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An Investigation Into The Viability Of Nanocrystalline Cellulose As A Packaging Material

By

John Glass

A Thesis Submitted In Partial Fulfillment Of The Requirements For The Degree Of Master Of
Science In Packaging Science

Department Of Packaging Science
College of Applied Science And Technology

Rochester Institute Of Technology

Rochester, NY

March 24, 2015

Committee Approval

Date: _____

Deanna Jacobs

Graduate Program Chair, Packaging Science

Date: _____

Changfeng Ge, Ph.D

Associate Professor, Packaging Science

Date: _____

Carlos A. Diaz, Ph.D

Assistant Professor, Packaging Science

Abstract

The focus of this proposal is to identify unexplored areas of research in the field of packaging science, specifically related to the incorporation of Nanocrystalline Cellulose (NCC) as a functional material in fiber based packaging, as well as to highlight some of potential risks and unknowns in the product lifecycle. This research hypothesizes that incorporating NCC into wood fiber-based c-flute corrugated packaging medium will show a sufficient performance improvement to justify additional research. Nanomaterials, as a whole, are still being understood, including those using naturally occurring bases such as NCC. Further incremental testing with NCC will help provide a performance and safety baseline for the necessary future research prior to mass production. NCC holds great promise for the future: a commonly available, naturally occurring material that's easily recyclable and biodegradable, yet has the strength of steel. Due diligence is required for this material to come to market in a safe and sustainable manner.

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Introduction

Significance and Problem Statement

This planet has a sustainability problem. It was been created by the overuse of natural resources by the human population with little to no regard for the long-term effects of these practices until the last few decades. Alternatives to the virgin materials that are being consumed so quickly need to be developed and brought to market sooner rather than later. Developing materials that are both sustainable, as in they can be easily renewed as a resource, as well as easy to manipulate as their virgin counterparts is proving to be a challenge, however, requiring scientists to modify of the base materials in an attempt to maintain performance (de Azeredo, 2009).

A promising recent development is the ability of scientists to effectively remove cellulose from plant matter. Cellulose is a naturally occurring polymer and a building block in the cell walls of nearly all plants (Klemm, Heublein, Fink, & Bohn, 2005). It is completely natural, biodegradable, can be used by itself or as an additive, and be synthesized into sugars to create fuel (Brunecky, et al., 2013). Cellulose by itself is also very strong, having a strength similar to steel (Venere, 2013) (Dufresne, 2013). However, this material in its raw form is incredibly tiny. As these particles are under 100 nanometers in size, they were named Nanocrystalline Cellulose (NCC) (Shatkin, Wegner, Bilek, & Cowie, 2014). The ability to remove cellulose in larger than lab-scale operations is a huge milestone, but the challenge lies in being able to take this material and effectively, safely, scale it up to sustainable mass production without further harm to the planet.

Of the plethora of potential uses for this material, packaging in particular could see significant improvements in sustainability (Shatkin, Wegner, Bilek, & Cowie, 2014). Packaging, almost by definition, is required to protect a product and is often designed to be disposable upon final destination. Any consumer that shops at a supermarket has experienced this phenomenon, but the scale of this problem is much greater than just Consumer Packaged Goods (CPG). While some research has been done incorporating cellulose-based or modified materials into packaging, there are significant gaps.

Purpose

The purpose of this proposal is to identify unexplored areas of research in the field of packaging science, specifically related to the incorporation of Nanocrystalline Cellulose (NCC) as a functional material in fiber based packaging, as well as to highlight some of potential risks and unknowns in the product lifecycle.

Hypothesis

This research hypothesizes that incorporating NCC into wood fiber-based c-flute corrugated packaging medium will show a sufficient performance improvement to justify additional research.

Literature Review

Manufacturing Methods and Material Types

Currently there are many methods of manufacturing cellulose derived materials, including TEMPO mediated oxidation, high pressure (e.g. 2,000 bar) homogenization (Kumar, et

al., 2014), acid hydrolysis (Lapidot, 2013), friction grinding and spray drying (Vartiainen, et al., 2011). For the purposes of this proposal we will focus on acid hydrolysis using sulfuric acid and aqueous mechanical grinding. In mechanical grinding, the base material, commonly wood, is ground between plates to create a material called Microfibrillated Cellulose (MFC). In this material, the fiber lengths are significantly shorter than at the beginning of the process. If it is prepared in an aqueous solution it imparts a semi-transparent look to the paste, but they have not been shortened enough to become completely transparent, such as in NCC. MFC generally has a fiber length of approximately 1 μm and a thickness of 3-100 nm, depending on the base wood chosen (Dufresne, 2013). It is important to note that MFC includes both amorphous and crystalline portions of the cellulose chains.

NCC is commonly prepared either from a chemical process or a combination of chemical and mechanical processes. One example of a chemical process is treating wood fibers with sulfuric acid (H_2SO_4) (Lapidot, 2013). This process eliminates the amorphous regions of the cellulose chains allowing the crystalline structure to separate. (Dufresne, 2013) (Lapidot, 2013). As the cellulose is very small, and is generally suspended in water, it takes on the form of a clear gel. NCC fibers are typically a few hundred nanometers in length and a width of a few nanometers. Dufresne (2013) mentions that the more important method of characterizing NCC fibers is their aspect ratio, which is the ratio of the length to the width. Aspect ratios vary between 10 and 67 depending on the source fiber. NCC can be prepared from MFC, but MFC cannot be created from NCC alone as the amorphous regions have been removed chemically.

It is important to note that MFC and NCC have similar but measurably different properties due to their physical makeup as well as how they are prepared. A study was completed comparing two films comprised of materials manufactured both processes. It was shown that

NCC had a much higher light transparency than MFC, and the additional processing and homogenization improved the ultimate tensile strength as well as the Young's modulus, but at a lower strain at break. In essence, the NCC is clearer and has superior ultimate strength, but the MFC is a notably tougher material, able to take more abuse before failure, even if its ultimate strength is lower (Kumar, et al., 2014). Lastly, as MFC and NCC can be manufactured from nearly any plant-based material, waste from the industrial processes, such as papermaking, suddenly become potential sources for feedstock (Lapidot, 2013) (Lyne, 2013).

Potential Applications

One of the more common potential applications of NCC is as an additive to flexible films, or a hybrid with other nanomaterials, in order to improve mechanical or barrier performance. Several publications list thin films destined for food packaging as a potential benefactor of this technology. (Jimenez & Ruseckaite, 2012) (Aulin, Salaza-Alvarez, & Lindstrom, 2012) (Guzman, 2012) (Shatkin, Wegner, Bilek, & Cowie, 2014) (Sirvio, Kolehmainen, Liimatainen, Jiinimaki, & Hormi, 2014) (Lyne, 2013). Although there are still many hurdles that need to be overcome before such a complicated material could achieve FDA approval. One of these challenges is the potential risk to both animals and the environment during or after use of nano-scale additives.

One of the areas that does not appear to be very well explored is using these materials as a reinforcement for fiber based materials. Some research has been done in Europe (Lindstrom & Aulin, 2014) and by the University of Maine that shows promise in both paper lightweighting and strength improvements (Shatkin, Wegner, Bilek, & Cowie, 2014), but it is not clear how

these improvements would trickle down to fiber based packaging production. This area is of particular interest and also the focus of this study.

Risks and Concerns

Based on the dearth of published articles on nanotoxicity, specifically in relation to NCCs, it appears that it is a fairly new field of study compared to the study of nanotechnology. Of the few articles found, the most relevant involved an experiment where a number of aquatic species were exposed to NCC. The study showed that while some species were sensitive to these materials, and being exposed to them had an effect on their reproductive ability, the conclusion was that NCC's have a "low toxicity potential and environmental risk" (Kovacks, et al., 2010). While this is a good start to the environmental research necessary prior to mass production and implementation, much more work must be completed.

Based on existing research, there is a heightened amount of interest for food contact plastics which has helped raise the issue of nanotoxicity in humans. In a study outlining nanobiocomposites, specifically combining bioplastics (e.g. Polylactic Acid or PLA) with nanomaterials, the authors created a list of risks and forward work, the chief amongst them being: "To develop, improve and validate in vitro and in vivo test methodologies to assess the toxicology of nanoparticles and their interaction with human cells" (Jimenez & Ruseckaite, 2012). It has been demonstrated that exposure to other types of nanoparticulates, such as titanium dioxide (TiO_2) can cause damage to DNA (Petkovic, et al., 2011). Research has been completed, however, to speed the detection process of damage to DNA by exposure to more common particulate of this size (Watson, Ge, Cohen, Pyrgiotakis, Engelward, & Demokritou, 2014). Put simply, the test methods to determine whether or not nanoparticulate such as NCC are safe do

not exist yet, let alone in a capacity to vet new materials prior to production. Even if the test methods existed, most nanoparticulates are not understood well enough for the nanotoxicity studies to truly be meaningful (Warheit, 2008).

At the very least, research has begun on detection methods for the particulates themselves. While research is being done in Europe to assess exactly how these materials may shed nanoparticulates and some possible ways to detect them (Simon, 2012), a US based team has developed a laser-based system that should be able to make use of these methodologies (Ozdemir, et al., 2014).

Lastly, it does not appear that much research has been done to address the end of life of this material. There is one group, however, that has identified an enzyme that can process cellulose-based material rapidly. This enzyme can break down cellulose into its base sugars, which could potentially be used for energy production or feedstocks for other processes. (Brunecky, et al., 2013). Theoretically, NCC will break down on its own accord when exposed to the environment, but the damage potential of these particulates between the time they are released and the time they break down is not understood.

Experiment Methodology

As the scope of the work left to be done is vast, this study hopes to focus its efforts in one place: Beginning to understand the benefits of incorporating NCC into fiber-based packaging materials as an additive. The results of this study will act as a go-no go gauge on this path of research. If the composite material does not perform as expected this path of research is not acceptable.

Research Design & Data Analysis

The path of least resistance for initial testing is incorporating NCC into an existing process as this will provide a direct comparison to off the shelf products. Regular Slotted Containers (RSC) are mass produced corrugated boxes and are a perfect candidate for this testing. RSC's consist of three components: The liner, the inner corrugated flutes, also known as the medium, and the adhesive. In this case, NCC could be incorporated into any of the components of an RSC, but the medium material itself should reveal interesting data as it provides a notable percentage of compressive strength of the package when it is corrugated and assembled into the RSC (ASTM Subcommittee D10.27, 2014). By adding NCC to an existing medium formulation we can directly observe the change in the performance of the composite material.

Previous research into biocomposite films has shown final part mixtures utilizing 0% NCC, as a control, up to 50% NCC for a test range, based on dry weight (Sirvio, Kolehmainen, Liimatainen, Jiinimaki, & Hormi, 2014), so this would likely be a good range for the independent variable of our experiment. For consistency, a single, NCC source should be chosen, comprised of the same type of tree from the same region. These fibers should be run through a pre-existing methodology for processing into NCC, for example the process Melodea utilized (Lapidot, 2013), in order to ensure consistent results.

After the source materials are obtained, a supplier capable of making short runs of corrugated should be found. This supplier should manufacture a sufficient quantity of C flute corrugated for material testing using the ASTM D5639 standard as the research instrument (ASTM Subcommittee D10.27, 2014). Specifically, at least 100 test cycles worth of material for each NCC/Kraft combination between 0% and 50%, in 10% increments, on the Edge Crush Test

and Mullen Burst test outlined in section 7 of the standard. This data will then be analyzed to find both the mean and standard deviation of each population to determine if, by using the NCC modified corrugated for our independent variable, a statistically viable improvement has been made over the control corrugated (0% NCC), as well as determining the approximate percentage gain, or respective loss, in performance due to the addition of these materials as our dependent variable.

The largest potential limitation in this research design is finding a corrugated manufacturing partner willing to create small, consistent runs of test materials. The fiber for the corrugated medium will likely not be a huge challenge as it is off the shelf, but finding a suitable quantity of NCC of consistent fiber length and quality will most likely be difficult due to the newness of the manufacturing process. As NCC is also only in pilot scale the cost of the base material may be a limiting factor as well. Several pilot plants exist across the globe, however, so this challenge is not insurmountable.

Future Work

As incorporating NCC into fiber-based packaging is still in its infancy, so there are several areas that this research could branch out into. Keeping along this particular research path, however, the two most logical next steps would be narrowing the band of NCC percentage testing then manufacturing boxes from the most ideal material. An example of narrowing of the percentage test band would work as follows. If the initial testing showed that the greatest gain in performance was between 20 and 30 percent, the next round of testing would create materials with a 20 to 30 percentage mixtures with a 1 percent change in each formulation. If the greatest strength material from the second round of testing was 22%, an additional batch would be

formulated, the corrugated would be converted into a standard box size, then sent off for ISTA testing with an off the shelf box as a control (0% NCC).

Summary

While great opportunity exists for these materials, it cannot be done without great caution. Nanomaterials as a whole are still just being understood, even after years of study. Rushing these items to market without due diligence from the scientific community could be disastrous. The other side of this coin, however, is that nanomaterials, specifically NCC, hold great promise for the future. A commonly available, naturally occurring material that's easily recyclable and biodegradable, yet has the strength of steel. It sounds like the stuff of science fiction, yet we are very close to seeing this material in mass production.

This testing, specifically, provides an opportunity to push the boundaries with fiber-based packaging, both increasing strength in existing products, and reducing the amount of material required for packages that are equivalently strong by reducing thickness. This incremental testing will help provide a baseline for other researchers and the industry as a whole moving forward.

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