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Update on Bio-Refining and Nanocellulose Composite Materials Manufacturing

Michael T. Postek and Dianne L. Poster

National Institute of Standards and Technology^{1,2}, Gaithersburg, MD 20899 USA

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. One of the factors limiting the potential of nanocellulose and the vast array of potential new products is the ability to produce high-volume quantities of this nano-material. However, recent research has demonstrated that nanocellulose can be efficiently produced in large volumes from wood at relatively low cost by the incorporation of ionizing radiation in the process stream. Ionizing radiation causes significant break down of the polysaccharides and leads to the production of potentially useful gaseous products such as H₂ and CO. Ionizing radiation processing remains an open field, ripe for innovation and application. This presentation will review the strong collaboration between the National Institute of Standards and Technology (NIST) and its academic partners pursuing the demonstration of applied ionizing radiation processing to plant materials for the manufacturing and characterization of novel nanomaterials.

Keywords

e-beam; nanocellulose; cellulose; wood; biomass; biorefining; paper; metrology

1.0 INTRODUCTION

Cellulose nanocrystals (CNCs) are one group of nanoparticles that have high economic value potential but present substantial challenges to high-volume manufacturing, and to the development of the measurement science necessary for production control. Cellulose is the world's most abundant natural, renewable, biodegradable polymer. Cellulose occurs as whisker-like microfibrils that are biosynthesized and deposited in plant material in a continuous fashion. The nanocrystals are isolated by hydrolyzing away the amorphous segments leaving the acid resistant crystalline fragments. Therefore, the basic raw material for new nanomaterial products already abounds in nature and is available to be utilized in an array of future materials. However, commercialization requires the development of efficient manufacturing processes and production-level nanometrology to monitor product quality.

Postek et al., 2008, reported on the initial developments of the manufacturing, imaging and

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metrology of cellulose nanomaterials and subsequent papers expanded upon that topic (Postek et al., 2010, 2013a). In 2013, enough research had been done, at that time, to elicit from the field, a compilation of over 100 research projects in the manufacturing cellulose nanomaterials (Postek et al., 2013b) which was reviewed at the 2014 SPIE Optics and Photonics Conference (Postek et al., 2014). New developments incorporating ionizing radiation in the nanocellulose manufacturing process were sufficiently exciting to warrant this additional update.

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, or interested in, separating the fibers into their smallest component parts. 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, Girl and Adhikari, 2013, Reboullat and Pla, 2013, Duferesne, 2013, Klemm et al., 2011, Bharimalla et al., 2015, Postek et al., 2013b) describing various current methods for isolation such as: homogenization, grinding, cryo-crushing electrospinning, enzymatic pretreatments, TEMPO-mediated (2,2,6,6-tetramethylpiperidine-1-oxyl radical) oxidation, carbomethylation and acetylation. Yet, none have included the use of ionizing radiation in the manufacturing of these 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.

Elucidating the mechanisms of the radiolytic decomposition of cellulose processing is a key element to tapping into this source array of nanocellulose for the growth of nanocellulosic-product development and the mass generation of nanocellulose by radiation treatment. 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 not well understood. 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.

2.0 DISCUSSION

2.1 Advantages Afforded by Ionizing Radiation

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 – excellent for biological and human health applications.

Efforts using ionizing radiation for the synthesis of a variety of advanced nanomaterials have been underway at the National Institute of Standards and Technology (NIST) and this work has been facilitated by the strong and long-standing collaborations between NIST, its academic partners and other Government Laboratories. Materials and the metrology under development include soft nanomaterials for drug delivery applications (An et al., 2011; Grimaldi, 2013; Takinami, 2014; Pazos 2016), magnetic nanocomposites for imaging and electrical functions (Pazos and Tsinas 2017, personal communication), adsorbents for environmental products (Dietz et al., 2016), and membranes tailored for fuel cell uses (Kim et al., 2017, personal communication). 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 (Wishart J. 2016, personal communications, Pazos et al., 2017, personal communication). 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 the materials, an important key component to understand and optimize the overall production and performance of products which ultimately make use such materials.

2.2 Demonstrated Need for Metrology

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, 2014). Isolation and characterization are needed to understand and optimize production and performance of nanocellulostic-products. This is largely due to the more rapid ability to synthesize materials, versus the more involved activities needed to isolate and determine accurately, via measurements, what is produced. Often, new or modified instrumentation is required, thus requiring substantial instrument development and optimization time. Metrology and new instrument developments need to be developed 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.”

2.3 Cellulose Nanomaterials and their Mega-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 (Figure 1) is a high-value material that can be used in many applications including paper making. 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. 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 as \$250 billion worldwide by CY 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 (Figure 2), fibers, fibrils, rods, or whiskers (Börjesson and Westman 2015).

2.4 Lignocellulosic-based Biorefinery

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). But, any widespread use of woody biomass as a feedstock for a biorefinery requires the development of an 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, Hendriks and Zeeman, 2009, Himmel et al., 2007 and 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 degree of cellulose polymerization, celluloses crystallinity and an increase in the rate and total cellulose hydrolysis. Additional, work has shown that the strength of wood is significantly reduced by electron beam irradiation and as the dose increases the amount of energy required for milling decreases. The reduction in strength is due to the de-polymerization of the cellulose by the ionizing radiation.

A biorefinery utilizes many plant products such as: wood, grasses and agriculture waste to produce economically beneficial materials and chemicals. Due to high oil prices, the initial chemical target for a biorefinery was glucose to produce ethanol for fuel. However, as oil prices fluctuate, the end goal must also reflect that variability and remain agile. So, other economically valuable chemicals and materials having greater market value can be alternatively produced. In either case, nanocellulose as a major by-product. The biorefinery concept, as shown in Figure 2, 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 reduced due to reduced milling and a reduction in the hot water/ steam processing time. The general mechanisms of the ionizing radiation effects on cellulose can be found in Postek et al., 2017.

3.0 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 ionizing radiation in the 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 H₂ and CO. Another advantage of pretreating the plant materials with ionizing radiation is that it 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. This presents a 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 break-down 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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Figure 1. Scanning electron micrographs of isolated cellulose nanocrystals. (Left) Secondary electron image. (Right) Bright field transmitted electron image (Field of View = 1.2 micrometers).

High-level Biorefinery Concept I

High-level Biorefinery Concept II

Figure 2. High level biorefinery concept showing the location of the ionizing radiation in the processing scheme.