. The amount of α-cellulose was deduced from the holocellulose content to obtain the hemicellulose content:

$$\text{Holocellulose}(\%) = \frac{(m_{hc} - m_c)}{m_{ub,b}} \times 100 \quad (1)$$

$$\alpha - \text{cellulose}\,(\%) = \frac{(m_{\alpha c} - m_c)}{m_{ub,b}} \times 100 \quad (2)$$

where m_{hc} is the oven-dried weight of holocellulose and of crucible, $m_{\alpha c}$ is the oven-dried weight of α-cellulose and of crucible, m_c is the oven dried weight of crucible, and $m_{ub,b}$ is the oven-dried weight of unbleached or bleached fibers.

2.4.2. Klason lignin determination

Klason lignin content was determined following a modified procedure in wood (Effland, 1977). A portion of oven dried bark (200 mg) was hydrolyzed with 2 mL of 72% sulfuric acid for 1 h by incubating the test tube at 30 °C and constantly stirring using glass rods. The reaction was stopped by adding distilled water and the diluted solutions were further autoclaved at 120 °C. Glass-crucibles 40–60 grade were utilized to filter the soluble fraction from the Klason lignin. The solid residues were oven dried at 105 °C to constant weight, cooled in a desiccator and weighed to determine the Klason lignin content.

2.4.3. Ash contents

Ash contents in the bark were determined according to the ASTM D1102-84 method. About 10 mg of oven-dried sample was weighed in a platinum pan and heated from room temperature to 580 °C at a heating rate of 10 °C/min using a thermal gravimetric analyzer (TGA-Q500, TA Instruments, New Castle, DE, USA). Ash contents were reported as the percentage of the remaining residues after treatment.

2.5. Fiber quality analyzer (FQA)

Fiber length and distribution were measured using a fiber quality analyzer (OpTest Equipment Inc., Hawkesbury, ON, Canada). Length distribution was obtained from five samples of 1000 fibers, each for both bleached and unbleached fibers.