MAKER: Use of Natural Products in Manufacturing Engineering Education at a Minority-based Land-grant Institution

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ABSTRACT

Near-term processing of cellulosic materials requires them to be scalable in material properties for scaled up manufacturing purposes. The use of cellulosic materials is gaining favor in production applications because the synthesis and extraction of cellulose can be a green process from start to finish and is renewable in nature. The implementation and integration of natural products into manufacturing engineering education at Central State University (CSU), an 1890 Land Grant Institution located in Wilberforce Ohio, incorporates a local supply chain found in the Tawawa Woods that is sustainable and minimizes waste recycle. Thus, undergraduate students enrolled in the College of Science and Engineering search out suitable starting cellulosic materials for use in manufacturing applications. They investigate different natural and synthetic cellulosic materials and then initiate various surface, chemical, electrical and mechanical property measurements with these materials. They identify readily available starting reagent materials (natural and synthetic) that are appropriate for extraction of cellulose. Following identification of test reagents, a statistical experimental design matrix is compiled. The matrix used guides the synthesis and extraction experiments. It is possible that the resultant cellulosic fibers may accept the natural and synthetic colorants. The purpose of color enhancement is to determine feasibility and longevity of its use with different celluloses as starting electrode materials. Promising results may lead to production of novel biomaterials, polymeric materials, and composite materials as well as compliant sensing materials capable of being modified for different applications. Assessment results point to greater engagement of minority learners. These students tended to spend more than eight hours per week in the laboratories, often well into the evening, working on their manufactured samples produced from natural resources.

Introduction

A recent study noted that the quality of diversity interactions were related to 2 different outcomes: the need for cognition and critical thinking skills.[1] Integration of research and development in the classroom and laboratory as a teaching strategy for student engagement and learning[2] is a practice that facilitates positive interactions among students, faculty, and the extended community.[1-6] Implementation of interdisciplinary research experiences that are real-world and team based combining undergraduate students from science and engineering disciplines with faculty in higher education alongside middle and high school in-service and pre-service science and engineering educators creates Capstone experiences that are of intellectual interest to the undergraduate student.

Research Conducted by CSU Research Teams

This multidisciplinary effort is aimed at conducting research related to cellulosic materials derived from a variety of resources for polymer fabrication, characterization, and application to engineering materials manufactured from natural products. It is of significant interest to the CSU community as a focus area for land grant research currently funded by agencies such as National Science Foundation Research Experience for Teachers (NSF-RET) and the United States Department of Agriculture (USDA). In the past two years, four CSU research teams have worked on natural product related projects.[7] Each team worked with a primary faculty research

mentor assisted by 2-3 other faculty members as the need arose. One undergraduate Science, Technology, Engineering, and Mathematics (STEM) major worked in tandem with two in service teachers and one pre-service teacher. Presented in Figure 1 is a research poster created by one of the four CSU collaborative research teams. This paper discusses that research along with a description of the work conducted by the CSU team.

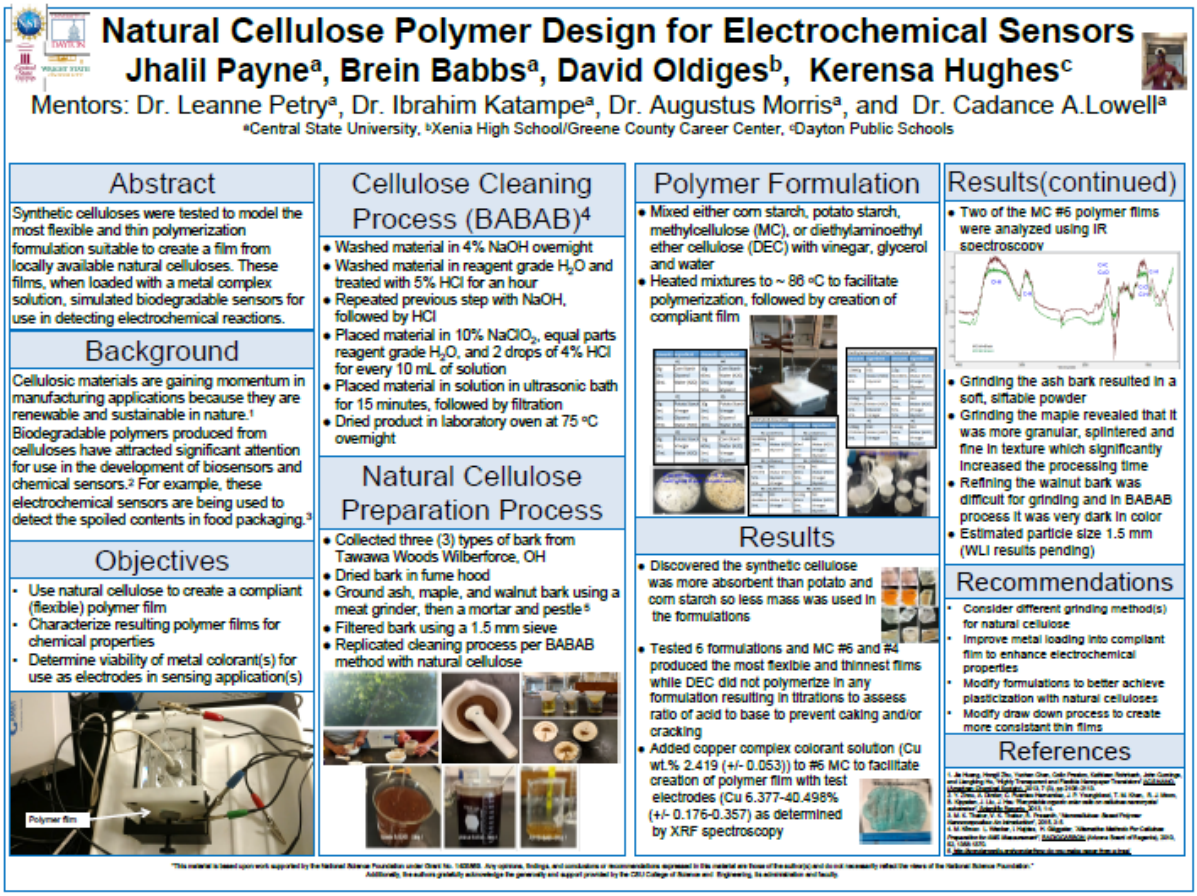

Figure 1. CSU collaborative team poster created for natural cellulose research.

CSU Team Project Title: Natural Cellulose Polymer Design for Electrochemical Sensors

Project Abstract: Synthetic and natural celluloses were screened and tested to model the most flexible and thin polymerization formulation suitable to create a film from locally available natural celluloses. These films, when loaded with a metal complex solution, simulated biodegradable sensors for use in detecting electrochemical reactions. Polymer films were assessed mechanically and spectroscopically. To date, some cellulose formulations resulted in brittle films while others a compliant material. Films averaged a thickness of 1.0 mm and, in some cases, exhibited a mechanical strength of 8.42-15.5 N. Spectroscopy results indicated incorporation of cellulose into the polymer. However, loading of metal complex for electrode purposes resulted in inconsistent distribution in the polymer film.

Project Background: The use of cellulosic materials is gaining momentum in manufacturing applications because they are renewable in nature, tunable in mechanical and chemical properties, and capable of being altered for diverse products. Cellulose-based polymer materials derived from both natural and petrochemical, a chemical obtained from petroleum and natural gas, resources are currently being extensively used in a wide range of products and in numerous applications.[8] Compared to their natural counterparts, synthetic polymers have been widely used in a vast number of applications such as films, flexible plastic bags, composites and rigid containers to name a few.[8] The use of celluloses as reinforcements in biodegradable polymers is a relatively new field in technology and has attracted significant attention during the last decade.[9] The use of cellulosic materials is gaining approval in production uses because the synthesis and extraction of cellulose is a green process that could be modified for scalable materials in manufacturing.[9] The properties of the cellulosic materials from natural resources (wood, bioresidues, and annual plants) have shown to be very similar independent of the original source, meaning that the size distribution of fibers is an important factor and that it can be modified for different applications.[10]

The main components of wood are cellulose (40–60%), lignin (16–33%), hemicelluloses, and minor easily extractive components (5–10%) like resins, waxes, etc.[11] Natural cellulose fibers with a diameter of 20–50 mm are made of thousands of microfibril· with a diameter of a few to tens of nanometers that can form a smooth film capable of scattering less light than regular paper.[12] Thus, these cellulose fibers can be dissolved and used to make transparent films by the same process as in the plastics industry.[13] A range of electronic devices on transparent paper substrate have recently been demonstrated, including organic light-emitting diodes (OLED), organic solar cells, touch screens, thin film transistors (TFTs), and antennas.[13] Despite the promising performance of cellulose fibers and their abundance, few studies have been performed on the utilization of cellulose microfibrils.[14] The main reason is the difficulty in extracting fibers from the complex plant cell wall.[14] The development of biosensors and chemical sensors for the detection of neurotransmitters has received attention due to the vital role in the metabolic system of mammals.[15] Due to its small size, the microelectrode has been proved to be significantly advantageous to electroanalytical chemistry.[16] The electrode materials that can be employed in manufacturing microelectrodes are usually limited to gold, platinum and carbon, primarily due to the 'heat sealing' process used in the fabrication of microelectrodes.[16] The use of metal electrodes capable of producing different oxidation states is of interest in this study because of the ability to produce a visual indication of the electrochemical reaction being monitored and still maintaining compliance of the film.

Screening Methods for Sample Design and Fabrication:
Cellulose Preparation - Three (3) types of tree bark were collected from The Tawawa Woods Natural Landmark, Wilberforce, Xenia Township, Greene County, OH (39° 43' N, 83° 52' W).[17] Maple, Ash, and Walnut tree bark were collected and dried in the laboratory fume hoods for seven (7) days. The bark was then mechanically grinded about ten (10) revolutions per minute (rpm), and refined with a mortar and pestle to produce a powder like substance. The resulting powder was sifted using a 1.5 mm sieve and collected for subsequent cleaning.
Cleaning Method - The BABAB, base-acid-base-acid-bleaching, method of cleaning the cellulose from the bark was used. This method is a modified version of the widely used ABA, acid-base-acid, method, extended with a bleaching step at the end of the cleaning process and

represents the current standard cleaning procedure for wood.[11] In between steps, reagent water (H_2O) was used for rinsing. The ground bark (25 mg) was first washed in 5 mL of 4% NaOH overnight. Product was then removed by gravity filtration and washed in 10 mL of reagent grade water followed by treatment with 5 mL of 4% HCl for 1 hour. The previous water rinsing step was repeated prior to another cycle with 5 mL 4% NaOH and 4% HCl for 1 hour each. The product was removed, rinsed, and soaked in a solution consisting of 5 mL of 10% $NaClO_2$, 5 mL of reagent grade water, and 2 drops of 4% HCl for 2 hours. After 2 hours of bleaching, the bleached cellulose was placed in an ultrasonic bath (25 ^oC) for 15 minutes. The resulting yellow colored suspension was collected using gravity filtration. The final product was dried at 75 ^oC in a standard laboratory oven overnight.

Polymer Formulation - Corn starch, potato starch, methylcellulose, or diethylaminoethyl ether cellulose was mixed in various ratios of 5 weight percent acetic acid (vinegar), glycerol, and water. The solution was then heated to ~86 ^oC and rapidly stirred to facilitate polymerization. The cellulosic polymer was poured onto a 5.0 x 5.0 cm^2 parchment paper square and flattened to create a 1.0 mm thick compliant film. Tables 1, 2, and 3 of Figure 1 show the corn and potato starch (baseline) formulations, methylcellulose (MC) formulations, and diethylaminoethyl ether cellulose (DEC) formulations, respectively. Compliant films containing metal electrodes substituted a 2.5 weight percent aqueous solution for water in the formulations.

Analytical Methods for Sample Characterization:

Spectroscopic Tests - A Buck Scientific Incorporated (Model 500) Infrared Spectrometer was used to determine the percent reflectance and estimate the degree of polymerization for the cellulosic films. The polymer film was sandwiched between two sodium chloride salt plates (25 x 4 mm) and scanned in the range from 4000 cm^{-1} to 600 cm^{-1}. A Thermo Scientific Niton XL2 XRF Analyzer was used to determine the weight percent of the loaded metal in compliant film. A 3 electrode setup was used for the electrochemical tests. The metal containing compliant film was used as the working electrode (sample). An Ag/AgCl probe filled with saturated KCl was used as the reference electrode. A platinum/ niobium mesh was used as the counter electrode. A 0.5 M KCl + 0.001 M $K_3Fe(CN)_6$ (1:1 mixture ratio) was used as the electrolyte. Several drops of 1.0 M sulfuric acid was added to every 300 mL of test electrolyte. The electrochemical flat cell had an exposure area of 1 cm^2. A Gamry Interface 1000 potentiostat was used for electrochemical measurements.

Mechanical Tests - An Instron 2716-020 was used for tensile testing and to estimate the modulus of elasticity.

Results and Discussion:

Polymer processing - Upon testing different formulations, it was determined that the synthetic cellulose was more absorbent than the baseline corn and potato starches. Thus, ratios of vinegar, glycerol, and water for each formulation were altered to enhance polymerization. As noted in Figure 1, methylcellulose formulations #4 and #6 produced the most compliant films and were therefore used to test metal electrode loading. Diethylaminoethyl ether cellulose did not polymerize in any formulations. Titration testing was done to assess the ratio of acid to base, to attempt to prevent the caking and/or cracking prior to the curing of the film. For every 5 grams of DEC it was determined that 5 weight percent acetic acid was the appropriate stoichiometric ratio for the formulations. Each cellulosic powder resulting from the three types of ground bark was slightly different from the other bark. The Ash produced a soft, siftable powder which

resembled a texture similar to that of the methyelcellulose. Maple bark produced a granulated texture, similar to that of very fine sand. However, it did splinter during the refining phase. Walnut produced a texture similar to the Maple, although it was by far the most difficult to filter during the cleaning procedure because the powder had a propensity to agglomerate. An estimated particle size of each cellulose was 1.5 mm. White Light Interferometry results confirming particle size are in progress.

Spectroscopic Results - Polymer films were assessed using Infrared spectroscopy (IR) to determine the degree of polymerization, different functional groups present, and associated bonding. Figure 1 in the presented poster notes the IR spectra for two replicate samples of the #6 MC formulation. Evidence of O-H, C-H, C=C, C=O, and C-O functionalization is noted. According to these results, the #6 MC formulation is ~ 70 percent reflective in the visible range. This result is in agreement with IR results by Jung et al.[18] Copper loaded films were highly absorbing and therefore could not be evaluated for percent reflectance but could be examined with X- Ray spectroscopy (XRF). Samples loaded with a copper (Cu) complex solution to provide an array of electrodes in the compliant film were analyzed via XRF and results indicate 6.377- 40.498 (+/- 0.176- 0.357) weight percent of Cu loaded into the #6 methylcellulose formulation. This wide range of weight percent Cu is interesting because the initial Cu complex solution showed 2.419 (+/- 0.053) weight percent of Cu in the liquid solution when tested by the XRF analyzer. These results suggest that upon curing a greater amount of Cu metal is imparted to the polymer film and may be unevenly distributed throughout its 1.0 mm thickness within the 1 cm diameter area of analysis. Figure 2 in the presented poster is an optical photograph of the electrochemical test cell set-up configured to date. As of the writing of this REU report, electrochemical test results are pending.

Mechanical Results - The Instron 2716-020 used for tensile testing and to estimate the modulus of elasticity was not sensitive enough to measure the strength of these films. Unistrut scaffolding was employed to fix the polymer films, apply increasing loads with statics weights, and estimate the mechanical force needed to break the polymer films. Using the scaffolding assembly, a functioning test apparatus was employed to mechanically test films and estimate mechanical strength in the 8.42-15.5 N range.

Conclusions and Recommendations: To speed up the process of grinding the bark and producing the amount natural cellulose needed for the synthesis of the compliant films, different grinding methods should be considered for the purpose of scaled up manufacturing. For better consistency, and to improve electrochemical properties, the loading of the Cu complex solution (or other metals) into the compliant films should be modified to incorporate a drawdown bar process thus improving metal dispersion and creating a uniform film thickness. The formulation ratios were altered to best account for the absorbance of liquid with the synthetic celluloses. Similar considerations should be made in the test matrix for natural cellulose formulations using the ground Ash, Maple, and Walnut bark for better plasticization during the curing process in making compliant films. Finally mechanical testing for stress versus strain in addition to the breaking point relative to the elastic modulus of the polymer formulation should be assessed. Currently, electrochemical and mechanical testing to determine extent of redox reaction based upon the metal complex loading and mechanical strength compared to degree of polymerization, respectively, are ongoing.

Summary
Four CSU research teams engaged in natural product related projects in materials and manufacturing over the course of two years. Teams worked collaboratively on a variety of natural product program initiatives in addition to the cellulose processing and polymeric characterization results presented here and included: (1) extraction of colorants for dyeing and sensing applications; and (2) antibacterial and antioxidant testing for medicinal applications. Assessment results point to greater engagement of CSU undergraduate students. These students spent more time per week in the laboratory, often well into the evening, working on their manufactured samples produced from natural resources. All teams gained a better understanding of team work and group dynamics which should aid them in facilitating team-based activities in the future among peers, faculty, and the extended community.

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