Radiation Physics and Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

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

Ionizing radiation processing and its potential in advancing biorefining and nanocellulose composite materials manufacturing☆

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ARTICLE INFO

Keywords:
e-beam
Cellulose
Wood
Biorefining
Nanocellulose
Lignin

ABSTRACT

Nanocellulose is a high value material that has gained increasing attention because of its high strength, stiffness, unique photonic and piezoelectric properties, high stability and uniform structure. Through utilization of a biorefinery concept, nanocellulose can be produced in large volumes from wood at relatively low cost via ionizing radiation processing. Ionizing radiation causes significant break down of the polysaccharide and leads to the production of potentially useful gaseous products such as H_2 and CO. The application of radiation processing to the production of nanocellulose from woody and non-wood sources, such as field grasses, bio-refining by-products, industrial pulp waste, and agricultural surplus materials remains an open field, ripe for innovation and application. Elucidating the mechanisms of the radiolytic decomposition of cellulose and the mass generation of nanocellulose by radiation processing is key to tapping into this source of nanocelluose for the growth of nanocellulostic-product development. More importantly, understanding the structural break-up of the cell walls as a function of radiation exposure is a key goal and only through careful, detailed characterization and dimensional metrology can this be achieved at the level of detail that is needed to further the growth of large scale radiation processing of plant materials. This work is resulting from strong collaborations between NIST and its academic partners who are pursuing the unique demonstration of applied ionizing radiation processing to plant materials as well as the development of manufacturing metrology for novel nanomaterials.

1. Introduction

Nanocellulose combines the desirable properties of cellulose with the new and exciting capabilities and applications presented by new, revolutionary nanoscale materials (Moon et al., 2016). Initially, the paper making process, credited to the discovery by the Chinese around 150 B.C, was not technologically capable of separating the fibers into their smallest component parts and this remained a “holy grail” until a discovery in 1977 by a research manager at the ITT Rayonier Eastern Research Division (ERD) Lab in Whippany, N.J. (Turbak, 2015). More recently, several reviews have been published on the preparation of nanocellulose (Lavoine et al., 2012; Giri and Adhikari, 2013; Rebouillat and Pla, 2013; Dufresne, 2013; Klemm et al., 2011; Bharimalla et al., 2015; Postek et al., 2013) describing various current methods for isolation such as: homogenization, grinding, cryo-crushing electrospinning, enzymatic pretreatments, TEMPO mediated oxidation, carbomethylation and acetylation. Yet none have included the use of ionizing radiation in the manufacturing of these economically valuable materials. Recently, Driscoll reported the application of ionizing radiation to the break-down of wood (Driscoll et al., 2009) and is also the first demonstration of the potentials afforded by the application of this technique to the liberation and production of nanocellulose from wood and potentially non-wood sources, such as field grasses, bio-refining by-products, industrial pulp waste, and agricultural surplus materials. Since the application of ionizing radiation to this field is so new, the use of ionizing radiation in cellulose manufacturing remains an open field, ripe for innovation and application. While the use of ionizing radiation, i.e., via electron beam, is new to the field of wood treatment, it is not

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http://dx.doi.org/10.1016/j.radphyschem.2017.09.015
Received 28 April 2017; Received in revised form 1 September 2017; Accepted 11 September 2017

new to other industrial applications. There are over 1400 high current electron beam systems in operation around the world providing an estimated added value to numerous products of > $85 billion. The largest areas of use include applications to wire, cable and tubing; surface curing, shrink materials; tires and medical device sterilization (International Irradiation Association, 2017, 2011).

Elucidating the mechanisms for the radiolytic decomposition of cellulose is a key element to tapping into the natural and abundant sources of nanocellulose. Such elucidation is necessary for the mass generation of nanocellulose by radiation treatment and growing the nanocellulosic-product market. Preliminary assessments have been reported (Tissot et al., 2013) but the structural break-up of the cell walls as a function of radiation exposure is still not well understood. However, it is widely believed that the breaking of glycosidic bonds in cellulose is the primary method of depolymerization (Al-Assaf et al., 2016). However, while the crystallinity of cellulose is changed by irradiation, doses above 200 kGy are required to see a large drop in crystallinity (Cheng et al., 2013; Driscoll et al., 2009). Comprehensive chemical characterization and dimensional metrology studies are central to unlocking the level of details that are needed to understand these mechanisms further and advance the large-scale radiation processing of plant materials.

2. Advantages afforded by ionizing radiation and measurement needs

Fundamental and applied research in the physical interactions of ionizing and non-ionizing radiation with matter is very important. Ionizing radiation affords several distinct advantages in materials engineering: 1) the process is easy to control; 2) the products can be tailored to have specific physical and chemical characteristics, 3) sterilization is performed simultaneously with the synthesis of the material; and 4) finally, there is an elimination of the need for a cross-linking agent for polymeric materials, rendering such systems free of impurities and potentially toxic residuals making it an excellent choice for biological and human health applications.

Efforts using ionizing radiation for the synthesis of advanced nanomaterials are underway at the National Institute of Standards and Technology (NIST). Materials under development include soft nanomaterials for drug delivery applications (An et al., 2011; Grimaldi, 2013; Takinami, 2014; Pazos et al., 2016), magnetic nanocomposites for imaging and electrical functions, adsorbents for environmental products (Dietz et al., 2016), and membranes tailored for fuel cell uses (Kim et al., 2017). The measurement aspects of the synthesis steps have been investigated, including the effects of temperature, dose, and the initial material concentrations and types on the control of the size, molecular weight, and functionality of the products. Material manipulations have also been undertaken, including polymer crosslinking and graft polymerization, and the kinetics of the formation and decay of transient species investigated using spectrophotometric pulse radiolysis, most recently with Brookhaven National Laboratory (Pazos et al., 2017). The over-reaching goal for all this work is the development of measurement methods and standards to support the precise and accurate synthesis and characterization of materials, an important key component to understand and optimize the overall production and performance of products which ultimately make use of such materials.

While rapid advances in the mass generation of nanocellulose by radiation processing may be possible near term with existing technologies, there remains an unfortunate lag time in the development of sophisticated methods to isolate and characterize the product (Postek et al., 2010; Postek, 2014). This is largely due to the inability to isolate and determine accurately via measurements what is produced. This will require new or modified instrumentation, substantial instrument development, or lengthy optimization time. Metrology and new instrument developments need to be done in concert. This is not a unique situation, the semiconductor industry had to overcome a similar technological barrier and has discovered that for advanced manufacturing: **“if you cannot measure it, you cannot manufacture it.”**

3. Wood and cellulose

Wood is a natural composite composed of cellulose, hemicellulose and lignin and other components. The first three are biopolymers, with cellulose and hemicellulose being polysaccharides. Wood is about 38–50% cellulose, 23–32% hemicellulose, and 15–25% lignin. The exact composition is species specific (Boerjan et al., 2003; Huber et al., 2006; Sjöström, 1993).

Cellulose is a linear, high molecular weight (MW) polymer of anhydro-d-glucopyranosyl units linked by β-(1→4) glycosidic linkages. The degree of polymerization (DP) is between 500 and 14,000 for wood celluloses (Mohnen et al., 2008). The linear chains of cellulose are highly ordered due to hydrogen bonding and high crystallinity, making them insoluble in conventional solvents and resistant to hydrolysis. The cellulose in wood and other lignocellulosic biomass acts as the “fibers” of the composite, giving the wood its stiffness (Panshin and de Zeeuw, 1980).

Hemicelluloses are irregular, complex polysaccharides which consist chiefly of heteroglucans (xyloglucans), heteroxylans, and heteromannans. For woody plants, glucomannans are the dominant components of hemicelluloses in softwood, while glucuronoxylans are the dominant components in hardwood (Harris and Stone, 2008). The principle sugars of hemicelluloses include: D-xylose, D-mannose, D-glucose, D-galactose, L-arabinose, d-glucuronic acid, 4-O-methyl-d-glucuronic acid and d-galactouronic acid. Hemicelluloses have lower DPs than cellulose, ranging from less than 70 to about 200 units and have a high percentage of short-branch chains (Kuhad et al., 1997, 2007, Kuhad and Singh, 2007). Due to their short-chain lengths, branching, low hydrogen bonding, and crystallinity, hemicelluloses are more easily hydrolyzed than cellulose. In wood, hemicelluloses act as a bonding agent between cellulose and lignin.

Lignin is an amorphous, highly-branched, three-dimensional, polyphenolic hetero-polymer synthesized by enzymatic dehydrogenative polymerization of 4-hydroxyphenyl propanoid units (Sasaki et al., 2004). The three-general monomeric phenylpropane units are coniferyl, p-coumaryl, and sinapyl alcohol. The relative proportions of the three cinamyl alcohol precursors incorporated into lignin vary with plant species as well as the locations of the lignin within the plant cell wall. These phenolic monomers are linked together mainly by alkyl–aryl, alkyl–alkyl, and aryl–aryl ether bonds. The MW of lignins can be 100 kDa or more (Kuhad et al., 1997). Lignin is extremely important because it acts as the cementing agent or resin in wood (Sjöström, 1993).

The strong interaction of these biopolymer components makes wood incredibly strong and durable. This leads to a high cost to process wood for uses other than a structural material. The major structural component of wood and plant fibers is cellulose and it is the most abundant polymer synthesized by nature. Despite its great abundance, cellulosic biomass has seen only limited application beyond its historical uses such as paper, and construction materials.

4. Cellulose nanomaterials and their impact

Cellulose nanomaterials can result when cellulose is processed to the smallest possible-size (~ 2 nm × ~ 100 nm). The produced nanocellulose (Fig. 1) is a high value material that can be used in many applications including paper making (Fig. 2). Nanocellulose enables products to be lighter and stronger, has less embodied energy, can require no catalysts in its manufacturing, is biologically compatible (providing a key characteristic for its eventual for disposal) and comes from a readily renewable resource. Economic studies (Shatkin et al., 2014) have shown that cellulose nanomaterials have the potential for a dramatic impact on the world economy – early estimates to be as much