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

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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 nanocellulose to the growth of a sufficiency 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.

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 byproducts, 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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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 \rightarrow 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: p-xylose, p-mannose, p-glucose, p-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 ($\sim 2 \text{ nm} \times \sim 100 \text{ nm}$). 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





Fig. 1. Scanning electron micrographs of isolated cellulose nanocrystals. (top) Secondary electron image. (bottom) Bright field transmitted electron image (Field of View = 1.2μ m).



Fig. 2. Scanning electron micrograph of nanocellulose paper (Field of View = 2.5 µm).

as \$250 billion worldwide by 2020 and it is possible to calculate the potential US market share as high as \$71 billion at \$5 per pound for nanocellulose (Cowie et al., 2014). Cellulose-based nanotechnology has created a pathway for expanded and new markets utilizing these renewable materials. These high value materials are a natural by-product of a lignocellulosic-based biorefinery, and can be isolated as crystals (Fig. 2), fibers, fibrils, rods, or whiskers (Börjesson and Westman, 2015).

5. Lignocellulosic-based biorefinery as a source for nanocellulose

Lignocellulosic-based biorefineries have the potential to reduce the

world's reliance on nonrenewable fossil fuels and chemicals. These biorefineries convert the stored chemical energy of lignocellulosic biomass to energy, chemicals, and materials (Amidon et al., 2008, 2011; Kamm et al., 2011).

Woody biomass is the largest source of organic carbon on Earth, with a production of over 5.6×10^{13} kg of organic carbon per year (Field et al., 1998). Only about 5% of the annual woody biomass produced each year is utilized (Thoen and Busch, 2006). This leaves a huge amount of renewable chemical energy that can be captured and used. If one looks at natural forest woody biomass in terms of energy, forests produce about 1.1×10^{18} kJ per year (Klass, 1998). This is more than two times the world's total annual energy consumption of 5.0×10^{17} kJ (Amidon et al., 2008). The above illustrates the potential of woody biomass as an excellent alternative energy source.

Any widespread use of woody biomass as a feedstock for a biorefinery would require the development of a highly economical way to separate the components of wood from the wood composite and to overcome the recalcitrance of cellulose (Agbor et al., 2011; Aita and Kim, 2010; Amidon et al., 2011; Hendricks and Zeeman, 2009, Himmel, 2007; Lynd et al., 2008). Electron beam irradiation has been shown to be an effective pretreatment method to reduce the recalcitrance of cellulose (Driscoll et al., 2009; Cheng et al., 2013; Smith et al., 2014), these studies have shown a decrease in the degrees of cellulose polymerization and cellulose crystallinity, and an increase in the rate and yield of cellulose hydrolysis. Additionally, the strength of wood is significantly reduced by electron beam irradiation. Fig. 3 shows the effect of electron beam irradiation on the ASTM D143 toughness test of hard maple and it is clear the wood toughness decreases with increasing absorbed dose ($R^2 = 0.89$). The toughness is reduced by 50% after 250 kGy exposure. Fig. 4 shows the energy required to mill 1 kg of 1 cm cube hard maple blocks to 40 mesh vs absorbed dose. As the dose increases, the amount of energy required for milling decreases. The reduction in strength in the two above tests is due to the de-polymerization of the cellulose.

A biorefinery utilizes many plant products such as wood, grasses and agricultural surplus and waste materials to produce economically beneficial materials and chemicals. Due to high oil prices, the initial chemical target for such a biorefinery was glucose for the production of ethanol for fuel. However, as oil prices fluctuate, the end goal must also reflect this variability and remain agile. So, other economically valuable chemicals and materials having greater market value can be alternatively produced. In either case, nanocellulose is a major by-product. The biorefinery concept, as shown in Fig. 5, can function with the standard Kraft processing approach where, in the early stages, a good deal of energy is necessary to break down the plant materials to the component parts. However, as stated above, pre-treatment of the lignocellulosic material with ionizing radiation can be successfully used to significantly reduce the recalcitrance of cellulose. The strength of the wood decreases with the amount of ionizing radiation applied, this results in an approximately 50% reduction in energy required for maceration due to reduced milling and a reduction in the hot water/steam processing time. A



Fig. 3. Graphical representation demonstrating the decrease in wood toughness with increasing absorbed dose. The test was conducted on $20 \times 20 \times 280$ mm samples equilibrated to 12% equilibrium moisture content before the test was conducted (*see* ASTM D143, Standard Test Methods for Small Clear Specimens of Timber, ASTM International, West Conshohocken, PA, 2014, www.astm.org for a full description of the test method). The error bars represent the standard deviation of the mean of five samples.





10 MeV electron beam has a total depth of penetration in unit density material of approximately 5 cm. Electron beam pretreatment of lignocellulose material is the most environmentally and energy friendly method. Electron beam pretreatment uses no chemicals and only about 3.5×10^{-7} kW-h per KGy at 80% electrical efficiency.

The advantage of pretreating the plant materials with ionizing radiation also removes the chemical/enzymatic step for some applications, adds no additional sulfur groups to the product and very importantly provides the ability to control dose, and to customize the particle size as demonstrated in the previous nanoparticle work cited.

6. The general mechanisms of the ionizing radiation effects on cellulose

In the absence of water and presence of oxygen, the direct effects of ionizing radiation on cellulose can be outlined through the following reactions (Ershov, 1988):

- Ionization of the cellulose molecules: This is a very fast reaction, and takes no more than a couple of femtoseconds: RH→RH⁺ + e⁻
- 2. **Recombination**: This reaction is also very fast and usually takes place at a very high dose rate and in the crystalline portion of the cellulose: $RH^+ + e^- \rightarrow RH^*$
- 3. Fragment formation and decomposition: This is the preferential cleavage of the C(1)-H and C(4)-H bonds of the glucopyranose ring: RH* $\rightarrow R \cdot + H$
- 4. Abstraction of hydrogen: This is the removal of hydrogen from other carbon atoms along the same chain (*R* •, hydrogen transfer) or from an adjacent chain (*R'*•, hydrogen hopping). The equation presented here represents hydrogen abstraction from an adjacent chain: *R* + *R'*H → *RH* + *R'*•
- 5. **Decomposition:** This pertains to the unstable $R \cdot$ radicals with cleavage of the glucosidic bond to give terminal radicals with scission of the glucopyranose ring. This scission results in the formation of CO₂ (or CO) and of polymeric compounds containing terminal carbonyl or carboxyl groups.

It is currently thought that in the presence of oxygen, the carboncentered radicals in the amorphous areas of the cellulose react very fast with molecular oxygen to produce the corresponding peroxyl radicals. This reaction is very fast, with a reaction rate constant of higher than 1 \times 10⁸ mol⁻¹ s⁻¹. These peroxyl radicals (RO₂•) undergo various types of reactions, including fragmentation reactions and abstraction of hydrogen from neighboring cellulose molecules, producing more C-centered radicals and hydroperoxides:

 $\mathrm{RO}_2 \bullet + \mathrm{RH} \rightarrow \mathrm{RO}_2\mathrm{H} + \mathrm{R} \bullet.$

In the presence of H₂O, the radiolytic products of water play an important role in the radiation chemistry of cellulose through producing R•. The radiation-chemical yields of H₂O (µmol/J) are: $G(e_{aq}) = G(\bullet OH) = G(H_3O^+) = 0.28$; G(H) = 0.06; $G(H_2) = 0.047$; $G(H_2O_2) = 0.07$. The hydroxyl radical (•OH) is the most efficient in abstracting H from the cellulose chain, producing R•. The H-atom (H) behaves

Fig. 5. High level biorefinery concept showing the location of the ionizing radiation in the processing scheme.



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similarly by abstracting an H atom from the cellulose molecules, leading to the production of R•. The hydrated electron e_{aq} is a very powerful species. It adds to the oxygen atom of the cellulose molecule leading also to the formation of R•. Fig. 6 shows the scission reactions of cellulose carbon centered radicals leading to degradation of cellulose.

7. Conclusion

Nanocellulose is a high value material which has gained increasing attention because of its high strength, stiffness, unique photonic and piezoelectric properties, high stability, and uniform structure. Nanocellulose can be produced in large volumes from wood and other precursor plant materials either by contemporary wet extraction or by application of radiation processing. Pretreating precursor wood materials with ionizing radiation during processing results in significant break down of the polysaccharide and, in parallel, leads to the production of potentially useful gaseous products such as H_2 and CO. This presents huge opportunity to the ionizing radiation community. Further research into the mechanisms of the radiolytic decomposition of cellulose and the mass generation of nanocellulose is vital to tapping into nanocellulose for the growth of nanocellulostic-product development. The successful application of radiation processing is a key and energy saving component.

Pretreatment with ionizing radiation is also an environmentally friendly method for bio-refining, production of biofuels, economically viable chemicals and nanomaterials from wood and non-woody sources. Ionizing radiation decreases the energy needed for the breakdown of the wood, improves the hot water extraction of lignin and hemicellulose, reduces the recalcitrance of cellulose, increases the rate of enzymatic hydrolysis, reduces the energy needed for milling and can be used to sterilize wood chips. However, success requires strategic alliances like those demonstrated in this work, between the Government, academia and industry. Advanced manufacturing and nanotechnology are a strong fit for such strategic alliances because they are naturally multi-disciplinary in nature, are enabling technologies, and present broad industry implications, however commercialization challenges remain and will require innovative partnerships and multi-scale pilot approaches.

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Fig. 6. The scission reactions of cellulose carbon centered radicals leading to degradation.

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