

ABSTRACT

SALAM, ABDUS. The Synthesis, Characterization, and Application of Polysaccharides-based Additives to Increase the Dry Strength of Paper. (Under the direction of Prof. Lucian A. Lucia and Prof. Hasan Jameel).

Paper recycling is a very visible and highly important conceptual framework in any effort to address environmental concerns, reduce expanding landfills, and reduce the need for virgin fiber manufacture with the concomitant expenditure of energy and resources. The major problem with recycling paper is the loss of its strength properties due to reduced inter-fiber bonding of reclaimed fibers relative to virgin wood pulp fibers is generally attributed to the drying phase of the first papermaking cycle. Petroleum-based dry strength agents are widely used for improved recycle paper strength properties. The widespread use of petroleum-based dry strength agent in the paper making industry has raised environmental concerns and prompted efforts towards developing alternatives.

The goal of this study is to therefore develop a new (natural and environmentally friendly) polysaccharide derivative to produce a polysaccharide-based dry strength additive featuring high strength recycled paper. These new polysaccharide dry strength additives are expected to significantly improve inter-fiber bonding and improve the antimicrobial activity of the final product. Soy flour is a very cheap complex polysaccharide, but it has a low number of free functionalities and poses a bacterial digestion problem as manifested by bad odors and potential paper strength losses. This dissertation is a fundamental study that focused on the modification (synthesis) of polysaccharides (soy flour, cornstarch, hydrolyzed protein and carbohydrate-based nano materials) with five different types of crosslinking agents for the introduction of carboxylic or and amine groups. The modified polysaccharides were complexed with chitosan as part of a general chemical strategy to reduce the bacterial digestion

of modified polysaccharides (especially soy protein flour) and improve its incorporation into a recycle pulp matrix to increase inter-fiber bonding.

To confirm the improvement properties of modified polysaccharide additive-treated pulp sheet, the inter-fiber bonding strength, amount and type of bond formation between additive and pulp fibers, mechanical strength, and antimicrobial activity were tested. The inter-fiber bonding strength increased 2.5-3 times, mechanical strength (tensile, bursting, and STFI index) increased 38-52%, the ester bonds formed were found to be 1.82-1.90 mmol/100g after curing at 110 °C, and a significantly enhanced antimicrobial activity was observed for both modified polysaccharide and modified polysaccharide additive-treated pulp sheet compared to the control sample (untreated pulp sheet). The composition and structure of additive-treated pulp sheet was also analyzed by TGA, DMA, FT-IR and SEM.

The current results confirm that modified polysaccharides have a potential opportunity in the papermaking industry as dry strength agents for paper.

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The Synthesis, Characterization, and Application of Polysaccharides-Based Additives to
Increase the Dry Strength of Paper

by
Abdus Salam

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DEDICATION

To my beloved parents- Abdur Razzak and Shahera Banu.

BIOGRAPHY

Abdus Salam was born in Dinajpur, Bangladesh. He is a graduated in Applied Chemistry and Chemical Technology in 2000 at University of Rajshahi, Bangladesh. After graduation, in August of 2000 he started to work in Progoti Composite Mill Ltd. as a Scientist. His major job responsibility was bleaching, dyeing, printing, and formulation of coating agent and pigment.

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CHAPTER 1

This chapter mainly focuses on general introduction, literature review and research objectives of the dissertation.

1. Introduction

Paper recycling has been practiced for many years. Often it is possible to substitute recovered fibers in place of virgin fibers used for the production of paper or paperboard. The major problem with recycling paper is the loss of its strength properties due to the change in basic fiber characteristics such as length, flexibility, swelling, bonding, and contamination [1]. The reduced inter-fiber bonding of reclaimed fibers relative to virgin wood pulp fibers is generally attributed to the drying phase of the first papermaking cycle [2]. Drying is a *de facto* papermaking protocol accompanied by partially irreversible closure of the small pores in the fiber wall (“hornification”), as well as increased resistance to swelling during rewetting [3]. Additionally, when hornification occurs within the pores of the fiber, the loss in swelling capacity results in stiffer fibers, which lack the conformability of virgin fibers, and thus have a reduced opportunity to maximize bonding strength as a result, decreases the mechanical strength [2, 4]. Figure 1.1 showing decreases the breaking length when paper sheet was drying and recycling with different temperatures (Cabalova et al., <http://www.intechopen.com>).

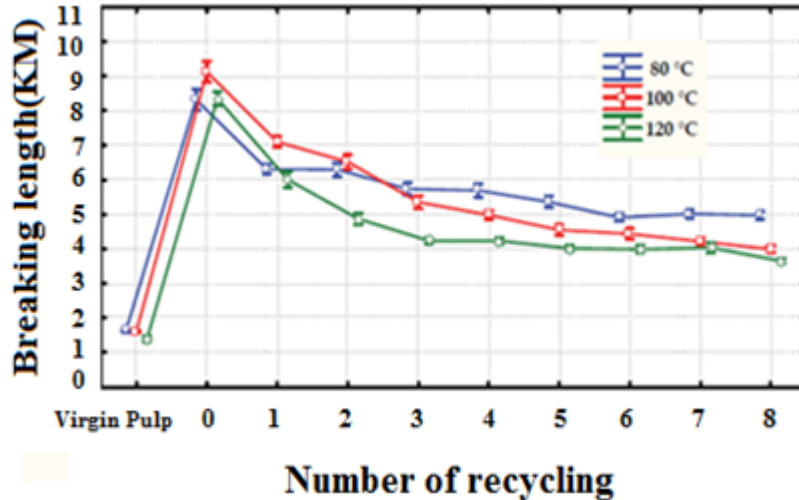


Figure 1.1: Alteration of the breaking length of the paper sheet drying at the temperature of 80, 100, 120 °C during eightfold recycling.

Different types of polysaccharide-based dry strength additives such as native (corn) starch, cationic starch, amphoteric starch, soy protein flour and petroleum based dry strength such as cationic polyacrylamide, anionic polyacrylamide, glyxolate polyacrylamide have been used over the course of time to increase the mechanical strength of recycle paper furnish. These types of commercial dry strength agents, however, have not been able to increase the strength properties of reclaimed pulp furnish to levels comparable to virgin pulp. In addition, native starch or cationic starch need to be well cooked before use but cooked starch has many drawbacks such as high viscosity and limited absorption on cellulose fiber substrate causes poor performance. Over soy protein flour has decomposition problem due to contain metabolic enzyme, and polyacrylamides is a petroleum-based dry strength that is costly and can contribute to pollution.

1.1. Introduction to polysaccharides

Origin of Soy flour

Soy flour is made by roasting and grinding soybeans. Soy flour is commercially available and contains approximately 33.7 % carbohydrate, 34.5% soy protein, 21.9% fatty acid and other components such as moisture, vitamin, mineral and biologically active or metabolic proteins such as enzyme [5]. The metabolic protein in soy flour is vital issue to decompose of soy protein. However, soybean is also an excellent source of soy protein that is highly digestible (92-100%). It has proteins (40%), lipids (20%), carbohydrates (35%), minerals (5%) and very small quantity of other nutrients [6]. Soy protein is a long chain polymer consisting of 18 different polar and nonpolar amino acids. Polar amino acids include cysteine, arginine, lysine, histidine and many others.

Origin of corn starch

Cornstarch is a carbohydrate-based polymer that is widely abundant and readily available in a number of commercial forms. It typically occurs as semi-crystalline granules composed of amylopectin and amylose. Amylose is a linear chain polymer and is composed of α -1-4-glucosidic units. But amylopectin is a branch chain polymer and composed of α -1-4-glucosidic units and β -1-6 glucosidic units [7].

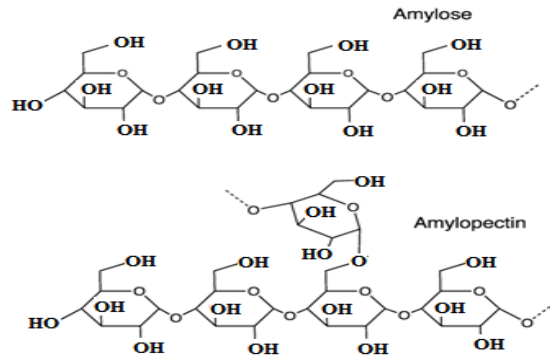


Figure 1.2: Chemical structure of amylose and amylopectin

Origin of cellulose nanocrystals

Cellulose is arguably the most important biopolymer on the planet because not only is it the most abundant biomaterial available, it is renewable, biodegradable, biocompatible, non-hypoallergenic, readily derivative, extremely strong, and eco-friendly. No other natural or synthetic polymer comes close to matching its highly functional mechanical and chemical properties. It is a carbohydrate polymer made up of repeating β -D-glucopyranose units that is characterized by three hydroxyl groups per anhydroglucose unit that is able to impart a high degree of functionality to the biomacromolecule (8).

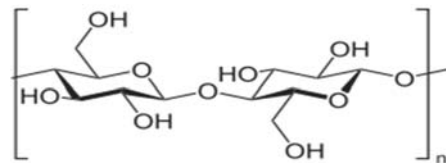


Figure 1.3: Chemical structure of cellulose nanocrystals.

1.2. Substitution of polysaccharide

Polysaccharides are polymeric carbohydrate molecules composed of long chains of monosaccharide units bound together by anhydroglucose linkages. Each glucose unit has three hydroxyl groups which may be substituted. The average number of substitutions per glucose unit in polysaccharide is called the degree of substitution. The hydroxyl groups in glucose unit may be substituted by anhydride, acetyl, or cationic groups via esterification or etherification reactions and produce anionic or cationic polysaccharides. The ionization of polysaccharide molecule to change the properties of polysaccharides [9] for example cationic starch, anionic starch etc.

1.3. Modification of polysaccharides

Modification is a common approach to improve the performance of polysaccharide for various applications. Corn starch, soy protein flour and cellulose nanocrystals have been modified with modifying agents, such as monochloro sodium acetate, succinic anhydride, citric acid, melic anhydride, butanetetracarboxylic acid, epichlorohydrin, alkyl ketene dimer, 1,2,3,4-diepoxybutane, and alkyl succinic anhydride to improve the mechanical properties and water stability of polysaccharide products[10]. The esterification reaction occurs between the hydroxyl group of polysaccharide and the anhydride group of the modifying agent.

However, if modifying agent contain more than two carboxyl groups, there is a possibility to have a cross linking reaction between the modifying agent and molecules of polysaccharide [11]. Typically, epichlorohydrin, sodium trimetaphosphate, sodium tripolyphosphate, epichlorohydrin and 1,2,3,4-diepoxybutane are used as crosslinking agents to cross link a

polysaccharide [12, 13]. Esterification or cross linking is a function of the acidic, alkali, aqueous and non-aqueous media and it may also be controlled by varying modifying agent concentration, polysaccharide percentage, pH, times and temperatures [11].

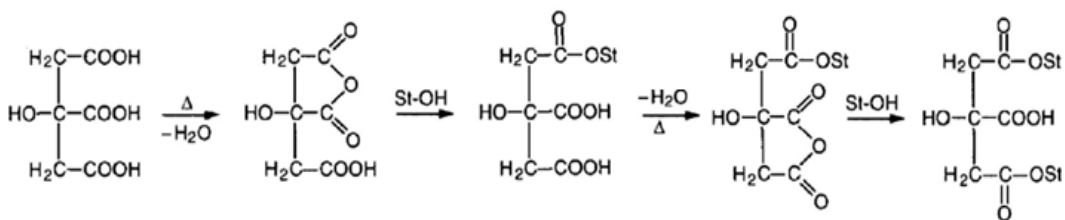


Figure 1.4: Esterification reaction between citric acid and starch.

This work has focused mainly on the development of new polysaccharide-based (soy flour, corn starch and cellulose nanocrystals)-based dry strength additives via chemical reactions with different types of modifying agent to provide high strength recycled and virgin paper furnishes. The mechanism is based on the incorporation of carboxylic acids and amine functionalities onto the polymeric backbone of polysaccharides to significantly contribute to improved inter-fiber bonding among pulp fibers by developing (1) hydrogen bonds between functional groups of polysaccharides and hydroxyl groups of pulp fibers, (2) ionic bonds among the amine groups of polysaccharides and carboxylic acid groups of pulp fibers and (3) covalent bonding or crosslinking among multi-carboxylic acid functionalized polysaccharides and hydroxyl groups of pulp fiber (the multi carboxylic acid group condense to form an anhydride at high temperature and subsequently lead to esterification with the hydroxyl groups of pulp fibers). The modification of the polysaccharide has shown the ability to reduce

bacterial digestion of the soy flour and corn starch, and recycled pulp sheets.

1.4. Literature review

Previous studies: For the last few decades several efforts have been made for improving the mechanical properties of recycle paper furnish at home and abroad. This section deals with past research work on the problem of recycle paper furnish, efforts to overcome the problem through modification of recycle paper furnishes, effect of dry strength additive and sizing agent on the recycle paper furnish, and bacterial resistance of recycle paper furnish.

RISI [14] has reported that global paper and paper board consumption has been growing quite steadily. While in 1950, about 50 million tons of paper was produced worldwide, global paper and board production was close to 400 million tons in 2010. Approximately over 210 million tons of waste paper was collected and re-used in 2010, an almost 30% increase from 1992. These values show that recovered paper is currently the most important raw material in the production of paper, paperboard, and corrugated paper.

Anon [15] has reported that the utilization rate of waste fiber (OCC) for recycled containerboard in 1963 was 21.1% in the US, whereas in 2001 it was 67% with a concomitant recovery rate of approximately 70%. Recently, the American Forest & Paper Association (AF&PA) released a 2011 recovery rate for Old Corrugated Containerboard (OCC) which has reached a new high of 91.2%.

Onusseit [16] reported that paper recycling is mostly external, meaning that the accumulated paper waste used is mostly generated outside of the paper mill, i.e., post- but also pre-consumer

recovered paper. The prime objective is to utilize the fibers contained in the recovered paper. Following the increase in paper industry needs, recovered paper collection has been extended to private households and the use of commingled instead of source-separated collection systems has become more popular. With these, there is a yield of recovered paper of considerable lower quality and greater amount of impurities.

Nazhad et al. [1] investigated that the major problem of OCC recycling paper is the loss of its strength properties because of reduced inter-fiber bonding resulting from the drying phase of the first papermaking cycle.

James et al. [17] reported that when hornification occurred inside the internal molecules of the fiber, it resulted in fibers that were stiffer and not as conformable as virgin fibers that ultimately deprived the sheet of an optimal opportunity to bond.

Diniz et al. [4] indicated that when wood pulp fibers are dried, the internal fiber volume compressed. Because of structural changes in wood pulp fibers, it lead to the removal of a significant amount of water, closed fiber pores, increased stiffness, and reduced surface area. In addition, when fibers were re-suspended in water, the original water swollen state was not regained.

Newman et al. [18] proposed that when adjacent cellulose crystalline regions were dried in contact, they coalesced.

Gullichsen [19] reported that after refiningg of recycle pulp, the pulp fibers collapsed and became more flexible, possessing increased bonding surface area with increases burst and

tensile index when increasing number of refining revolutions. Besides, refining produced a higher amount of fines which tends to slow down the dewatering of the wet web of paper. However, refining also decreases the length of fiber which lead to a decreased tear strength and folding endurance [18].

James et al [17] investigated that the inter-fiber bonding depends on polysaccharide molecules and the surface functional groups such as hydroxyl, carbonyl, and carboxyl. A few researchers tried to increase inter-fiber bonding through the beating or refining of pulp fiber [21], blending with virgin fibers [22], chemical derivatization of pulp fibers [23], etc. But strength improvement is still very low relative to that of virgin pulp sheet [24].

Biermann et al. [25] reported that modifications of wood pulp fibers is a very active research area, and several methods have been developed over the last few years. Various investigators indicated that modification changed many physical properties of fibers such as absorbency, strength, stiffness and water resistance [26].

Dimitri et al. [27] reported that two carboxylic acid moieties formed an anhydride at high temperature. This anhydride later reacted with cellulose hydroxyl groups via a traditional esterification reaction. (Fig.1.5).

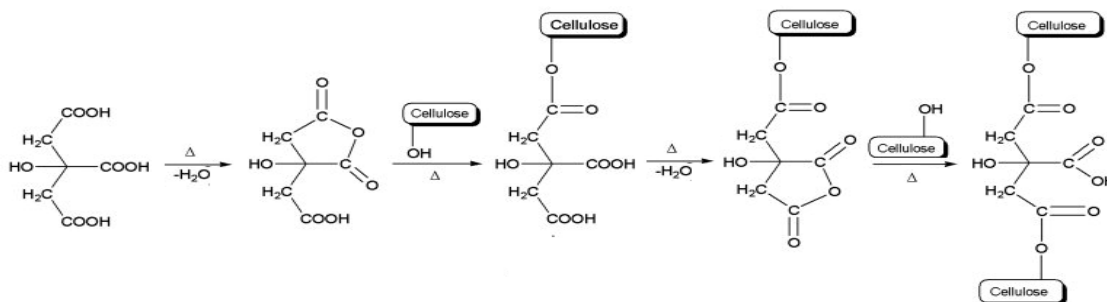


Figure 1.5: Possible crosslinking reaction mechanism of citric acid with cellulose.

Abbas [28] reported that native starch is widely used in food applications every day. It is also used in the textile industry for sizing and finishing of cloth, pharmaceutical, medical and cosmetic industries. But native starch is not widely used in the paper making industry as dry strength agent due to wide variation of viscosity and it is nearly nonionic, and thus unable to adsorb on fiber effectively. Therefore, the native starches have limited use in the paper industry.

Ayoub et al. [29] investigated that native starches normally required modification such as mechanical, chemical, or enzymatic to enhance essential properties. The modifications of starch changed pasting temperatures, reduced viscosity, improved resistance to processing conditions, and added desirable functional groups.

Wing [11] carried out research on modification of starch with citric acid. Their esterification carried out at high temperatures allow citric acid to form anhydrides which reacted with the hydroxyl groups of starch. It was indicated that the degree of substitution of starch depended on reaction factors such as reactant concentration, catalyst concentration, pH, time, and

temperature.

Jensen et al. [30] investigated that cationic starch is widely used in recycle fiber to retain fines, fillers, and internal sizing agents at the wet end of the paper machine for increased paper strength.

Heydari et al. [20] found that a dry strength agent such as polyacrylamide enhances the bonding area in recycle pulp fibers. The inter fiber bonding between fibers increased due to intermolecular hydrogen bonding provided by the dry strength agents functionalities (carbonyl oxygens) compared to the hydrogen bonding between fiber hydroxyl groups. However, the polyacrylamide can promote the fiber-fiber interactions by ionic or covalent interactions from amine groups [23].

Grigoriev et al. [31] reported that G-PAM was increased dry strength properties of pulp sheets because G-PAM is a reactive polymer and its reactive functional groups can covalently bind with cellulose upon dehydration.

Riaz [32] reported that soybean is an excellent source of highly digestible soy protein (92-100%). It contains proteins (40%), lipids (20%), carbohydrates (35%), minerals (5%) and a very small quantity of other nutrients [33]. Soy flour is made by roasting and grinding soybeans. Defatted soy flour is commercially available and contains approximately 33% carbohydrates, 51% soy protein, 3% fats, and other components such as moisture, vitamin, mineral and biologically active or metabolic proteins [34]. Soy protein is a long chain polymer consisting of 18 different polar and nonpolar amino acids. Polar amino acids include cysteine,

arginine, lysine, and histidine among others.

Li et al. [35] found that soybean proteins are used in paper coating and sizing operations. Twenty different proteins increase the wet strength of paper. The proteins and polypeptides, which have a reinforcing function, have a high content of five important amino acids. The first two are polar amino acids with a hydroxyl group on each, and the other three are common basic amino acids with active amine groups [36].

Xu et al. [37] carried out research on chemically modification of soy protein flour with succinic anhydride and later with the polyamidoamine-epichlorohydrin used to cross-link the soy adhesives for improving bond strength. The author also mentioned that the FT-IR results of modified soy protein flour contained acetylated or succinylated spectral signatures.

Jin et al. [38] investigated that soy protein flour can be used as a dry strength additive in recycled OCC pulp furnishes. But the strength improvement of OCC pulp sheet was very low compared to virgin pulp. However, soy protein flour is susceptible to bacteria digestion.

1.5. Research objectives

The **overall objectives** of this study were to synthesize, characterize, and study the fundamental function of a new class of polysaccharide-based dry strength additives to improve the mechanical properties of low strength recycle paper furnish (OCC).

Hypothesis: It was proposed that carboxylic and/or amine functionalized polysaccharides may contribute to improving inter fiber bonding among OCC pulp fibers by developing an extensive hydrogen, ionic bonded, and a chemically crosslinked network.

Therefore, the hypothesis was tested as follows:

- Developing a polysaccharide dry strength additive capable of forming hydrogen bonds, ionic bonds and chemically crosslinkages with recycled OCC pulp fiber.
- Measurement of the resultant properties:
 - Inter-fiber bonding strength, fiber length, mechanical strength
- The fundamental reasons for improvements observed were obtained by quantification of the amounts and types of bonds formed.

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CHAPTER 2

This chapter presents the selection of modifying agent and optimizing modification conditions. This chapter also focuses on the optimizing additive dosage and pH to produce better paper sheet.

2.1. Introduction

Chemical modification of polysaccharides has been widely studied for the production of anionic, cationic and amphoteric materials for paper, textiles, and food applications. Esterification is one of the chemical modification possible for the polysaccharides using acetic anhydride, octenyl succinic anhydride, citric acid, sodium monochloro acetate, fatty acid, epichlorohydrin, pentafluorobenzyl chloride, or fatty acid chlorides [1-5]. Etherification is also a common reaction of polysaccharides especially for starch with vinyl monomers in the production of hydrophobic starch for textiles [6]. Amphoteric starch has negative and positive charged functional groups prepared through chemical reaction with 3-chloro-2-hydroxypropyltrimethylammonium chloride and sodium tripolyphosphate [7]. Cationic starch was prepared by reacting starch with 3-Chloro-2-hydroxy propyl amine [8].

In this present investigation, the selection of modifying agent and optimum reaction conditions were attempted. Modifiers such as succinic acid, carboxymethy-adipic acid, butanetetracarboxylic acid, ethylenediaminetetraacetic acid and diethylenetriaminepenta acetic acid were reacted with soy flour in presence of sodium hypophosphite separately and then complexed with chitosan. A fixed amount of each modified soy flour additive was mixed with pulp slurry to generate hand sheets.

2.2. Experimental

2.2.1. Selection of Modification Agent

5 g of different kind of modifying agent namely succinic acid, carboxymethy-adipic acid, butanetetracarboxylic acid, ethylenediaminetetraacetic acid and diethylenetriaminepenta acetic acid was dissolved in 20 mL deionize water in a 50mL Petri dish separately. 1 g of SHP was then added at each modifying agent solution Petri Dish. Soy flour (5g) was combined with each modifying agent solution in the Petri Dish and manually mixed vigorously with a glass rod. The mixture was placed in an air oven at 130°C for 4 hours. Reaction products were washed with DI water and filtered several times to remove unreacted materials. The product obtained was modified soy flour that was air dried at 50°C in an air oven overnight. Thereupon, the modified soy flour was complexed with chitosan using a known procedure [9]. Briefly, 1g of chitosan was dissolved in 50mL of 1.5 % acetic acid solution. Modified soy flour (1g) was also dissolved with 50 mL water and then added to a 50 mL chitosan solution in a 250 mL round bottom flask. The reaction mixture was stirred using a magnetic stirrer at 80°C for 90 minutes [10]. Approximately 2% modified soy protein flour additive by mass of OCC pulp-based slurry was thoroughly mixed before generating a two-dimensional hand sheet for physical testing.

2.2.2. Optimization of Synthesis Conditions

The modification (synthesis) of soy flour was carried out in 50mL Petri dish. Modification was done with 10–50% diethylenetriaminepenta acetic acid (DTPA) and 5% sodium

hypophosphite based on the weight of diethylenetriaminepenta acetic acid, at pH 8-12, 100–140 °C for 1–5 hours in the soy flour –liquor ratio of 1:10. At the end of the desired reaction period, the DTPA-soy protein flour product was thoroughly washed with distilled water and dried in air oven [11]. Thereupon, the DTPA-soy flour was complexed with chitosan [12]. The blend ratio (chitosan/modified soy flour) was prepared at varying chitosan percentage 10-50% to determinate the optimum chitosan ratio with soy flour-DTPA. Approximately 2% DTPA-soy flour/chitosan by mass of OCC pulp-based slurry was thoroughly mixed before generating a two-dimensional hand sheet for physical testing.

2.2.3. Optimization of Additive Dosage and pH

The hand sheet was prepared at varying DTPA-soy flour/chitosan additive concentration e.g. 0.5, 1, 1.5 and 2% based on the weight of OD OCC pulp at pH 7. The additive-treated OCC pulp sheet was tested tensile strength to find out optimum additive dosage. Similarly, additive-treated OCC pulp sheet was prepared with 3, 4, 5, 6, 7 and 8 pH separately, and the optimum pH was selected based on highest tensile strength of additive-treated OCC pulp sheet.

2.3. Results and discussion

It was observed from Table 2.1 that diethylenetriaminepentaacetic acid modified soy flour-treated OCC pulp sheet exhibit better tensile index compare to other modifying agent. The tensile properties of modifier are in the order diethylenetriaminepenta acetic acid > ethylendiaminetetraacetic acid > butanetetra-carboxylic acid > carboxymethy-adipic acid > succinic acid.

Table 2.1: Effect of modifying agent on mechanical properties into recycle OCC pulp hand sheet.

Modifying agent	Additive	Pulp Furnish	Tensile Index (Nm/g)
Succinic acid(SA)	Soy Flour-SA/Chitosan	OCC	43.00
Carboxymethyl-adipic acid(CMA)	Soy Flour-CMA/Chitosan	OCC	45.08
Butanetetracarboxylic acid (BTCA)	Soy Flour-BTCA/Chitosan	OCC	46.72
Ethylendiaminetetraacetic acid (EDTA)	Soy Flour-EDTA/Chitosan	OCC	50.10
Diethylenetriaminepenta acetic acid (DTPA)	Soy Flour-DTPA/Chitosan	OCC	52.58
No modifying agent	No additive	OCC	38.15

It was observed from Figure 2.1, 2.2, 2.3 and 2.4 that the tensile index of DTPA-soy flour/chitosan additive-treated OCC pulp sheet increased up to 20% DTPA, time 3hrs, temperature 120°C and pH 10, and afterward, it become very slow. From an economic point of view, 20% DTPA, time 3 hrs, temperature 120°C and pH 10 were selected. It is also seen from the Figure 2.5 that the tensile index of soy flour-DTPA/chitosan-treated pulp sheet increases with the increased chitosan percentage into soy flour-DTPA up to 30% and then decreases. The optimum soy flour-DTPA/chitosan ratio was selected 70:30.

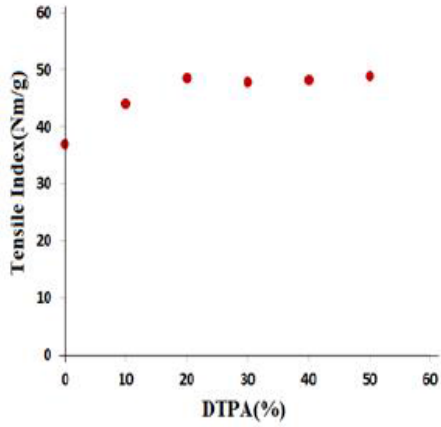


Figure 2.1: Effect of DIPA concentration vs tensile index of additive-treated pulp sheet

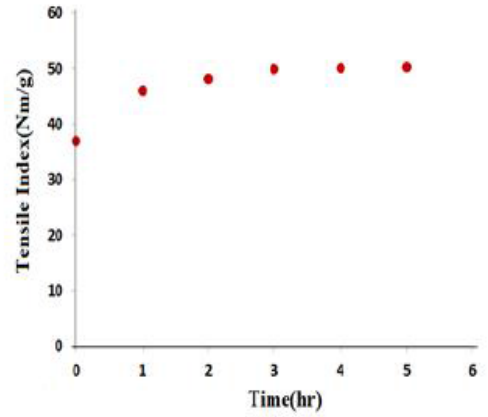


Figure 2.2: Effect of time vs tensile index of additive-treated pulp sheet

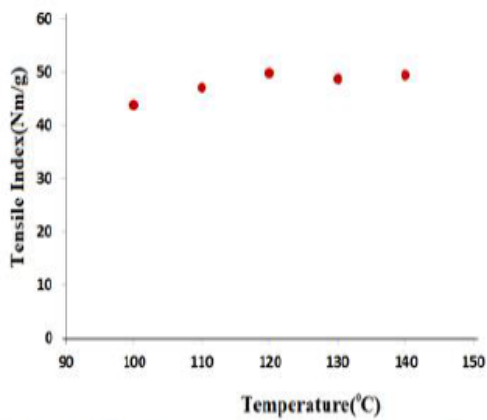


Figure 2.3: Effect of temperature vs tensile index of additive-treated pulp sheet

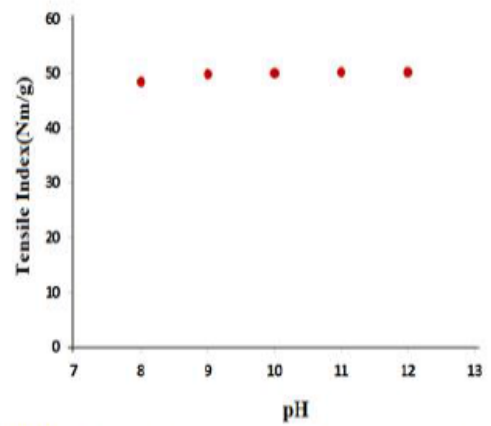


Figure 2.4: Effect of pH vs tensile index of additive-treated pulp sheet

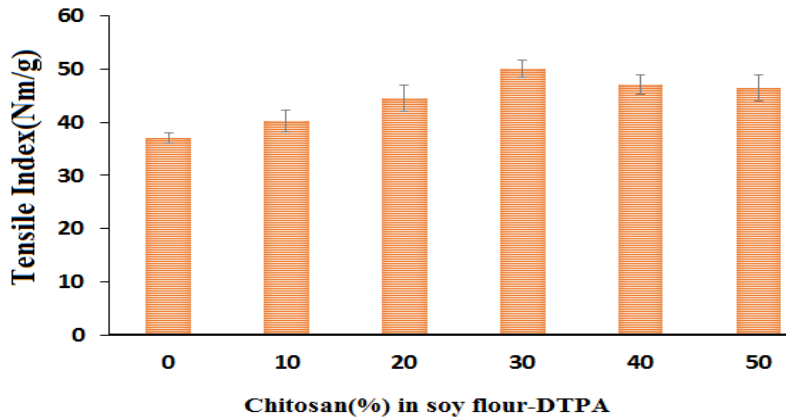


Figure 2.5: Effect of chitosan percentage vs. tensile index of additive-treated pulp sheet

From Figure 2.6, it is shown that the tensile index of OCC pulp sheet increases with increased additive concentration up to 1.5% and then decreases. It is also observed from Figure 2.7 that the tensile index of additive-treated pulp sheet decreased with increased pH up to 6 and then increased. Based on tensile properties and economics, the optimum additive dosage and pH were 1.5% and 4 & 8, respectively. However, the drainage ability was tested in sheet molder machine based on how fast drainage the pulp slurry water. The drainage ability was increased about 18% and the additive retention was found to be 65%.

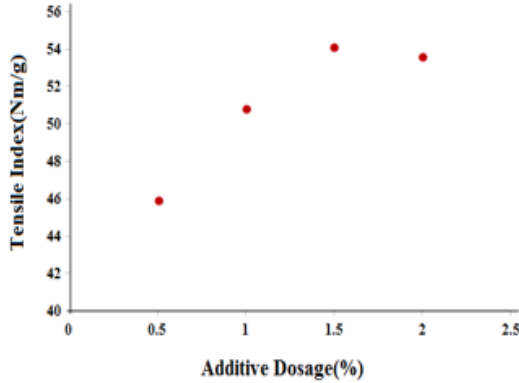


Figure 2.6: Effect of additive dosage percentage vs. tensile index of additive-treated pulp sheet.

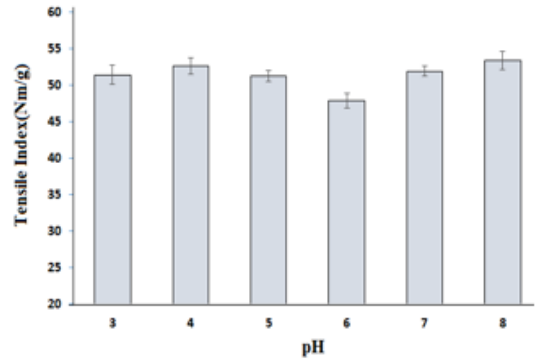


Figure 2.7: Effect of pH vs. tensile index of additive-treated pulp sheet

2.4. Conclusion

Five different types of modifying agent treated modified soy flour additive were mixed with pulp slurries to generate hand sheets. Diethylenetriaminepentaacetic acid (DTPA)-modified soy flour additive-treated OCC pulp sheets exhibited better tensile indices compared to other modifying agents. Four factors including agent concentration, time, temperature, and pH were considered. From an economic point of view, 20% DTPA, 3 hrs, 120 °C, and pH 10 were selected. The modified soy flour was blended with different percent chitosan to determinate the optimum blend ratio. The optimum chitosan blend ratio was found 30%. The optimum additive dosage, pH, drainage rate and additive retention were studied. Based on tensile properties, the optimum additive dosage and pH were 1.5% and 4 & 8, respectively. The drainage ability increased 18% and the additive retention was found to be 65%.

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CHAPTER 3

Complex Soy Bean Flour-Based Additives to Increase the Dry Strength of Recycled Paper.

This chapter focuses on the hydrolysis of soy protein isolates from acid, alkali, and enzymatic treatments, modification of hydrolyzed soy protein isolate and soy flour with modifying agents in the presence of a catalyst and further complexed with chitosan, and finally the characterization of modified hydrolyzed soy protein isolates and modified soy flour additives. In addition, it also focuses on the characterization of the modified hydrolyzed soy protein isolate and modified soy flour additives-treated recycled paper furnish (OCC) by examining the inter-fiber bonding strength, quality and quantity of bond formation (hydrogen, ester, ionic), and mechanical properties.

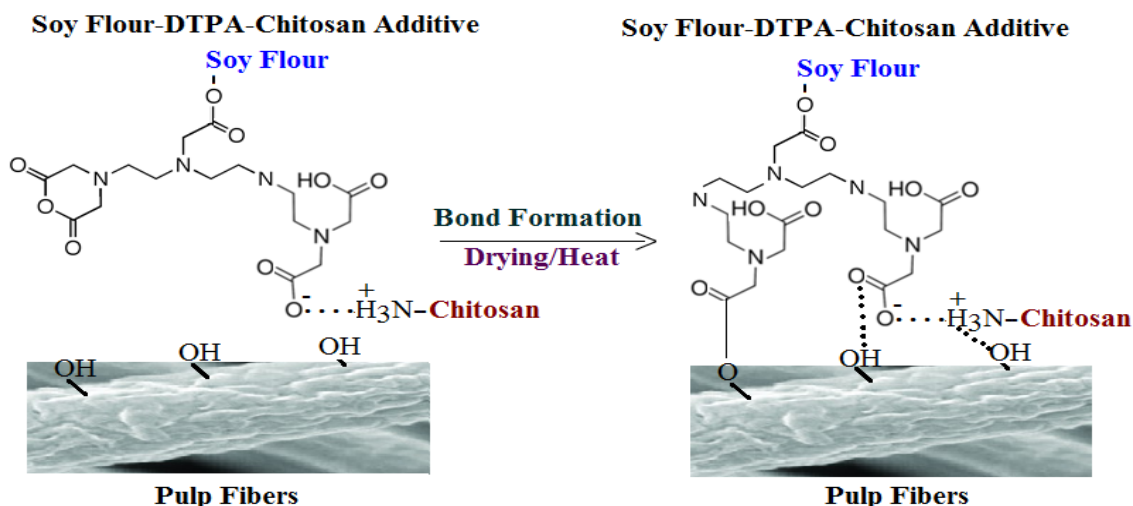
Two article and one book chapter has been published from this chapter.

1. Abdus Salam, Hasan Jameel, Lucian A. Lucia. The Synthesis, Characterization, and Application of Soy-Based Macromolecules: A New Generation of Materials for Paper Dry Strength Enhancement. *ACS Sustainable Chem. Eng.* 2015, 3, 524–532.
2. Abdus Salam, Lucian A. Lucia, Hasan Jameel. A preliminary assay of the potential of soy protein isolate and its hydrolysates to provide interfiber bonding enhancements in lignocellulosic furnishes. *Reactive and Functional Polymers*, 2014, 85, 228-234.
3. A. Salam, H. Jameel, Y. Liu, L.A. Lucia. Novel Class of Novel Class of Soy Flour Biobased Functional Additives for Dry Strength Enhancements in Recovered and Virgin Pulp Fiber Networks. Soy-Based Chemicals and Materials, *ACS Symposium Series* Vol. 1178, Chapter 11, pp 255-264, 2014.

The Synthesis, Characterization, and Application of Soy-Based Macromolecules: A New Generation of Materials for Paper Dry Strength Enhancement

Abdus Salam, Lucian A Lucia,* Hasan Jameel

Graphical Abstract



Abstract

The goal of the current effort was to develop a new soy-based derivative (from soy flour) to impart high fiber-fiber strength improvements to reclaimed paper materials. The success of the research hinged on successful proliferation of carboxylic and/or amine functionalities onto the polymeric backbone (proteins and carbohydrates) of the soy flour residues to significantly contribute to improved inter-fiber bonding of reclaimed paper fibers. Diethylenetriaminepentaacetic acid (DTPA) was reacted with soy flour in presence of sodium hypophosphite and then complexed with chitosan as part of the development of a new generation of dry strength agents to improve integration into reclaimed pulp fiber matrices and

increase inter-fiber bonding. The reclaimed paper materials incorporating the DTPA cross-linked (modified) soy flour agent demonstrated unprecedented tensile strength indices. The synthetic conditions including surface modifier concentration, time, temperature, pH, and material-to-liquor ratio, were optimized. A 1.5% soy flour-DTPA-chitosan agent by mass of pulp-based slurry was thoroughly mixed before generating two-dimensional hand sheets whose tensile indices increased 52.6, 53, and 57.8% for recovered (OCC, Old Corrugated Containerboard) pulp sheet, NSSC (virgin) pulp sheet, and a kraft (virgin) pulp sheet, respectively, versus the controls. The inter-fiber bonding strength of soy flour-DTPA-chitosan agent-treated pulp sheets (OCC, NSSC and kraft) increased 2.5-3.0 times, a landmark finding relative to past work. The modified soy flour-agent treated pulp sheets also provided significantly increased gloss and water repellency with concurrent diminished roughness compared to the control sample.

Keywords: *Soy flour, crosslinking/synthesis, dry strength agents, recovered fibers, kraft pulp, inter-fiber bonding, mechanical properties*

3.1.1. Introduction

Pulp is a lignocellulosic-based fibrous material that is generally prepared by chemically or mechanically separating predominantly cellulose fibers from their natural bundled state in crops fiber, woody fiber, or waste paper. Their morphology, mechanical or chemical stability, and/or optical properties can change significantly when formed into a wet web of paper and subsequently subjected to processes such as pressing, drying, printing, storage, repulping, and deinking.¹ Typically, the responses of various paper blends or materials to different external

stresses vary, but generally, “virgin” or never-reclaimed fibers tend to significantly outperform reclaimed (or recycled) fibers. Paper reclamation has been practiced for many years as a means to demonstrate good environmental stewardship practices and national/regional energy concerns. Often, it is possible to substitute reclaimed fibers in place of virgin fibers for the production of equivalent paper or paperboard. It has been reported that the utilization rate of OCC (Old Corrugated Containerboard), a popular and widely used grade of paper, in 1963 was 21.1% in the US, whereas it increased to 67% during the early part of the last decade with a concomitant reclamation rate of nearly 70%.² Recently, the American Forest & Paper Association (AF&PA) has divulged a reclamation rate for OCC of over 91%. The major problem with attaining the goal set by AF & PA for OCC reclamation is the inherent loss of strength that occur from changes in basic fiber qualities such as length, flexibility, swelling, bonding, and purity (contamination).³ The reduced inter-fiber bonding of reclaimed fibers relative to virgin wood pulp fibers is generally attributed to the drying phase of the first papermaking cycle.⁴ Drying is a *de facto* papermaking protocol accompanied by partially irreversible closure of the small pores in the fiber wall (“hornification”), as well as increased resistance to swelling during rewetting.¹ Additionally, when hornification occurs within the pores of the fiber, the loss in swelling capacity results in stiffer fibers, which lack the conformability of virgin fibers, and thus have a reduced opportunity to maximize bonding strength.⁴⁻⁵ The most universally acknowledged property loss in reclaimed paper fibers is mechanical, manifested as a loss of inter-fiber bonding measured by tensile and burst strengths. Inter-fiber bonding is characterized primarily by hydrogen bonding between surface carbohydrate macromolecules of neighboring fibers. The strength of inter-fiber bonding

critically depends on the chemical nature of the polysaccharide molecules with particular emphasis on functional groups such as hydroxyl, carbonyl, and carboxyl. Not surprisingly, it also depends upon the extent of surface contact among fibers.⁴

Therefore, a number of research efforts have attempted to improve the strength of reclaimed paper by addressing either one or both of the latter aspects given that reclaimed fibers are mechanically inferior to their virgin equivalents. Past research has demonstrated that high intensity (PFI) refining increases tensile and bursting strength of reclaimed paper, but at the expense of the production of a high level of fines (typically, *sub*-mm sized particles from the S2 layer of wood fibers) that tend to slow down dewatering of the wet web of paper. A loss of fiber length and coarseness can lead to compromises in tear strength and folding endurance.⁶⁻

⁷ Earlier research efforts have identified several chemical treatments that contributed to significant improvements in the inter-fiber bonding strength of a recycled pulp sheet.⁸ Within those studies, a few have demonstrated that chemical modification of pulp fibers may obviate strength losses.⁹⁻¹⁰

The interest, therefore, in chemical derivatization continues unabated to this day, with much research devoted toward discovering viable agents that can significantly augment fiber-fiber bonding. Soybean-based byproducts have recently been identified by our group as potentially viable agents or the next generation (bio-based) of additives for paper dry strength enhancements.¹¹ The US produced nearly 88 million metric tons of soybean in 2013 (USDA) of which soy flour is the second pass by-product (after defatting the soybeans), that can be characterized as a complex carbohydrate made by roasting the soybean, removing the coat,

and grinding it into flour. Defatted soy flour is commercially available and contains approximately 32% carbohydrates, 51% soy protein, 3% fat, and a host of other components that include water, vitamins, and minerals.¹²

The soy protein component is a long polymer chain consisting of 18 different polar and nonpolar amino acids; amongst the polar amino acids are cysteine, arginine, lysine, and histidine which can be used as a chemical "hook" to crosslink the protein and thus improve its mechanical, thermal and physical properties as well as reduce water sensitivity and hydrophilicity.¹³ Earlier research has related that soy proteins can be cross-linked by incorporation of aldehydes such as glyceraldehyde, formaldehyde and glutaraldehyde by employment of *Maillard* reactions.¹⁴ Crosslinked isolated soy protein has previously been used to develop biodegradable polymers that possess enhanced mechanical properties.¹⁵ A cursory study conducted by Jin et al.¹¹ applying soy bean protein flour as a dry strength additive showed promise for papermaking. The results of such studies have pointed to increased tensile strength from hydrogen bonding networks between soy protein and pulp fibers. However, the strength improvement was not comparable to commercial dry strength agents likely due to the very low density of hydrogen bonding functionalities on the soy flour. Dry strength additives are very important as a class of chemical reagents because they allow for a reduction in the overall basis weight of the paper product to achieve the same dry strength and thus save on the cost of cellulosic raw materials. Selecting the correct dry strength agent to minimize costs is key for success in papermaking. Different types of dry strength additives such as native starch, cationic starch, carboxymethyl cellulose, guar gum, and polyacrylamides have been used over the course of time. These types of commercial dry strength agents,

however, have not been able to increase the strength properties of reclaimed pulp furnish to levels comparable to virgin pulp. The key to dry strength enhancements is a complex function of successful homogeneous blending of a reagent with hornified fibers, providing surfaces for interfacial bonding, and appropriate economics. DTPA (diethylenetriaminepentaacetic acid) is a reagent that could provide successful crosslinking because it contains five carboxyl groups and two amine groups. At higher temperatures, these carboxyl groups may condense to form an anhydride and may esterify with the amine or hydroxyl group of soy flour. These available functionalities may form hydrogen, ionic or covalent bonding networks within the reclaimed pulp fibers and thus improve inter-fiber bonding strength.

The present study therefore focuses on the synthesis, characterization, and functional understanding of a newly developed generation of soy flour-based dry strength additives for improving the mechanical properties of low strength reclaimed paper materials (OCC). In the present investigation, the modification of soy flour with DTPA in presence of sodium hypophosphite represents the first agent of this class studied to determine its potential to achieve high strength gains. The DTPA-modified soy flour was complexed with chitosan as part of a general chemical strategy to facilitate its integration into a reclaimed OCC pulp fibers matrix and increase inter-fiber bonding. This research also focuses on the characterization of the modified soy flour agent-treated reclaimed paper furnish (OCC) by examining the inter-fiber bonding strength, quality and quantity of bond formation (hydrogen, ester, ionic), and mechanical properties. Commercial cationic starch and polyacrylamide dry strength agents were used for comparison purposes.

3.1.2. Experimental procedure

3.1.2.1. Materials

Soy flour was provided by Archer Daniel Midland (ADM, Decatur, IL). Corn starch, was supplied by Cargill Incorporated, Minneapolis, MN. Reclaimed OCC, NSSC (virgin) and kraft (virgin) pulp were supplied by Georgia Pacific Innovation Research Institute, Norcross, GA. Crosslinking agents, i.e., diethylenetriaminepentaacetic acid (DTPA) and chitosan, were purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphate, (SHP) CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2; denatured alcohol and acetic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water.

3.1.2.2. Methods

Chemical Modification of Soy Flour

Approximately 2 g of the modifying agent (DTPA) was dissolved into 20 mL alkali solution in a 50 mL Petri dish to which 0.4 g of sodium hypophosphite (SHP) was added. Soy flour (8 g) was added to the Petri Dish and vigorously mixed with a glass rod. The mixture was placed in an air oven set at 120°C over a time course of 3 hours. Reaction products were washed with DI water and filtered several times to remove any unreacted materials. The product obtained was a modified soy flour that was air oven dried at 50 °C overnight. Thereupon, the modified soy flour was complexed with chitosan using a previously described procedure.¹⁸ Briefly, 0.6 g of chitosan was dissolved into 50 mL of a 1.5% acetic acid solution. Modified soy flour (1.4

g) was also dissolved into 50 mL water and then added to the existing 50 mL chitosan solution previously placed within a 250 mL round bottom flask. The reaction mixture was stirred using a magnetic stirrer at 80 °C for 90 minutes.¹⁹ The proposed reaction schemes for the reactions with DTPA are shown in Figures 3.1.1 and 3.1.2.

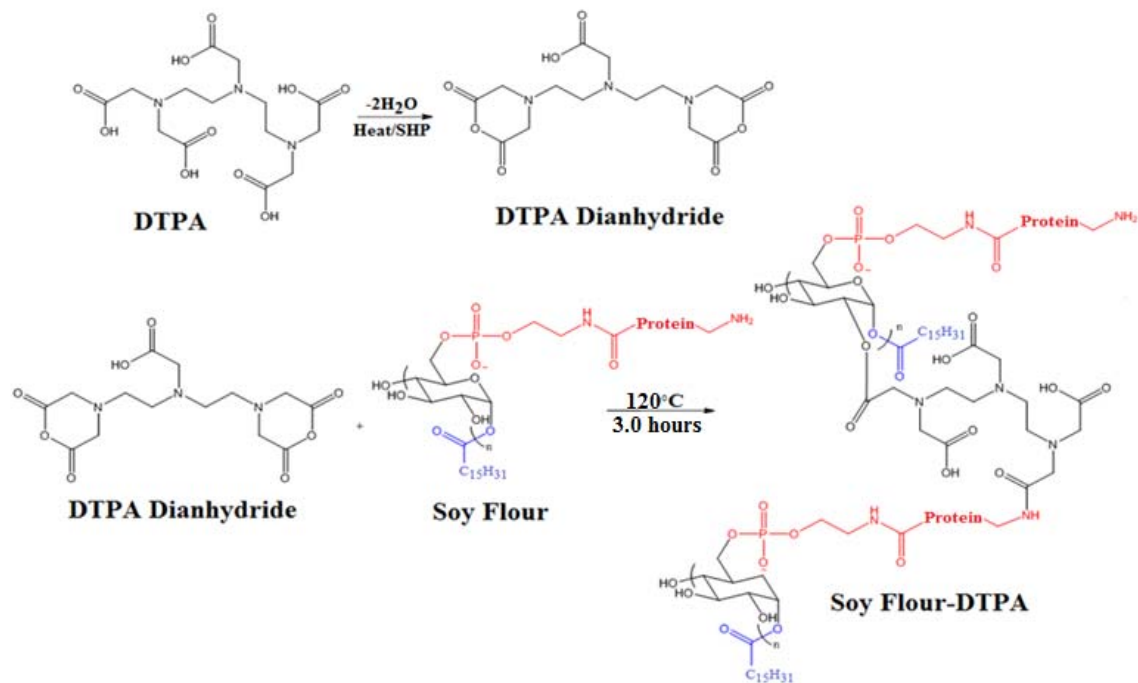


Figure 3.1.1. A suggested esterification route for soy flour and DTPA.

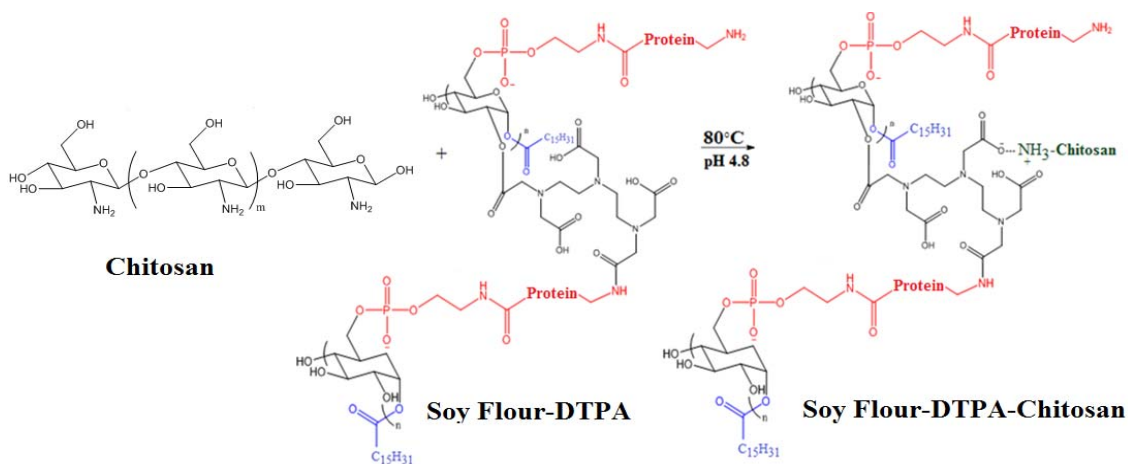


Figure 3.1.2. A suggested complexation reaction of the soy flour-DTPA reagent with chitosan.

3.1.2.3. Characterization of Modified Soy Flour

Determination of Carboxylic Acid Content:

A fixed amount of soy flour-DTPA was dissolved into 20 mL of 0.1 N NaOH and hydrolyzed for one hour. The excess NaOH was determined by titration with 0.1 N HCl and phenolphthalein as the indicator²⁰ in which the carboxyl content in milli-equivalents of acidity per 100 grams was calculated by the following equation:

$$\text{Carboxylic Acid Content (meq)} = \frac{(V_2 - V_1) \times N \times 100}{W}$$

where

N = Normality of HCl

V_2 = Volume of HCl without sample

V_I = Volume of HCl with sample

W = Weight of Sample

FT-IR Analyses

IR spectra of all modified soy flour samples were recorded on a Perkin Elmer FT-IR spectrophotometer.¹⁷

Thermal Gravimetric Analyses (TGA)

The TGA used in this study was a TGA Q500. A nitrogen atmosphere was used. The temperature range and heating rate were 30-600 °C and 5 °C/min, respectively, followed by isothermal heating at 600 °C.²¹

Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter DSC Q100 with a Hermetic pan (T 090127) was used to determine the thermal behavior of all samples. Samples were subjected to a 2 °C/min temperature ramp from 30–200 °C followed by isothermal heating at 200 °C for 15 minutes.²²

Measurement of Storage Moduli:

Dynamic mechanical analysis was performed using a DMA Model 2980 in the film tension mode. The specimen dimensions were 30 mm in length, 10 mm in width, and 0.3 mm in thickness. Samples were heated from 30 to 250 °C using a temperature ramp of 2 °C/min (20µm amplitude, at 1 Hz).²³

Contact Angles

Dynamic contact angle measurements were performed with a Phoenix 300 Contact Angle Analyzer (Seo Co., Ltd., Korea). Deionized water was used as the probe fluid.²⁰

3.1.2.4 Preparation and Characterizations of OCC Pulp Hand Sheets

The sheet was prepared according to TAPPI Standard Method T 205 using a 900 ml pulp slurry (2.7 g OCC having a freeness of 400 CSF) in a sheet molder in the presence or absence of a modified soy flour additive. The pulp slurry was diluted with 10 L of water to produce a uniform sheet. The sheet was dried in a condition room and subsequently cured at 25-110 °C for 1 hour.¹⁹ In addition, the additive dosage percentage and pH were optimized based on the tensile strength of the additive-treated OCC pulp sheet.

Scanning Electron Microscopy (SEM)

Morphological characterization of modified soy flour additive-treated OCC pulp hand sheets was performed using images acquired using a scanning electron microscope (SEM), Hitachi S-3200N.¹⁸

3.1.2.5. Physical Properties Test of Additive-Treated Recycled OCC Pulp Hand Sheet.

The tensile, burst, STFI, gloss and roughness of additive treated OCC pulp hand sheet were tested according to TAPPI T 220, TAPPI T 810, TAPPI T826, TAPPI T 480, and TAPPI T 538 test methods, respectively.

3.1.2.6. Inter Fiber Bonding Strength of Additive-Treated Reclaimed OCC Pulp Sheets

The inter-fiber bonding strength of additive-treated OCC pulp hand sheets was obtained using a standard T 569pm-00 (provisional method-2000@ 2000 TAPPI) testing protocol.

3.1.2.7. Quantification of the Amounts and Types of Chemical Bonds

The total unbound carboxylic acid contents of additive-treated OCC pulp sheet were determined by the methylene blue adsorption method.²⁴ Approximately 1 g of pulp was suspended in 25 mL flask of aqueous methylene blue chloride with the addition of 25 mL of borate buffer solution and filtered through sintered-glass. Approximately 10 mL of the filtrate was transferred to a 100mL calibrated flask to which 10mL of 0.1 N HCl was added. The flask was filled to 100 mL with DI water and the methylene blue in the solution was determined photometrically using a calibration curve. The free dye concentration was determined from experimental results (X , see below). A Perkin Elmer UV/VIS spectrophotometer was employed to determine the dye concentration in solution. The carboxyl group content of the sample was obtained according to:

$$COOH = \frac{(7.5-X) \times 0.00313}{Z} \text{ (mmol/g)}$$

where, X is the total amount of free methylene blue (mg) and Z is the weight of oven-dry sample (g). In addition, the total carboxylic acid content (bonded and unbounded) of additive-treated OCC pulp sheet was determined by acid base titration.¹⁹ (Note: the ester bond between the additive and the OCC pulp fiber can be cleaved by saponification with sodium hydroxide to allow measurement).

Calculations

The total esterification degree (bonds formed) was found using the following relationship:

$$\text{Total ester bonds formed} = (A - B) \text{ of additive} - \text{treated OCC pulp sheet}$$

Where A is the total carboxyl content (unbound and bonded) of additive-treated OCC pulp sheet (mmol/g) and B is the total unbound carboxyl content of additive treated OCC pulp sheet (mmol/g).

3.1.3. Results and Discussion.

3.1.3.1. Synthesis& Characterization of the Soy Flour-DTPA-Chitosan Agent

Soy flour is a complex glycoprotein that is replete with the typical spectrum of functional groups such as alcohols, carboxamides, thiols, thioethers, carboxylic acids and a great diversity of amino acids. These functional groups are excellent chemical pivots for surface modification through reactions with a variety of modifying agents, especially the ones used in the current study. Indeed, the central hypothesis is that significantly increasing the sites for hydrogen bonding would cause a significant appreciation in the bondability of the final product. This latter goal was accomplished by the modification of soy flour with DTPA via an esterification reaction in the presence of sodium hypophosphite and followed by subsequent complexation with chitosan. For the purposes of clarity and simplicity, the characterization of the DTPA-based complex will be representative of the modifying agent reactions. The carboxyl content of the DTPA cross-linked soy flour increased from 260 meq/100 g to 450 meq/100 g. It was found that the OCC fiber-fiber bonding as a result of the DTPA cross-linked

soy flour was much better than the control as demonstrated by a comparison of the tensile strength indices.

FT-IR Spectral Support. The FT-IR spectra of the soy flour (A), soy flour-DTPA (B), and soy flour-DTPA-chitosan (C) are shown in Figure 3.1.3. The spectrum of soy flour shows a prominent peak at 1715 cm^{-1} , which can be attributed to a carboxyl group from the soy protein. Not surprisingly, when the soy flour reacts with the DTPA, an additional peak is observed at 1748 cm^{-1} , while after further complexation with chitosan, signature peaks appeared at 1748 cm^{-1} and 1664 cm^{-1} that are attributable to the ester carbonyl functionality and amide of the chitosan, respectively. Amide bands in the spectrum appeared because the soy flour-DTPA derivatives undergo a complexation with chitosan followed by an amide reaction that occurs from drying the sample to over $105\text{ }^{\circ}\text{C}$. This latter result implicates the linking of the soy flour-DTPA to chitosan by a coupling reaction between the amino groups of chitosan and the carboxylic groups of soy flour-DTPA derivatives.

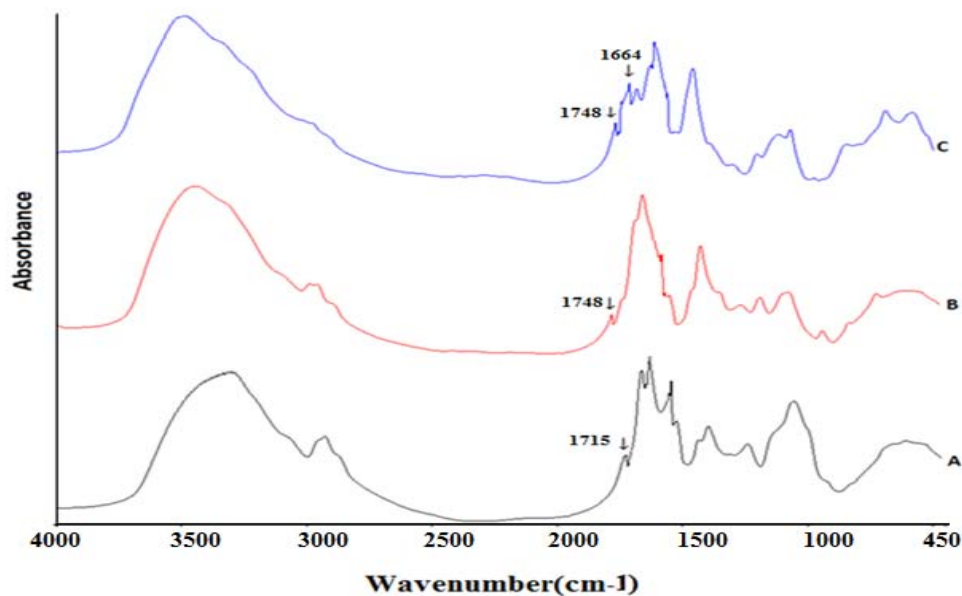


Figure 3.1.3. FT-IR spectra of soy flour (A), soy flour-DTPA (B), and soy flour-DTPA-chitosan (C). The prominent 1748 cm^{-1} band derives from the ester carbonyl stretch.

Thermal Analysis. The thermogravimetric behavior of the soy flour derivatives is shown in Table 3.1.1. For several of the samples, a weight loss ca. $100\text{ }^{\circ}\text{C}$ was attributable to water evaporation.²⁰ However, weight loss above $100\text{ }^{\circ}\text{C}$ was likely caused by the thermal decomposition of the soy flour and its derivatives themselves.¹⁸ DTPA had a single sharp decomposition peak at $280.3\text{ }^{\circ}\text{C}$, whereas the soy flour had a single weight loss peak at $310.2\text{ }^{\circ}\text{C}$; however, all derivatives of soy flour display a decrease in the maximum weight loss temperature and a concomitant significantly higher residual mass after heating to $600\text{ }^{\circ}\text{C}$. The latter result may be explained by soy flour surface-modifying agents possessing a lower decomposition temperature that is on the surface of the soy flour and the materials derived from the esterification possessing a lower temperature of degradation.¹⁴⁻¹⁵ The thermal behavior obtained from a differential scanning calorimetric analysis of the soy flour

derivatives are shown in Table 3.1.1. DTPA displays a very sharp endothermic peak at 217.5 °C, whereas for the soy flour an endothermic peak was observed at 188.6 °C. The endothermic peak increased for the reaction products as illustrated in Table 3.1.1. The increase in the magnitude of the endothermic peak may originate from changes in chemical composition characterized by increased hydrogen bonding and plasticization as well as an increase in the robust molecular organization obtained from the esterification reaction.²²

Table 3.1.1. Thermal analysis of soy flour and derivatives.

Sample	TGA maximum (DTG) degradation temp. (°C)	Residual char at 600°C (%)	DSC Endothermic Peak (°C)
DTPA	280.26	25.10	217.53
Soy Flour	310.20	23.40	188.57
Soy Flour-DTPA	300.32	27.15	199.20
Soy Flour-DTPA-Chitosan	293.75	29.03	200.54
Chitosan	290.0	26.0	268.35

3.1.3.2. Application of Soy Flour-DTAP-Chitosan Agent to Reclaimed and Virgin Pulp Furnishes for Mechanical Property Improvements

High mechanical properties in a two-dimensional paper sheet are likely the most important criteria for generating typical paper substrates. The substrates must display sufficient resistance to tolerate the stresses introduced by packaging (e.g., boxes), wrapping (e.g., linerboard), or sealing (e.g., liquid packaging). In general, macroscopic resistance can be ascribed at the molecular level to the development of a hydrogen-bonding network. Also, it is dependent on the quantity and surface area of the bonding sites. Reclaimed fibers have been

irreversibly damaged by usage that can affect final paper strength properties. Figures 3.1.4 shows the tensile indices of OCC (reclaimed), NSSC (virgin), and kraft(virgin) pulp hand sheets before and after the addition the soy flour-DTPA-chitosan additive. It can be observed that the tensile index of soy flour-DTPA-chitosan additive-treated OCC, NSSC, and kraft pulp sheets increased by about 52.6, 53.0, and 57.8% respectively, relative to the control. Similarly, the bursting index and STFI (compression) index of soy flour-DTPA-chitosan additive-treated OCC, NSSC, and kraft pulp increased 39.2, 43.5 and 42.5% respectively, and 39.9, 38.1, and 48.6%, respectively (Fig. 3.1.5 and 3.1.6). The increased strength properties are likely to have resulted from higher inter-fiber bonding between fibers and the soy flour-DTPA-chitosan additive. Soy flour-DTPA-chitosan contains a very large quantity of free -OH, -COOH and -NH₂ functional groups. These groups are intimately involved in hydrogen and ionic bonding with pulp fibers who themselves possess a sizable quantity of -OH groups (both cellulose and lignin), which significantly contributes to the relative bonded area between fibers and the additive. In addition, when the additive-treated pulp sheet is dried at $T > 105\text{ }^{\circ}\text{C}$, the -COOH groups of soy flour-DTPA-chitosan additive may form anhydrides that can proceed to react with the hydroxyl groups of pulp fibers to generate esters.¹⁷ The combination of hydrogen bonding and esterification can account for the increased bonding phenomena between fiber and additive during sheet formation manifested as increased mechanical properties, e.g., tensile strength.

The t-Test of paired samples (for the mean) was measured to confirm if the significance of the improvements in tensile indices of the additive treated pulp hand sheets. In each of the cases, an untreated sheet was compared to a sheet formed from the treated fibers. The t-Test

values for the OCC (control and additive-treated OCC pulp sheets), NSSC (control and additive-treated NSSC pulp sheets), and kraft (control and additive-treated kraft pulp sheets) samples were 15.23, -23.56 and -30.08, respectively. P values were 0.0000012, 0.000000063, and 0.0000000016, respectively. Because these p values were significantly lower than the α value 0.05 ($p < 0.05$), there was a basis to posit significant differences between the test performances results (tensile indices) between the control and soy flour-DTPA-chitosan additive-treated pulp sheet samples.

A comparative study of the mechanical properties of OCC pulp hand sheet results using the soy flour-DTPA-chitosan dry strength additive and several commercial dry strength additives is shown in Table 3.1.2. In comparison to the commercial dry strength additive results, the soy flour-DTPA-chitosan additive results convincingly demonstrate significant improved performance in tensile, bursting, and STFI (compression) index. This latter finding indicates that the chemistry introduced into the soy flour-DTPA-chitosan enhances bonding between pulp fibers. Thus, it appears that soy flour-DTPA-chitosan can potentially provide a viable alternative as a dry strength agent; moreover, soy flour and chitosan are renewable materials, extremely cheap, readily abundant, and environmentally compatible materials and offset the use of the more relatively expensive starch reagent as a dry strength agent (millions of tons/year) so that starch may be used for human consumption.

The optimum dosage for the soy flour-DTPA-chitosan additive was 1.5%, while the optimal pH was found to be 4 and 8 to yield the relative maxima tensile indices of the additive-treated OCC pulp hand sheets. The basis for the latter phenomena is firmly grounded in pH-dependent

electrostatics: at pH 4, the amine groups of the additive are nearly all protonated (their pK_a is about 1 unit higher), while at pH 8, the carboxylic groups (pK_a 4.75) are also nearly all deprotonated; the charged species are therefore much more likely to interact favorably with the diversity of groups and charges on pulp fibers via coulombic interactions.

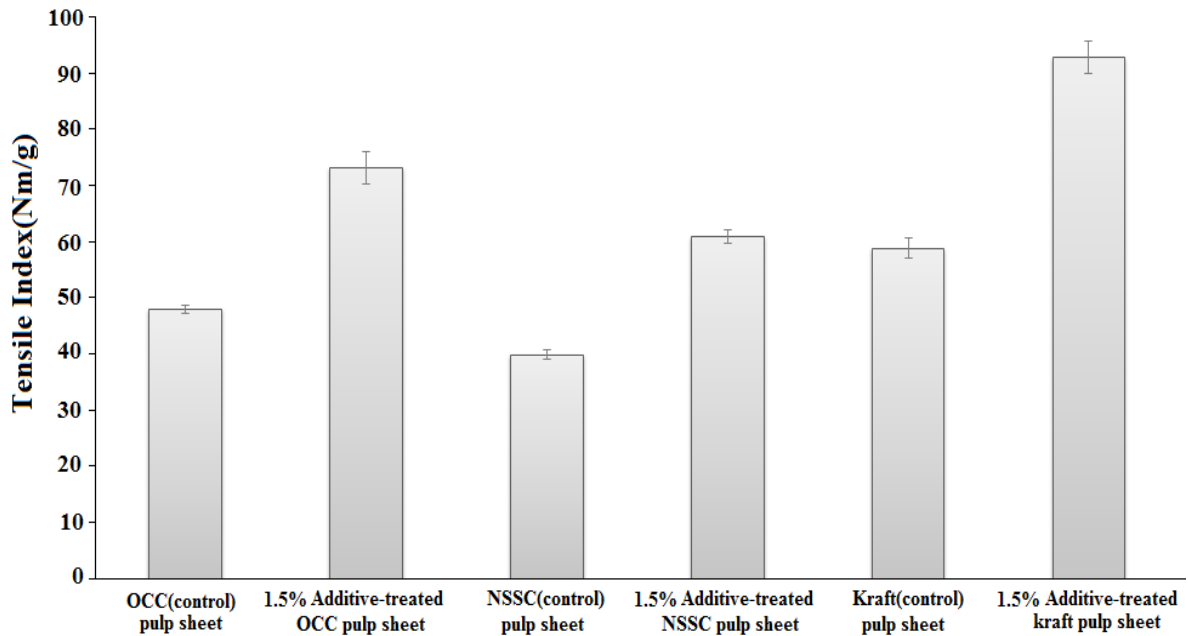


Figure 3.1.4. Tensile indices of the controls and respective modified soy flour-DTPA/chitosan additive-treated pulp hand sheets (The margin of error was calculated at the 95% confidence interval).

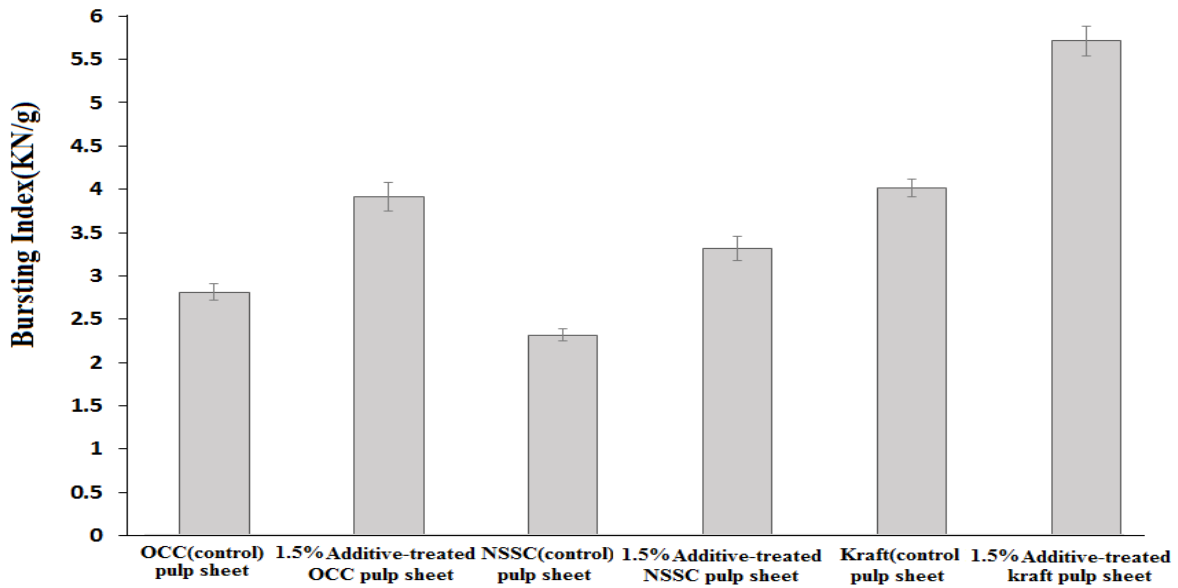


Figure 3.1.5. The bursting indices of the controls and respective modified soy flour-DTPA/chitosan additive-treated pulp hand sheets (The margin of error was calculated at the 95% confidence).

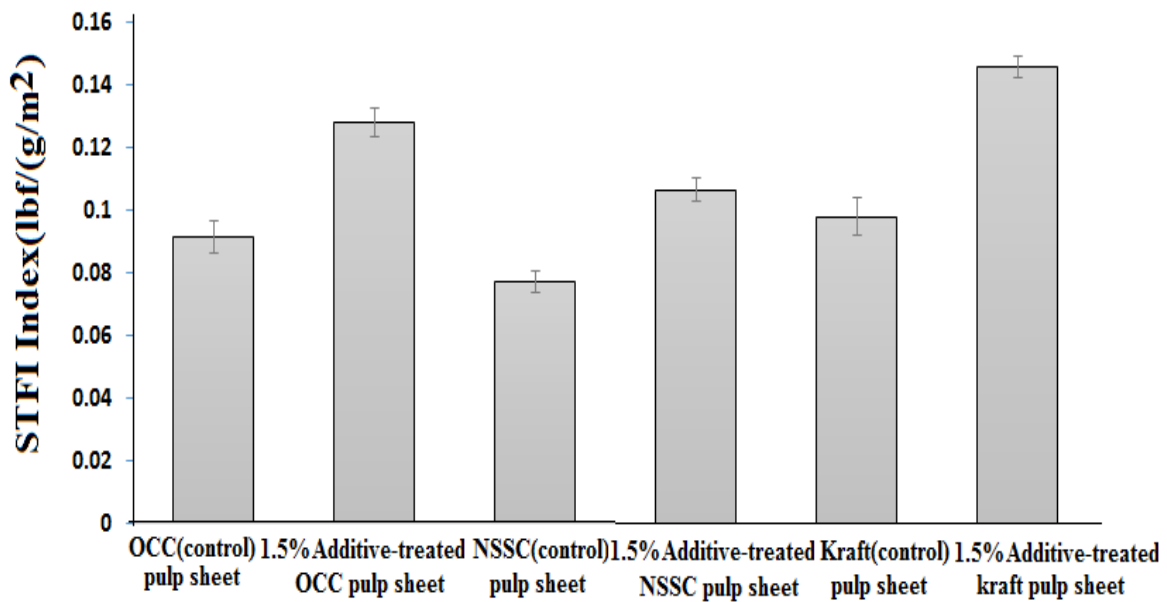


Figure 3.1.6. STFI indices of the controls and respective modified soy flour-DTPA/chitosan additive-treated pulp hand sheets (The margin of error was calculated at the 95% confidence interval).

Table 3.1.2. Mechanical properties of reclaimed OCC pulp hand sheets with different dry strength reagents (at the 1.5 % addition level, dried at room temperature, and cured at 105 °C).

Dry Strength Additive	Tensile Index (Nm/g)	Bursting Index (KN/g)	STFI Index (lbf/(g/m²))
No additive	47.9	2.8	0.091
Soy Flour-DTPA-Chitosan	73.1	3.9	0.128
Soy Flour-Chitosan	52.8	3.4	0.109
Soy Protein Flour-DTPA-Chitosan	71.25	4.0	0.130
Soy Protein Flour-Chitosan	57.00	3.3	0.110
Soy Protein Flour	49.28	2.7	0.093
Acid Hydrolyzed Soy Protein Flour	48.5	2.8	0.091
Soy Flour (commercial)	50.29	2.9	0.096
Native Starch (commercial)	51.73	3.0	0.098
Cationic Starch (commercial)	55.1	3.1	0.102
Cationic Polyacrylamide (commercial)	56.0	3.2	0.107
Anionic Polyacrylamide (commercial)	50.7	2.9	0.092

3.1.3.3. Bond Formation with Reclaimed OCC and Virgin Pulps

The inter-fiber bonding strength was measured by an Internal Bond Tester (Scott). Each pulp hand sheet (control and additive-treated) was cured at three different temperature: 25, 90 and 110 °C for one hour. The inter-fiber bonding strength for the control OCC, NSSC, and kraft pulp handsheets increased approximately 10-12% when they were cured at 90 °C or 110 °C versus 25 °C. The inter-fiber bonding strength of soy flour-DTPA-chitosan additive-treated OCC, NSSC and kraft pulp hand sheet showed nearly the same results when the samples were cured at 25 and 90 °C, but their strengths were significantly lower versus the soy flour-DTPA-chitosan additive-treated pulp sheet cured at 110 °C (Fig.3.1.7). The temperature dependence,

nature of the system, and ensuring chemistry dictate that a condensations (anhydride) reaction is occurring; at 110 °C temperature, two carboxylic acid groups condense to form an anhydride. Anhydrides can subsequently lead to other chemical reactions (esterification, amides) that can additionally improve inter-fiber bonding strength. However, curing temperatures between 25 °C and 90 °C are not sufficient to thermodynamically favor ester bonds because it has been reported that at temperatures below 100 °C, carboxylic acid groups do not yield anhydrides likely because of equilibrium effects (Le Chatelier's Principle) from excess moisture.¹⁷

It may be observed from Figure 3.1.7 that the inter-fiber bonding strength of all cured (25-110 °C) soy flour-DTPA-chitosan additive-treated OCC, NSSC, and kraft pulp hand sheets increased about 2.5-3 × relative to their respective controls. The significantly increased inter-fiber bonding strength which ultimately increases the relative bonded area between fibers can be attributed to electrostatic interactions and hydrogen bonding with the paper fibers during the paper making process.¹⁹ The combined interactive effects also contributed to an increase in macroscopic tensile strength.

The ester bonds as measured by titration (see Experimental Section for details) are shown in Table 3.1.3. The totals were found to be 1.82, 1.96 and 1.90 mmol/100 g, respectively, when soy flour-DTPA-chitosan additive-treated pulp hand sheets were cured at 110 °C for 1.0 hour. The anhydrides formed at this temperature lead to esters.¹⁷ However, as already noted, for curing temperatures between 25 °C and 90 °C, no esters formed. This is because no anhydrides formed at curing temperatures below 100 °C. Further evidence for the presence of ester

linkages between reclaimed OCC pulp fibers and dry strength reagent was obtained by ATR. A peak was observed at 1734 cm^{-1} at $110\text{ }^{\circ}\text{C}$ -cured soy flour-DTPA-chitosan additive-treated pulp hand sheets *NOT present at the lower temperatures*. The peak observed is not large in magnitude because a low quantity of carboxylic acid groups are present in OCC pulp because the applied level of additive (1%) was low. In addition, a high residual char value was observed in the soy flour-DTPA-chitosan-treated OCC pulp sheet compared to the control (OCC pulp sheet) after heating at $600\text{ }^{\circ}\text{C}$ (Fig. 3.1.8) which originates from strong and intransigent soy flour-DTPA-chitosan crosslinking (covalent linkages) to the OCC pulp fibers. The SEM (scanning electron microscopy) photomicrographs of OCC hand sheets and soy flour-DTPA-chitosan-treated OCC recycle pulp hand sheet are shown in Figure 3.1.9. The OCC control has a continuous smooth pore structure that contains plate-like solid pore walls, whereas the soy flour-DTPA-chitosan-treated OCC pulp hand sheet sample reveals a rougher surface with smaller irregular fragments on the fiber surfaces. It may be that these are aggregations of modified soy flour-DTPA-chitosan additive and fines/fibrils increasing the bonded area among the OCC pulp fibers to provide more compact fiber assemblies.

A dynamic mechanical analysis of OCC pulp sheet and soy flour-DTPA-chitosan additive-treated OCC pulp sheet were performed in tension mode and the results are illustrated in Figure 3.1.10. The storage modulus and loss storage modulus of the OCC pulp sheet, and soy flour-DTPA-chitosan additive treated OCC pulp sheet both decreased with increasing temperature. It is also observed from the Figure 3.1.10 that the storage modulus of soy flour-DTPA-chitosan additive treated OCC pulp sheets increased 135.9% ($2.35\times$) at $30\text{ }^{\circ}\text{C}$ temperature, but decreased 135.9% to 128.87% when the sample was heated to $245\text{ }^{\circ}\text{C}$ over 5 minute isotherms

relative to the control OCC pulp sheet. This latter result reflected increased bonding likely from crosslinking between fibers and the additive.¹⁸ However, the loss modulus for the OCC pulp hand sheet from 30 to 245 °C decreased about 34%, and for soy flour-DTPA-chitosan additive-treated OCC pulp sheet decreased about 21%. These results indicate that the soy flour-DTPA-chitosan additive was cross-linked with the OCC pulp fibers.

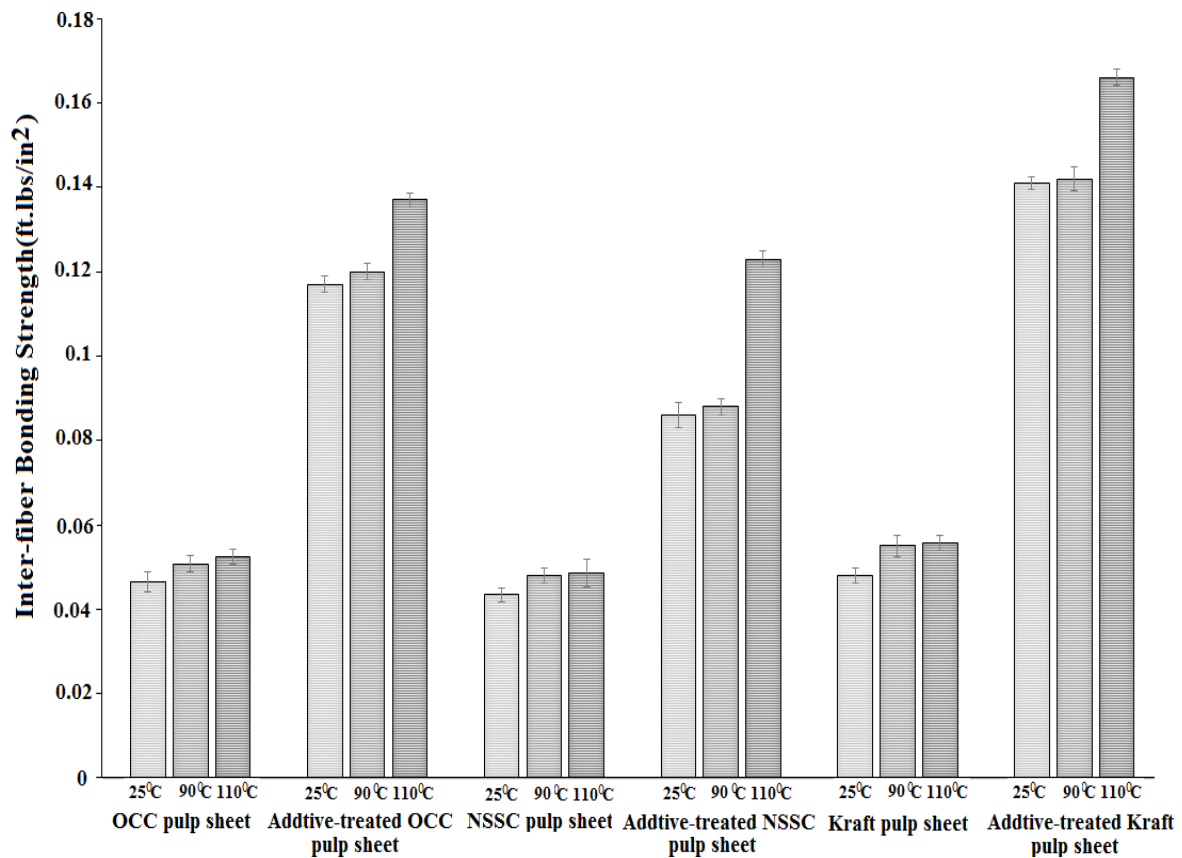


Figure 3.1.7. Inter-fiber bonding strength for 25, 90, and 110° C cured controls and soy flour-DTPA/chitosan additive-treated pulp hand sheets (The margin of error was obtained at the 95% confidence interval).

Table 3.1.3. Quantity of ester bonds formed in the soy flour-DTPA/chitosan additive-treated pulp hand sheet.

Curing Temperature (°C)	Ester bonds formed(mmole/100 g) in the additive-treated pulp sheet		
	Additive-treated OCC pulp hand sheet	Additive-treated NSSC pulp hand sheet	Additive-treated kraft pulp hand sheet
25	0.0	0.0	0.0
90	0.0	0.0	0.0
110	1.82	1.96	1.90

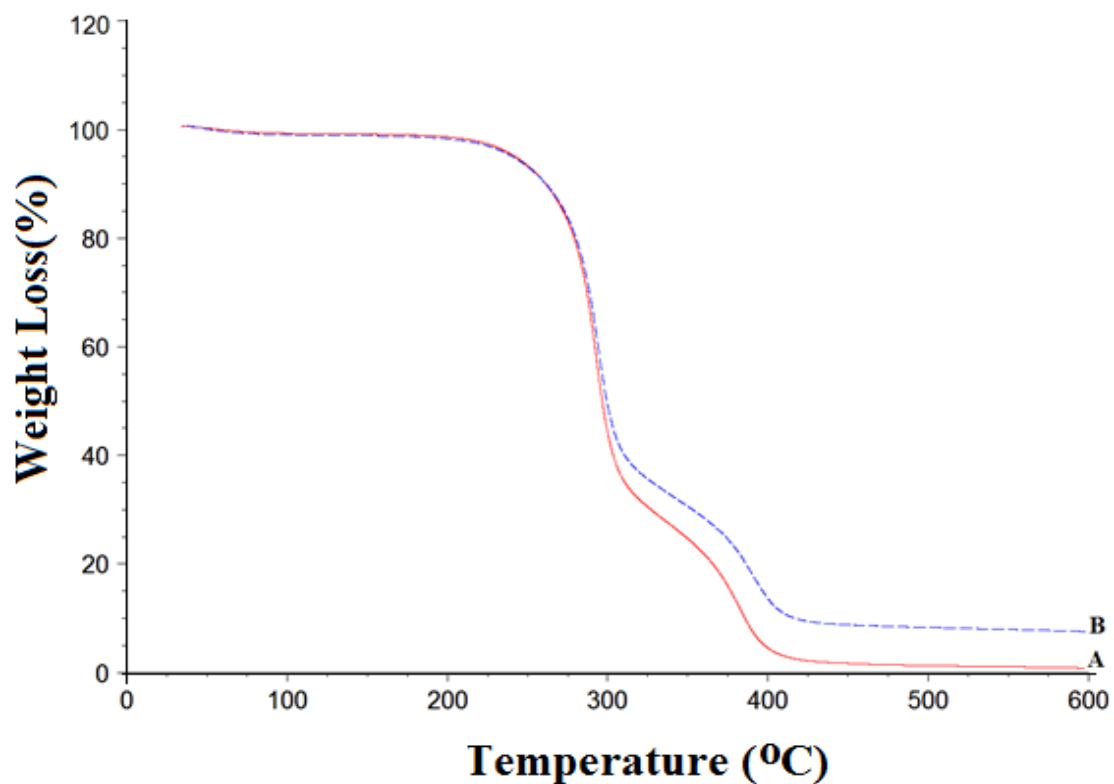


Figure 3.1.8. Thermo gravimetric analyses of OCC pulp sheet (A) and soy flour-DTPA-chitosan additive-treated OCC pulp hand sheet (B).

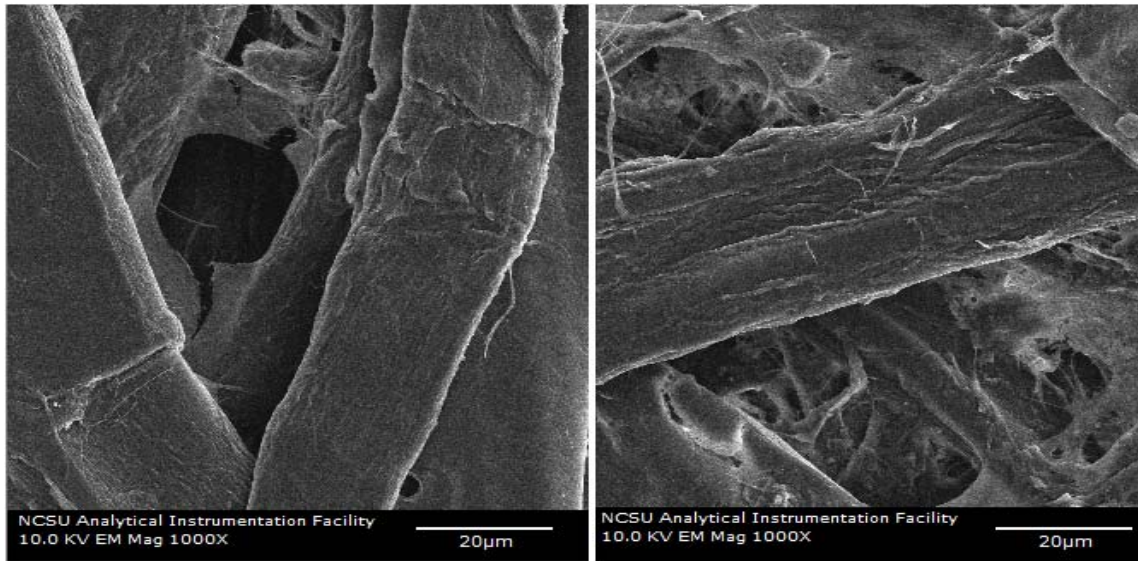


Figure 3.1.9. SEM image of OCC pulp sheet (left) and soy flour-DTPA-chitosan additive-treated OCC pulp hand sheet (right).

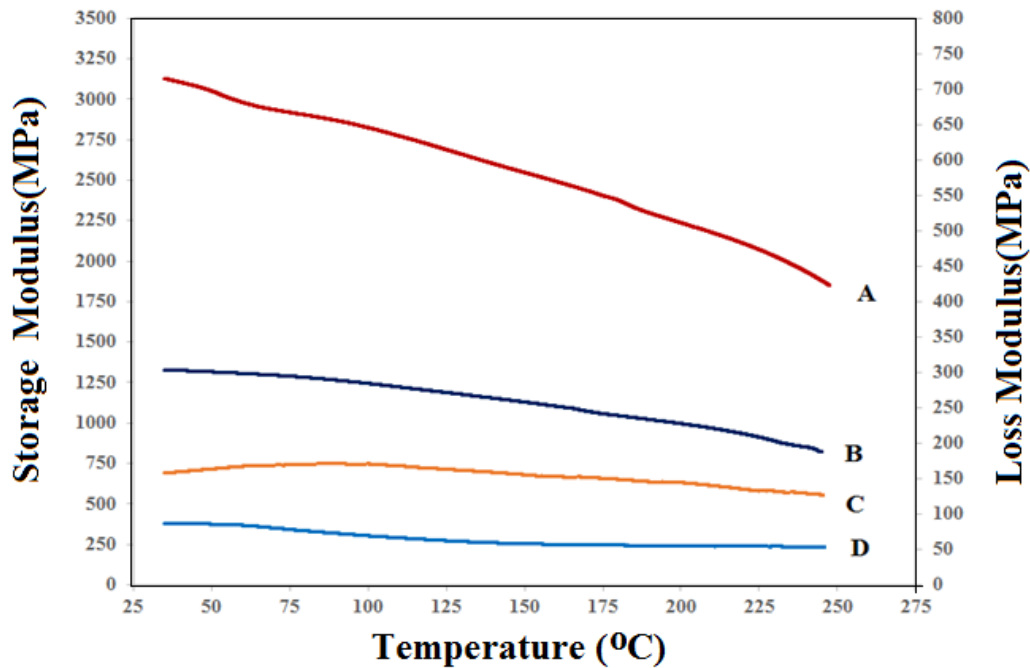


Figure 3.1.10. DMA of A = Storage modulus of soy flour -DTPA-chitosan treated-OCC pulp hand sheet, B = Storage modulus of OCC pulp hand sheet, C = Loss modulus of soy flour-DTPA-chitosan treated-OCC pulp hand sheet, and D = Loss modulus of OCC pulp hand sheet.

3.1.4. Interactions with Water

The dynamic contact angle of DI water droplets at 20 seconds was determined to be 46° for OCC pulp sheet hand sheet (control) although it significantly dropped to 4.5° after approximately 380 seconds (Fig. 3.11). In contrast, the dynamic contact angles at 20 seconds for Soy flour-DTPA-Ch-treated OCC pulp sheet were 106° , which later dropped to approximately 85° after 2000 seconds and finally reached 31° after approximately 3700 seconds. This reflects the significantly decreased water absorbency of the soy flour-DTPA-chitosan additive-treated OCC pulp sheet relative to the control pulp sheet. Although the control OCC has an irregular surface and is quite hydrophilic, the soy flour-DTPA-chitosan contains chitosan that is very hydrophobic and generates a sticky gel under wet acidic pHs that adopts a plastic-like character under dry conditions. When a pulp sheet with the additive is produced under pressing, it distributes very evenly over the rough surface to cover it uniformly to produce a paper surface that is smooth with increased gloss (Fig.3.1.11). Thus, because the additive-treated sheet surface is hydrophobic because of the plastic-like chitosan under dry conditions, the contact angle increases.

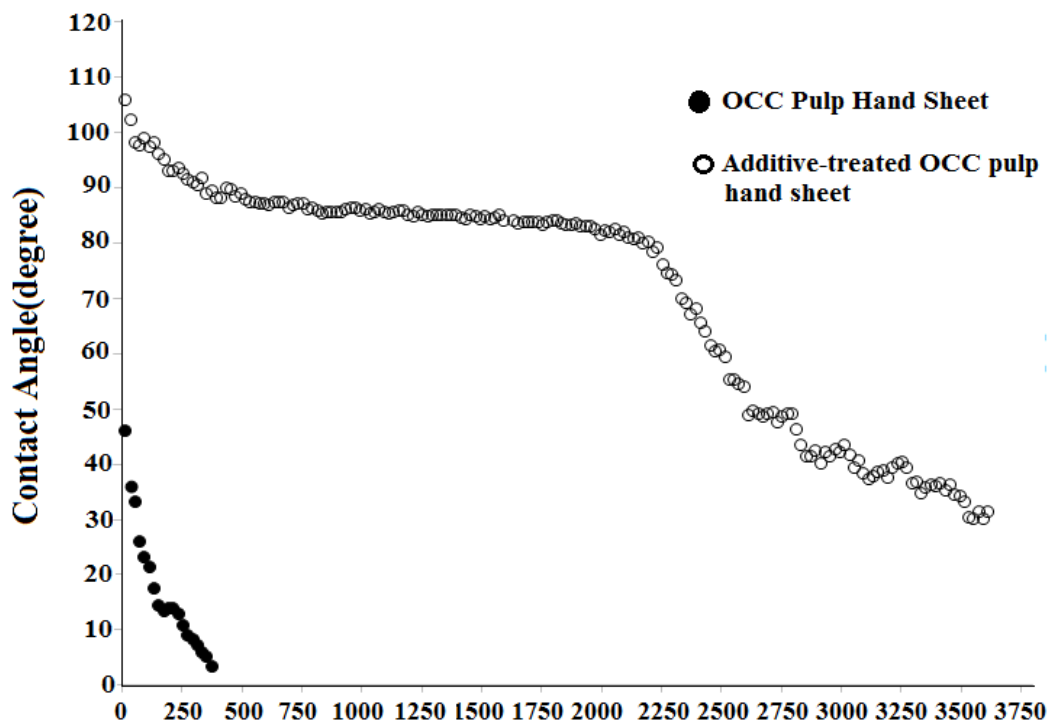


Figure 3.1.11. Contact angle of OCC pulp hand sheet (●) and Soy flour-DTPA/chitosan-treated OCC pulp hand sheet (○).

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A preliminary assay of the potential of soy protein isolate and its hydrolysates to provide inter-fiber bonding enhancements in lignocellulosic furnishes

Abdus Salam, Lucian A Lucia, Hasan Jameel

Abstract

Soy protein isolate (SPI) was extracted from soy flour and hydrolyzed with hydrochloric acid, sodium hydroxide, and enzyme, separately, to provide a series of hydrolysates. The SPI and its hydrolysis products were later cross-linked with ethylenediaminetetraacetic acid (EDTA) in the presence of sodium hypophosphite (SPH) after which they were complexed to chitosan as part of an on-going general chemical strategy in our laboratories to improve their incorporation into an *old corrugated container* (OCC) matrix and thus increase inter-fiber bonding. Approximately 2% SPI-EDTA-chitosan and hydrolyzed SPI-EDTA-chitosan additives by mass (OCC-based slurry) were thoroughly mixed before generating a sheet for physical testing. The tensile and burst indices of the SPI-EDTA-chitosan additive-treated OCC pulp sheet increased 46.3 and 61.85%, respectively, while the inter fiber bonding of SPI-EDTA-chitosan additive-treated OCC pulp sheet increased 74.86% compared to the control, albeit having a decreased tear strength and roughness, with significantly increased gloss. The additive-treated pulp sheet was characterized by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and ATR to provide evidence for product synthesis.

Keywords: *Soy protein isolate, hydrolysates, chitosan, complexation, OCC pulp, physical properties*

3.2.1. Introduction

Soy protein isolate is a long chain biopolymer consisting of 18 different polar and nonpolar amino acids. Polar amino acids such as cysteine, arginine, lysine, histidine and others can act as effective chemical pivots to crosslink the protein and improve the mechanical, thermal, and physical properties, while reducing water sensitivity and hydrophilicity [1]. Earlier research reported that isolated soy proteins may be cross linked with aldehydes such as formaldehyde, glutaraldehyde (GA), glyoxal, and glyceraldehyde through *Maillard* reactions [2]. Isolated soy proteins cross linked with GA yield biopolymers with enhanced mechanical properties [3]. Chemical modification of pulp fibers within the pulp & paper market is currently a common practice for improving printing quality, surface gloss, surface sizing, and calendaring. In addition, mechanical property improvements tend to be regulated by relatively costly chemical additives such as cationic starch or polyacrylamides. The low cost, commercial availability, and chemical derivatization power of soy protein flour (> 50% protein), not surprisingly, is extremely attractive for the development of novel functional soy protein derivatives for paper strength improvements. Typically, starch is used for printing and writing grade papers for surface sizing, *i.e.*, for improving paper surface resistance to uneven penetration and flow of inks/liquid media and acceptable printability [4]. The reclaimed paper market has been mostly focused on attaining improved mechanical strength properties.

Within the reclaimed paper market, the utilization rate of waste old corrugated containers (OCC) (recycled containerboards) in 1963 was 21.1% in the US, while in 2001 it increased to 67% with a recovery rate of nearly 70% [5]. Recently, the American Forest & Paper

Association (AF&PA) released a 2011 recovery rate for OCC with a new high of 91.2 percent. Therefore, research in this area is necessary to improve the strength of OCC because waste fibers are typically mechanically inferior to their virgin equivalents. Early work identified several chemical treatments that yielded improvements in the bonding strength of recycled sheets [6,7]. Further innovative studies have shown that fiber surface chemical derivatization can prevent strength losses [8, 9]. The paper industry is currently using commercial dry strength agents such as cationic starch, polyacrylamide, and glyoxylate polyacrylamide to improve the strength of OCC, but the improvement is still very low relative to virgin pulp [10,11]. In addition, a number of these studies have been conducted with nonrenewable inorganic fillers and petroleum-based matrices for applications that include packaging, a high value sector of the pulp market. Increasing environmental concerns have led to new flexible barrier bio-based packaging materials and the potential uses of renewable resources to offset the use of the inorganic fillers and petroleum-based materials [12].

The present study focuses on the application of an isolated soy protein derivative for improving the mechanical properties of OCC. It will focus on the characterization of the soy protein derivatives and explore their applicability with OCC.

3.2.2. Experimental

3.2.2.1 Materials

Soy flour was provided by Archer Daniel Midland (ADM, Decatur, IL). The OCC pulp was furnished by Azko Nobel Pulp and Performance Chemicals, Marietta, GA. Commercial dry strength agents such as Glyoxylate-PAM and cationic starch were supplied by Azko Nobel

Chemicals, Marietta, GA and Cargill Incorporated, Minneapolis, MN, respectively. Cross linking agents such as ethylenediaminetetraacetic acid (EDTA) and chitosan (Ch) were purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphite, (SHP) CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2, *Alcalase* product no. 126741, and denatured alcohol and acetic acid from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water as the medium.

3.2.2.2. Method

3.2.2.2.1. Extraction of the Soy Protein Isolate

Soy flour was carefully added into acidified water so that solution pH was within the isoelectric range of the soy protein (pH 4.0-4.8) so that only the soluble fraction of the soy flour dissolved. The resulting mixture was centrifuged to separate the protein-rich precipitate from the supernatant to give a high quality concentrate soy protein [13].

3.2.2.2.2. Hydrolysis of the Soy Protein Isolate

For hydrolysis of soy protein isolate, three different routes were followed: acid, alkali, and enzymatic treatments. Approximately 1 g of soy protein isolate was added into 50 ml of 1N HCl or NaOH solution and heated at 70 °C for 3 hours. The suspension was centrifuged at 5300 rpm for 15 min. to concentrate the hydrolyzed soy protein isolate and remove the excess aqueous acid or alkali. The resultant precipitate was rinsed and re-centrifuged until constant neutral pH was achieved [14]. The enzymatic hydrolysis was carried out with *Alcalase* as follows: soy protein isolate was dissolved in water at 50 °C for 10 min. When the protein

solution temperature reached 50 °C, the Alcalase (2.4U/g) was added. The soy protein isolate and enzyme ratio was 1:0.002. pH of solution was maintained at 7 by adding 1N NaOH during the first 15 min. of reaction while at the end of reaction, pH was adjusted to 4.5 using 1N HCl. The mixture was cooled, adjusted to pH 7.0, and heated at 95 °C for 15 min. to inactivate the enzyme. The enzymatic hydrolyzed soy protein isolate was centrifuged, rinsed, and re-centrifuged until constant neutral pH was achieved [15]. The mixture was freeze-dried and stored until further use.

3.2.2.3. Chemical Modifications of Soy Protein Isolate (SPI) and Hydrolyzed Soy

Protein Isolate

Into 15 mL of 1N sodium hydroxide solution in a 50 ml Petri Dish, 5 g of EDTA and 1 g of SHP were dissolved. Soy protein isolate or hydrolyzed soy protein isolate (5 g) was added to the solution and manually mixed with a glass rod. The mixture was placed in an oven at 130 °C for 3 hours. Reaction products were washed with water and filtered several times to remove unreacted materials. The product obtained was modified soy protein isolate that was air dried at 50 °C in an oven overnight [16]. The proposed reaction scheme is shown in Figure 3.2.1.

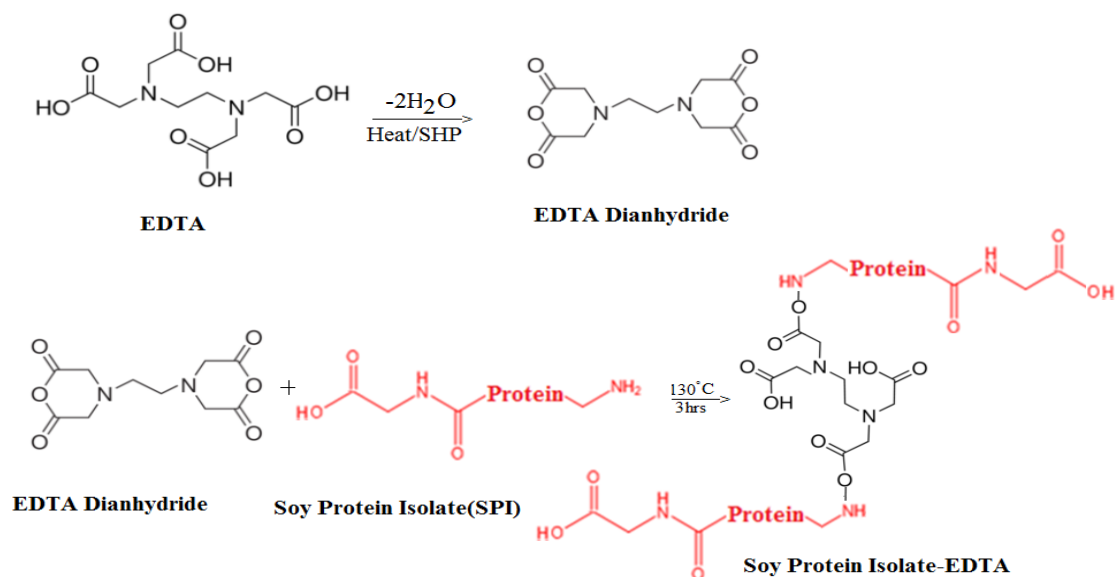


Figure 3.2.1. Esterification reaction of soy protein isolate with EDTA.

Polyelectrolyte Complexation

Chitosan (Ch, 1g) was dissolved into 50 ml of 1.5% acetic acid solution. Modified soy protein isolate (1 g) was dissolved with 50 ml water and added to a 50 ml chitosan solution in a 250 ml round bottom flask. The reaction mixture was stirred at 70°C for 90 minutes [17]. The proposed reaction scheme is shown in Figure 3.2.2.

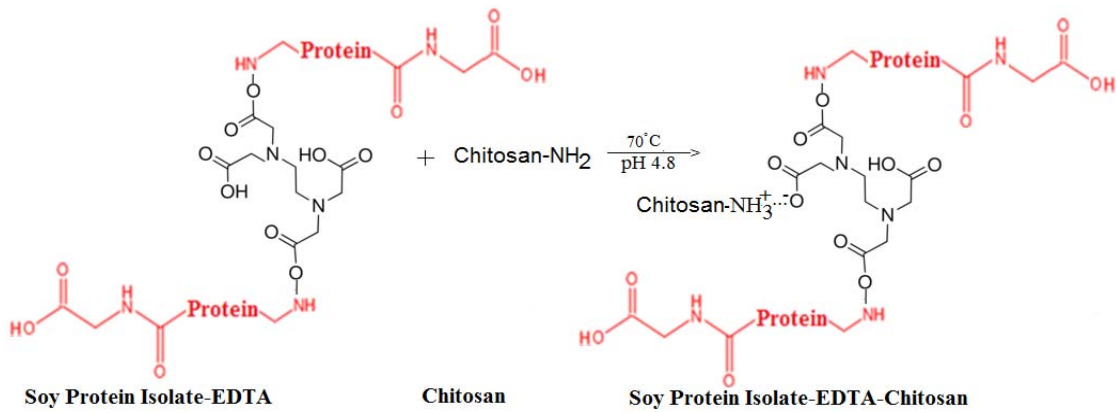


Figure 3.2. 2. Polyelectrolyte complexation of soy protein isolate-EDTA with chitosan

3.2.2.4. Preparation of OCC pulp sheet

The sheet was prepared according to TAPPI Standard Method T 205 using a 600 ml pulp slurry (1.8 g oven dried OCC pulp) in a sheet molder machine. The pulp slurry was diluted with 10L of DI water in a sheet molder to produce a uniform sheet. The sheet was conditioned and cured at 105 °C for 1.0 hour [17].

3.2.2.5. Testing Methods

Determination of Carboxyl Content

A known amount of soy protein isolate derivative was dissolved in 0.1N NaOH and hydrolyzed for one hour. The excess amount of NaOH was determined by titration with 0.1N HCl using phenolphthalein as an indicator [18] while the carboxyl content in milliequivalents (meq.) per 100 g was calculated as follows:

Tear Strength

The tear strength of OCC pulp hand sheet was tested with an L & W tester according to ASTM D 689 test method.

Inter Fiber Bonding Strength

The inter-fiber bonding strength of additive-treated OCC pulp hand sheets was obtained using a standard T 569pm-00 (provisional method-2000@ 2000 TAPPI) testing protocol.

ATR Analyses

IR Spectra of all modified soy flour samples were recorded on a Perkin Elmer ATR spectrophotometer [19].

Thermal Gravimetric Analyses (TGA)

The TGA used in this study was a TGA Q500 (TA Inc., New Castle, DE) under a nitrogen atmosphere. The temperature range and heating ramp were 30-600°C and 5°C/min, followed by isothermal heating at 600°C [20].

Measurement of Storage Modulus

Dynamic mechanical analysis was performed using a DMA Model 2980 (TA Inc., New Castle, DE) in the film tension mode. The specimen dimensions were 30 mm in length, 10 mm in width, and 0.3 mm in thickness. Samples were heated from 30 to 200 °C using a temperature ramp of 3 °C/min (20 μm amplitude, at 1Hz) [21].

3.2.3. Results and Discussion

3.2.3.1. Characterization of Soy Protein Isolate Derivatives

Soy protein isolate possesses a highly chemically rich surface covered with amine groups that allow for facile surface decoration using appropriate reactive species. The reaction pathways that were chosen for surface functionalization are shown in Figures 1 and 2. The carboxyl content of the soy protein isolate increased from 210 meq./100 g in the control to 430 meq./100 g in the test sample as a result of surface functionalization.

ATR Analysis

The ATR spectra of the soy protein isolate and soy protein isolate-EDTA are shown in Figure 3.2.3. The spectrum of soy protein isolate shows a prominent peak at 1635 cm^{-1} which arises from the amide linkage of the soy protein isolate, although the carbonyl region does not clearly show a carbonyl stretch. However, when the soy protein isolate was reacted with EDTA, a peak appeared at approximately 1740 cm^{-1} that is attributable to the carbonyl group. The appearance of the peak indicated that EDTA is cross linked to the soy protein isolate [18].

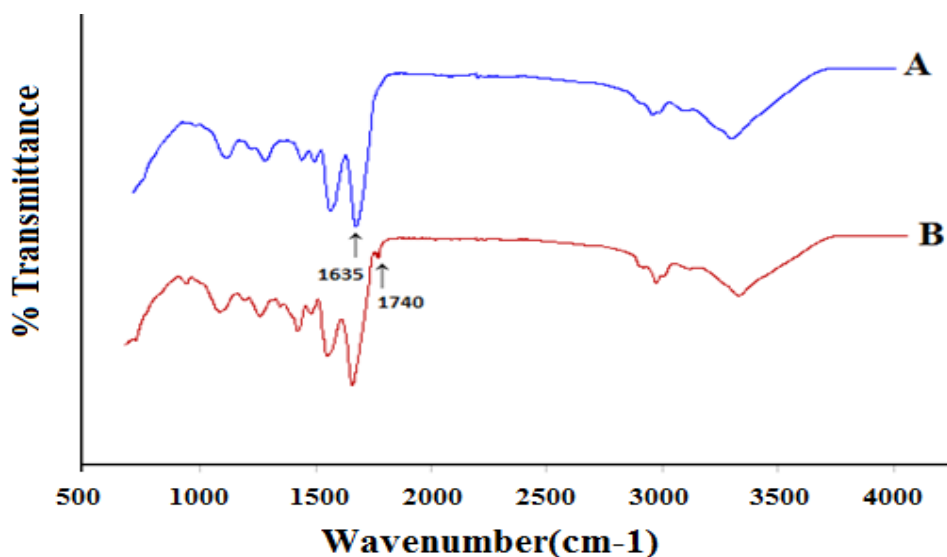


Figure 3.2.3. Shown are ATR spectra of soy protein isolate (A) and soy protein isolate-EDTA (B). The 1740 cm^{-1} band can be attributed to the ester carbonyl stretch, whereas the 1635 cm^{-1} band is representative of the carbonyl groups in an amide bond of the soy protein isolate.

Thermal Behavior

The thermogravimetric behavior of the soy protein isolate derivatives was evaluated over a $5\text{ }^{\circ}\text{C}/\text{minute}$ heating ramp under nitrogen and shown in Figure 3.2.4. The weight loss below and near $100\text{ }^{\circ}\text{C}$ was attributed to water evaporation [20]. However, the weight loss above $100\text{ }^{\circ}\text{C}$ was due to thermal decomposition of the soy protein isolate derivatives [22]. EDTA had a single sharp decomposition peak at $228.6\text{ }^{\circ}\text{C}$, whereas the soy protein isolate showed a single weight loss peak at $301.15\text{ }^{\circ}\text{C}$; however, all derivatives of soy protein isolate show a decrease in their respective maxima for degradation temperature and weight loss, and also significantly higher residual mass after heating to $600\text{ }^{\circ}\text{C}$. This may be explained by the fact that the soy protein isolate surface-modifying agents on the surface of the soy protein isolate have a lower

decomposition temperature and are attached via relatively labile ester bonds that also have a lower temperature of degradation [18].

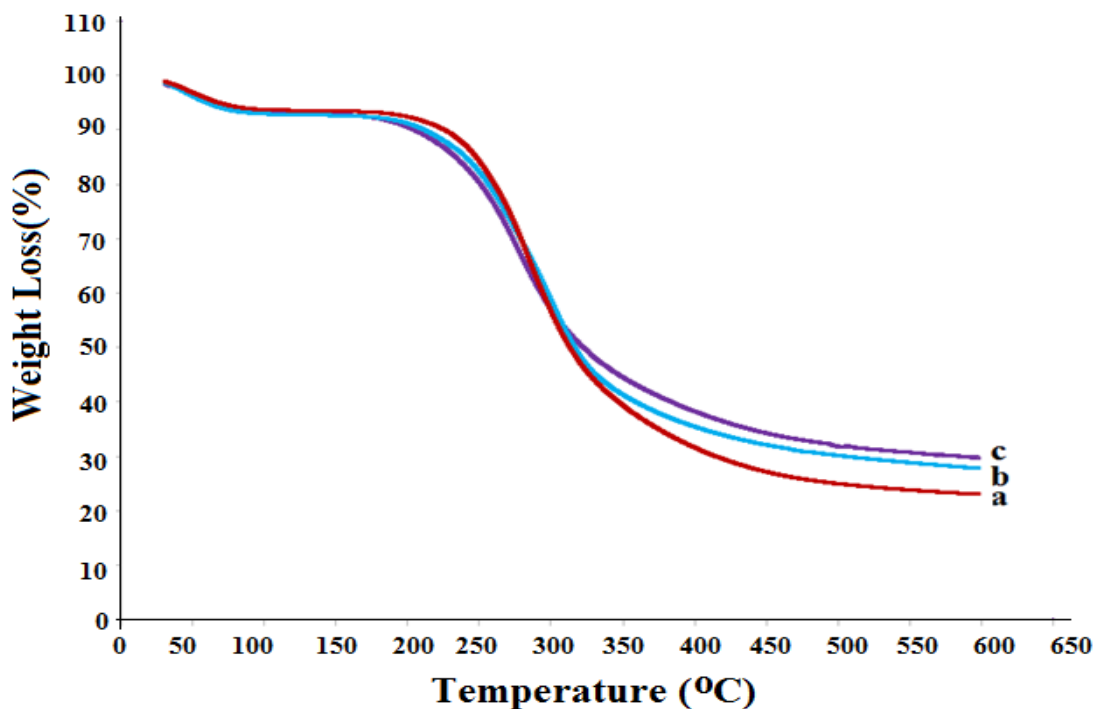


Figure 3.2.4. Thermogravimetric analyses of soy protein isolate (a), soy protein isolate-EDTA (b), and soy protein isolate-EDTA-chitosan (c).

3.2.3.2. Application of Soy Protein Isolate-EDTA-Chitosan Derivatives for OCC

Strength Improvement

Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need to display sufficient resistance in packaging, wrapping, or sealing. In general, such gross resistance can be attributed at the molecular level to a network of hydrogen

bonds. Also, it depends on the quantity and area of the overall bonding sites. In recycling, fibers are irreversibly damaged, a fact which affects their final paper resistance properties. Figure 3.2.5 shows the tensile index of OCC recycled pulp hand sheet that results after the addition of either virgin (non-recycled) pulp or dry strength agents.

Virgin pulp has in theory a much higher mechanical resistance because the fibers have not been reclaimed. The control for these studies was the base OCC recycled pulp (CSF = 400, a measure of the adsorption of water, *i.e.*, higher value, less adsorption). Earlier research reported that the range of tensile index (Nm/g) for OCC pulp sheet is 20-35 [23]. Defibrillated or non-defibrillated virgin softwood kraft pulp (revolutions = 5000, CSF = 530) was blended with OCC recycle pulp (50:50) to increase strength properties. In addition, 2% SPI derivatives (based on the mass of dried pulp) were mixed with a separate batch of OCC pulp slurry. The non-defibrillated virgin pulp sample demonstrated a decreased tensile index, but the defibrillated virgin pulp blend sample had a significantly increased tensile index compared to the control sample (Fig. 3.2.5). This may happen due to a significant decrease in the fiber size and an increase in the bonded area at the high revolutions (defibrillations). The SPI and hydrolyzed SPI did not affect the tensile index of the OCC pulp hand sheet (Fig. 3.2.5).

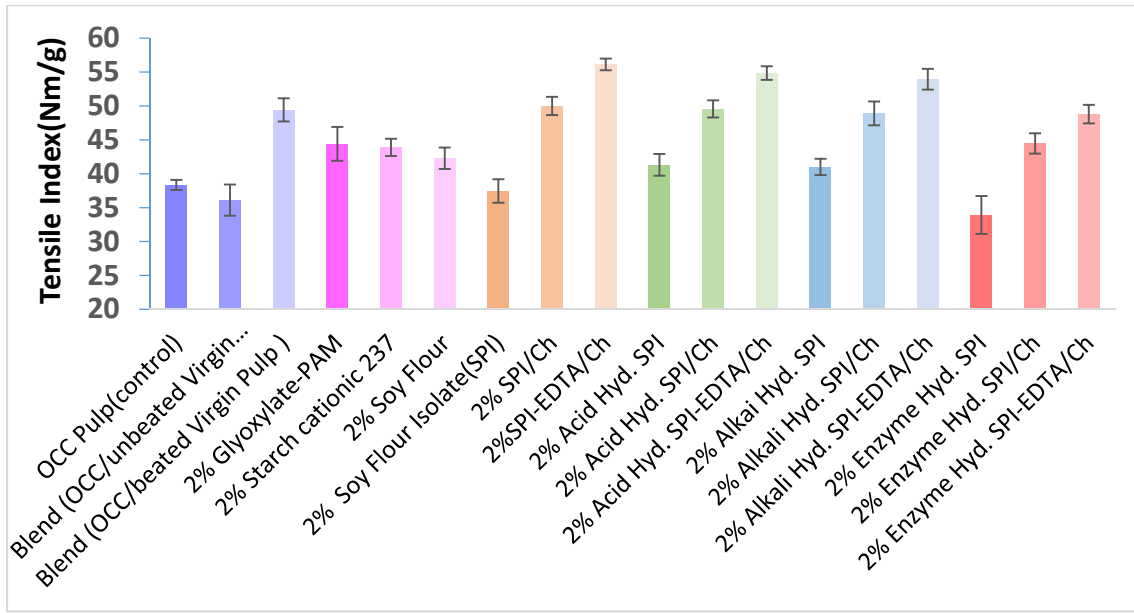


Figure 3.2.5. Tensile strength of soy protein isolate derivative-treated OCC recycle pulp hand sheets.

The tensile indices observed in Figure 3.2.5 from the application of 2% SPI derivatives-treated OCC pulp are shown as follows where “(%)” is the percentage that the system is superior to the tensile index of the control (non-treated) sample: SPI-Ch (30.4), SPI-EDTA-Ch (46.3); acid hydrolyzed: SPI-Ch (29.2), SPI-EDTA-Ch (43.0); alkali hydrolyzed: SPI-Ch (27.5), SPI-EDTA-Ch (38.4), and enzymatic hydrolyzed: SPI-Ch (15.9), SPI-EDTA-Ch (27.2). However, the STFI index (compression) was tested only for control and acid hydrolyzed SPI-EDTA-Ch treated pulp sheet. The STFI index was found to be 0.055 and 0.8, respectively. The results were significantly higher than what has been found for commercial dry strength additives such as glyoxylate polyacrylamide, cationic starch, and soy flour. This may be because of the extremely high level of carboxylic acid and amine groups in soy protein isolate derivatives that give rise to stronger interactions with OCC pulp when the sheet is generated with soy

protein isolate derivatives [24, 25]. In contrast, the tensile indices of 2% SPI-EDTA-Ch, acid hydrolyzed SPI-EDTA-Ch and alkali hydrolyzed SPI-EDTA-Ch derivatives-treated OCC pulp samples were also better than defibrillated virgin pulp blends (Fig. 3.2.5). Similarly, the burst strength %-age gains of the SPI derivatives-treated OCC pulp sample systems were “(%)” higher than the control: SPI-Ch (44.3), SPI-EDTA-Ch (61.8); acid hydrolyzed: SPI-Ch (60.7), SPI-EDTA-Ch (64.6); alkali hydrolyzed: SPI-Ch (40.8), SPI-EDTA-Ch (57.4), and enzymatic hydrolyzed: SPI-Ch (53.9), SPI-EDTA-Ch (65.5), while all the cases provided better results compared to the commercial dry strength additive (Fig. 3.2.6).

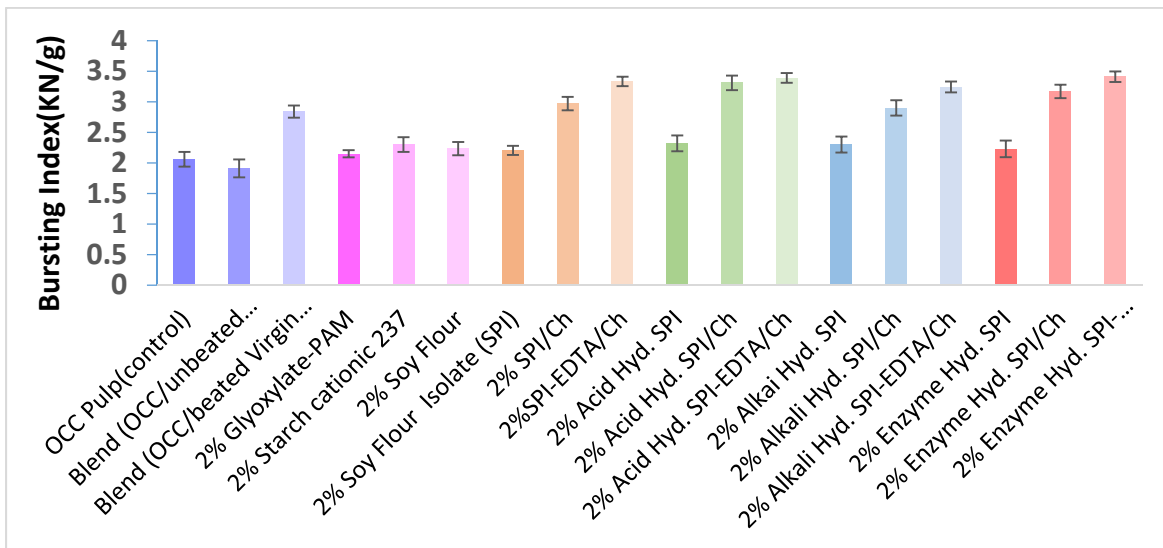


Figure 3.2.6. Bursting strength of soy protein isolate derivative-treated OCC recycle pulp hand sheets.

It is also observed from Figure 3.2.7 that the tear strength of all soy protein isolate and soy protein isolate derivatives-treated OCC pulp samples were lower than the control sample, but higher than the glyoxylate polyacrylamide-treated sample.

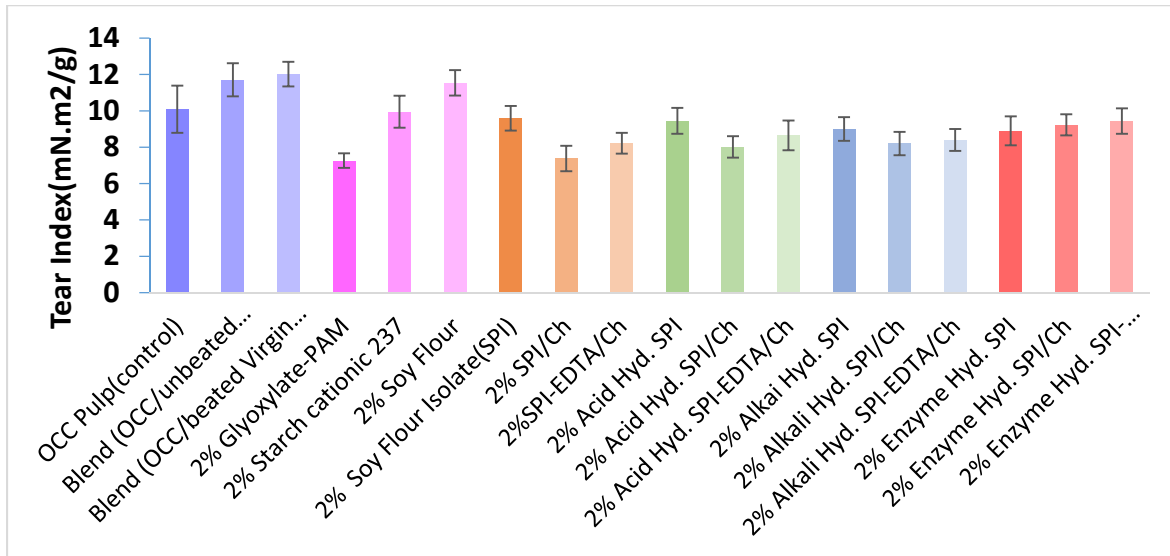


Figure 3.2.7. Tear strength of soy protein isolate derivative-treated OCC recycle pulp hand sheets.

The t-Test of paired samples (for the mean of the tensile index) was measured to confirm the significance of the improvements in tensile index of the additive treated pulp hand sheets. In each of the cases, an untreated sheet was compared to a sheet formed from the treated fibers. The *t* values for the OCC pulp sheet (control) and SPI-EDTA-Ch, acid hydrolyzed SPI-EDTA-Ch, alkali hydrolyzed SPI-EDTA-Ch, and enzymatic hydrolyzed SPI-EDTA-Ch-treated OCC pulp sheets were significantly negatively lower than the negative *t* table distribution value. The *p* value of OCC pulp sheet (control) and SPI-EDTA-Ch, acid hydrolyzed SPI-EDTA-Ch, alkali hydrolyzed SPI-EDTA-Ch, and enzymatic hydrolyzed SPI-EDTA-Ch-treated OCC pulp sheets were much lower than α value 0.05 ($p < 0.05$). Therefore, there was significant difference in tensile indices between the control and soy protein isolate derivatives-treated pulp sheet samples. In addition, SPI-EDTA-Ch-treated pulp sheet had significantly increased

gloss, but decreased roughness. This may happen due to increased density of SPI-EDTA-Ch-treated pulp sheet compared to control sample [26].

3.2.3.3. Bond Formation with OCC Recycle Pulp

The basic groups (-NH₂) on every ring in soy protein isolate-EDTA-chitosan derivatives develop positive charges when they are in a sufficiently acidic medium and can form ionic or covalent bonds with negatively charged cellulose in paper fibers during paper making [27]. In addition, the EDTA in soy protein isolate-EDTA-chitosan derivatives contains a number of free carboxyl groups (protonated in acidic medium) that can engage in hydrogen bonds with the fiber surface of pulp and increase the relative bonded area between fibers. The combined interactive effects attributable to the carboxylic acid and amine groups for increasing bonding between fibers during sheet formation also contributed to an increase in tensile strength [28].

The inter-fiber bonding strength of soy protein isolate-EDTA-chitosan additive-treated OCC pulp hand sheets increased approximately 74.86% compare to a control OCC pulp hand sheet. It is likely partially attributable to condensation reactions mediated by the high temperature (105 °C) that causes two carboxylic acid groups in EDTA to form an anhydride. Anhydrides can subsequently lead to other chemical reactions (*e.g.*, esterification) with the enriched surface hydroxyl groups of OCC pulp and can contribute to inter-fiber bonding strength [29]. In addition, a 1.35% higher residual char value was observed in the soy protein isolate-EDTA-chitosan-treated OCC pulp sheet compared to the control (OCC pulp sheet) after heating at 600 °C (Fig. 3.2.8). This higher residual char points to the likelihood that soy protein isolate-EDTA-chitosan is cross linked to the OCC pulp fibers.

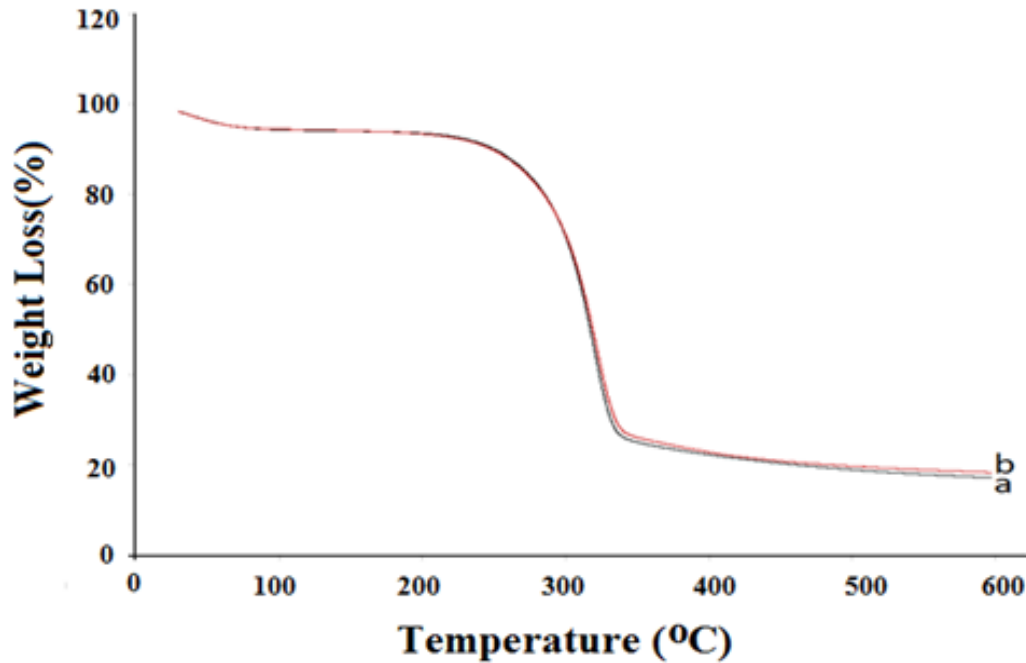


Figure 3.2.8. Thermogravimetric analyses of OCC pulp sheet and soy protein isolate-EDTA-chitosan additive-treated OCC pulp sheets.

The storage modulus and loss modulus both decrease with increased temperature as shown in Figure 3.2.9. It was observed that the storage modulus of the soy protein isolate-EDTA-chitosan-treated OCC pulp sheet was 25-27.3% higher when the temperature range was between 35-197 °C. The higher storage modulus is likely a result from the additive treated OCC pulp sheet being more flexible due to cross linking with the soy protein isolate-EDTA-chitosan additive [16]. However, the loss modulus for the OCC pulp hand sheet over the same temperature range decreased approximately 10%, while for the soy flour isolate-EDTA-chitosan additive-treated OCC pulp sheet, it decreased roughly 14%.

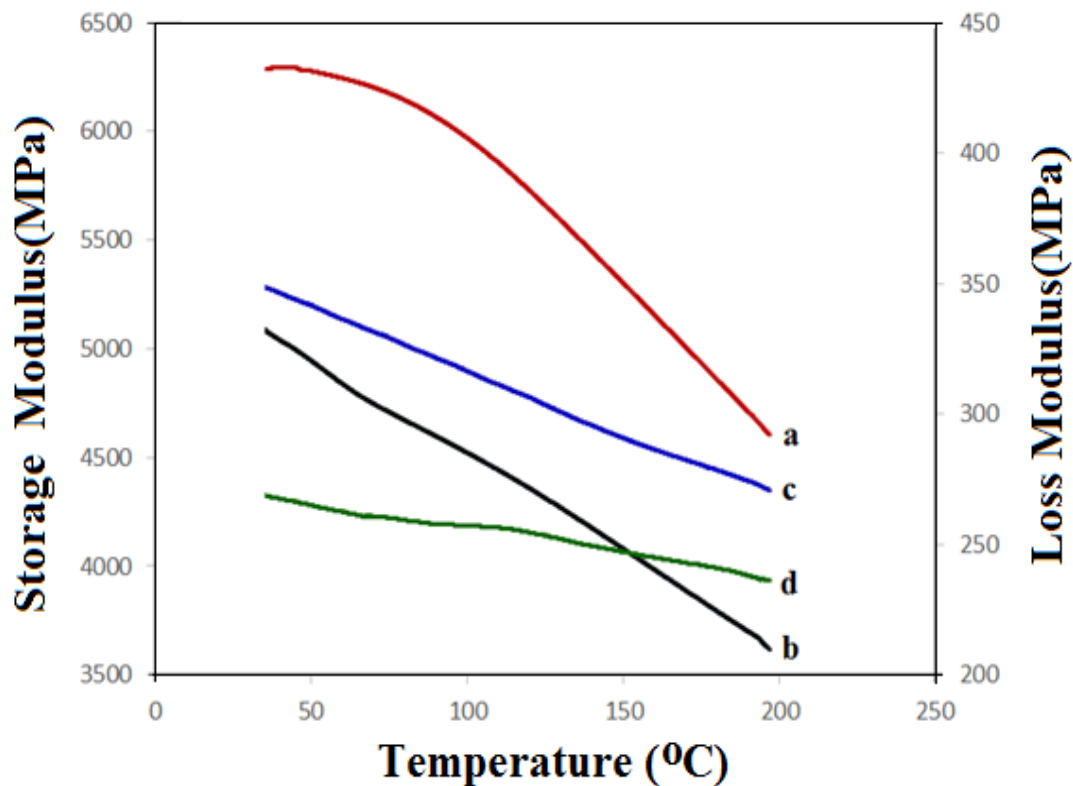


Figure 3.2.9. DMA of a = Storage modulus of SF-EDTA-chitosan treated-OCC pulp hand sheet, b = Storage modulus of OCC pulp hand sheet, c = Loss modulus of SF-EDTA-chitosan treated-OCC pulp hand sheet, and d = Loss modulus of OCC pulp hand sheet.

3.2.4. Conclusions

Soy protein isolate (SPI) from soy flour and its hydrolysates from separate treatments of acid, alkali, and enzyme was studied for its effect on OCC pulp sheet dry strength. Soy protein isolate and hydrolyzed soy protein isolate were modified with EDTA in the presence of sodium hypophosphite (SHP) to increase their ability to better bond recycled fibers during paper formation. It was found that the carboxyl group content of modified soy protein isolate significantly increased relative to the unmodified soy protein isolate, a driving hypothesis for

the observed strength gains. The EDTA coupled soy protein isolate and hydrolyzed EDTA coupled soy protein isolate were later cross linked with chitosan (Ch). Approximately 2% of soy protein isolate-EDTA-chitosan and their derivatives (acid hydrolyzed SPI-EDTA-Ch, alkali hydrolyzed SPI-EDTA-Ch, and enzymatic hydrolyzed SPI-EDTA-Ch) were blended with OCC recycle pulp separately before making samples. The tensile and burst strengths increased 46.3, 43.02, 38.35, and 27.2%, and 61.85, 64.56, 57.42, and 65.5%, respectively, compared to the control samples. These results were also significantly higher than what was typically found for commercial dry strength agents and blended OCC pulps. The t-test of paired samples (for the mean of tensile index) confirmed the significance of the improvements in tensile index of the additive treated pulp hand sheets. The inter-fiber bonding strength of a soy protein isolate-EDTA-chitosan additive-treated OCC pulp hand sheet increased approximately 74.86% relative to a control OCC pulp hand sheet. It displayed significantly increased gloss (100%), but decreased roughness (17%) and tear strength.

Acknowledgments

The authors would like to cheerfully acknowledge the support of the members of *The Laboratory of Soft Materials & Green Chemistry* at NC State University (USA) and Qilu University of Technology (P.R. China) as well as partial support of this work from a research grant administered by Smith-Bucklin & Assoc., LLC, through the United Soybean Board (Internal Grant No. 2013-0248/1340-512-5257).

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CHAPTER 4

Corn Starch-Based Dry Strength Additives to Increase the Dry Strength of Recycled Paper Furnish.

This chapter presents the modification of corn starch with modifying agents in the presence of a catalyst and further complexed with chitosan. It also focuses on the characterization of modified corn starch additives and modified corn starch additives-treated recycled paper furnish (OCC) by examining inter-fiber bonding strength and mechanical properties.

Synthesis, Characterization, and Application of Modified Corn Starch/Chitosan-Complexed Additive for High Strength of Recycled Paper

Abdus Salam, Lucian A Lucia, Hasan Jameel

Abstract

The objectives of the current research were to synthesize and characterize modified starch-chitosan complexed and examine their effect on the physical performance of recycled OCC pulp. This new approach provides a uniquely renewable and useful approach to enhance mechanical properties of pulp. The corn starch was reacted with diethylenetriamine pentaacetic acid (DTPA) in the presence of sodium hypophosphite. Thereupon, the modified corn starch was complexed with chitosan as part of a general chemical strategy to improve their incorporation into an OCC matrix and increase inter-fiber bonding. The characterization of the modified corn starch was done using TGA, DSC, SEM and FT-IR to analyze their composition and structure. Approximately 1.5% modified starch-chitosan complexed additive (by mass of OCC dry pulp) was thoroughly mixed before manufacturing a two-dimensional sheet for physical testing. The tensile index, burst index, STFI index and inter-fiber bonding strength of the modified OCC pulp sheet increased 49.5, 48.7, 49.5 and 176% respectively, albeit having a decreased tear strength, roughness but significantly increased gloss compared to the control sample.

Keywords: Corn starch; chitosan; esterification; complexation; OCC pulp; mechanical properties.

4.1.1. Introduction

Corn starch is a carbohydrate-based polymer that is widely abundant and readily available in a number of commercial forms. It typically occurs as semi-crystalline granules composed of amylopectin (70%) and amylose(30%).¹ Its multihydroxyl chemical make-up offers a number of derivatization opportunities for the chemical community. The low cost, commercial availability, and chemical derivatization opportunities of corn starch in the market not surprisingly attract a number of researchers attempting to develop new functional starch derivatives for industrial applications. However, chitosan is another carbohydrate polymer which structure is chemically build by glucosamine repeating unit. The amine group in glucose unit has lot of advantage such as disinfectants, a higher antibacterial activity etc.²

Chemical modification of a paper surface in the pulp and paper arena is currently a common practice for improving printing quality, surface gloss, surface sizing, and calendaring. Typically and especially for printing- and writing-grade papers, starch is used for surface sizing, with the main goal of improving paper surface resistance (to uneven penetration and flow of inks/liquid media) and printability.³ Recycling is a very visible and highly important conceptual framework in any effort to address environmental concerns, reduce expanding landfills, and reduce the need for virgin fiber manufacture with the concomitant expenditure of energy and resources. Hence, it is a highly sustainable approach that demands increased research efforts for future success. For old corrugated containerboard (OCC) paper, a major component of the recycled market, the market is primarily concerned with improving mechanical strength because of the compromised nature of the fibers utilized. OCC pulp is a

category of pulp fibers which have previously passed through at least two recycling processes. As a result, its fibers are much more degraded (shorter and/or thinner) and weaker than the original fibers. The bonding between these shorter fibers is significantly weaker which leads to very poor quality in terms of paper strength, such as burst strength, tear strength, and tensile strength. OCC also carries a significant amount of anionic trash which causes strength agents to lose their efficiency.⁴

Approximately 70 million tons of paper and paperboard are used per year in the United State (2011 MSW Characterization Reports). The utilization rate of waste fiber (OCC) for recycled containerboard in 1963 was reported to be 21.1% in the US, whereas in 2001 it was 67% with a concomitant recovery rate of approximately 70%.⁵ Recently, the American Forest & Paper Association (AF&PA) released a 2011 recovery rate for Old Corrugated Containers (24.1 million tons recovered) which has reached a new high of 91.2%. Therefore, much research in this area attempts to improve the strength of OCC because waste fibers are typically mechanically inferior to their virgin equivalents. Early research work identified several types of chemical treatments that yielded measurable improvements in the bonding strength of recycled sheets.⁶⁻⁷ A few innovative studies have shown that chemical derivatization of fiber surfaces can sometimes prevent strength losses from occurring,⁸⁻⁹ while refining and chemical treatments improved the mechanical properties of OCC pulp.³ The papermaking industry is currently using existing commercial dry strength agents such as cationic starch, amphoteric starch, carboxyl methyl cellulose(CMC) cationic polyacrylamide, anionic polyacrylamide, amphoteric polyacrylamide and glyoxylate polyacrylamide to address potential improvements in the strength of OCC, but strength improvement is still very low relative to that of virgin

pulp despite the current efforts.¹⁰⁻¹¹ Meanwhile, nontraditional approaches for strength improvements in such materials as OCC are available. For example, nanomaterials offer a promising alternative to tackling the issue of low OCC strength because of the nanometric size effect compared to conventional bulk fillers even at low filler content. Nanofillers have strong reinforcing effects, and studies have also shown their positive impact in barrier packaging. However, for decades studies have been conducted with nonrenewable inorganic fillers and a petroleum-based matrix for a number of applications including packaging, a high value sector of the pulp market.¹² Increasing environmental concerns have led to, for example, developing new flexible barrier bio-based packaging materials and investigating the potential uses of renewable resources for such applications.¹²

The present study focuses on the synthesis, characterization, and application of a newly developed corn starch-based dry strength additives for improving the mechanical properties of low strength recycled paper materials (OCC). In the present investigation, the modification of corn starch with diethylenetriamine pentaacetic acid in the presence of sodium hypophosphate (SHP) and later complexed with chitosan. This research also focuses on the characterization of the modified corn starch/chitosan additive-treated recycled OCC paper furnish by examining the inter-fiber bonding strength and mechanical properties.

4.1.2. Experimental Methods

4.1.2.1. Materials

The linear board (OCC) pulp was furnished by Georgia Pacific, Atlanta, GA. Corn starch (S)

was supplied by Cargill Incorporated, Minneapolis, MN. Chitosan (Ch), CAS no. 9012-76-4, was purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphate (SHP), CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2, and diethylenetriamine pentaacetic acid, CAS no. 67-43-6. Thyl alcohol denatured and acetic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water as the medium.

4.1.2.2 Chemical Modifications of the Corn Starch

Diethylenetriamine pentaacetic acid (2g) and SHP (0.4 g) were dissolved into 20 ml sodium hydroxide solution in a 50 mL Petri Dish. Corn starch (8 g) was boil at 100°C for 15 minutes and then combined with diethylenetriamine pentaacetic acid solution and manually mixed vigorously with a glass rod. The mixture was placed in an air oven at 120 °C for 3 h. Reaction products were washed with water and filtered several times to remove unreacted materials. The product obtained was modified corn starch that were air dried at 50 °C in an air oven overnight.¹⁴

The proposed reaction scheme of interest is shown in Figure 4.1.1.

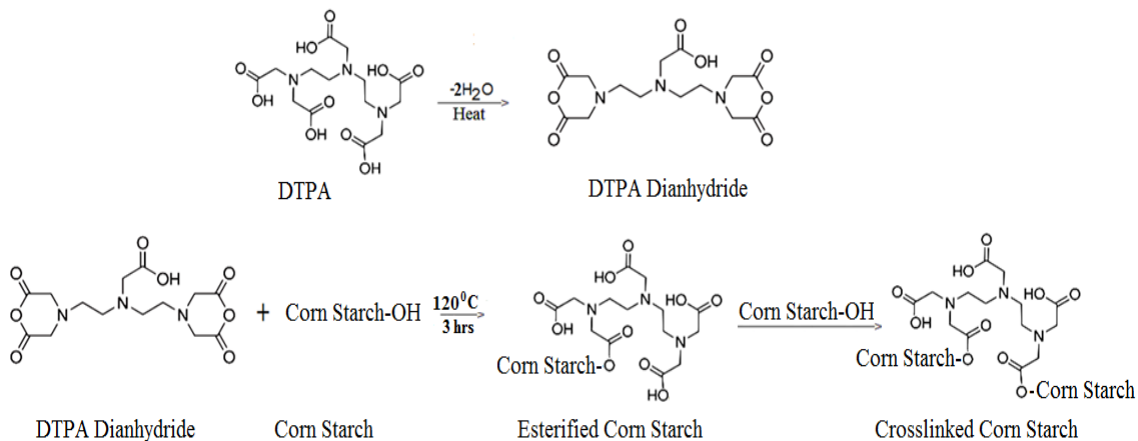


Figure 4.1.1. Esterification reaction of corn starch with DTPA.

4.1.2.3. Polyelectrolyte Complexation

Modified corn starch (1.4 g) were also dissolved with 50 mL of water. Chitosan (0.6 g) was dissolved into 50 mL of 1.5 % acetic acid solution and then added to a 50 mL corn starch solution in a 250 mL round-bottom flask. The reaction mixture was stirred using a magnetic stirrer at 80 °C for 90 min.¹⁵ The proposed reaction scheme is shown in Figure 4.1.2.

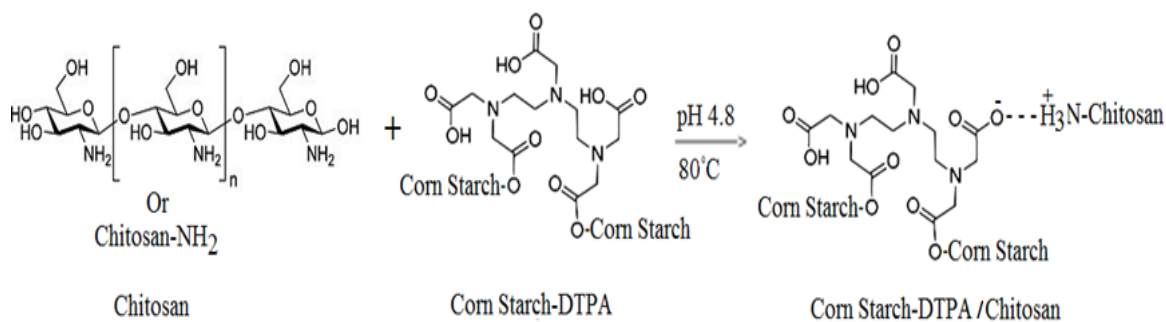


Figure 4.1.2. Polyelectrolyte complexation of corn starch-DTPA with chitosan.

4.1.2.4. Preparation of the OCC Pulp Sheet

The pulp hand sheet was prepared according to follow TAPPI Standard Method 205. 1.5% additive dosage (based on oven dry pulp) was properly mixed with 10 L of the pulp slurry (0.3% consistency) in a plastic bucket and then stirred (400 rpm) for 10 min. The sheet was prepared using a 600 mL pulp slurry in a sheet molding machine. The sheet was dried in a condition room and subsequently cured at 105 °C for 1.0 h.

4.1.2.5. Testing Methods

4.1.2.5.1. Determination of Carboxyl Content:

A known amount of corn starch derivative was dissolved in 0.1 N NaOH and hydrolyzed for one hour. The remaining excess amount of NaOH was determined by titration with 0.1 N HCl using phenolphthalein as an indicator,¹⁶ and the carboxyl content in milliequivalents of acidity per 100 g was calculated as follows:

$$\text{Carboxyl Content (meq)} = \frac{(V_2 - V_1) \times N \times 100}{W}$$

Where

N = Normality of HCl

V_2 = Volume of HCl without sample

V_1 = Volume of HCl with sample

W = Weight of Sample

4.1.2.5.2. Determination of Degree of Esterification and Degree of Substitution:

The corn starch derivative was dissolved in DMSO in a conical flask for 10 h, and then excess 0.1 N NaOH was added to the solution to saponify the ester over 2 h. The excess NaOH was determined by titration with 0.1 N HCl¹⁷⁻¹⁸ to determine the percent esterification and the degree of substitution shown below:

$$\text{Degree of Esterification (\%)} = \frac{6.005(V_2 - V_1) \times N}{W}$$

N = Normality of HCl

V_2 = Volume of HCl without sample

V_1 = Volume of HCl with sample

$$\text{Degree of Substitution} = \frac{162 \times A\%}{100M - (m - 1)A\%}$$

$A\%$ = Degree of esterification

W = Weight of sample

M = Molecular weight of crosslinking agent

m = Molecular weight of the crosslinking part of crosslinking agent

4.1.2.6. Physical Properties Test of Additive-Treated Recycled OCC Pulp Hand Sheet

The tensile, burst, tear, STFI, gloss and roughness of additive treated OCC pulp hand sheet were tested according to TAPPI T 220, TAPPI T 810, ASTM D 689, TAPPI T826, TAPPI T 480, and TAPPI T 538 test methods, respectively.

4.1.2.7. Inter Fiber Bonding Strength of Additive-Treated Reclaimed OCC Pulp Sheets

The inter-fiber bonding strength of additive-treated OCC pulp hand sheets was obtained using a standard T 569pm-00 (provisional method-2000@ 2000 TAPPI) testing protocol

4.1.2.8. Characterization

1.2.8.1. ATR Analysis

IR spectra of all modified corn starch samples were recorded with a Perkin Elmer FT-IR spectrophotometer. All the spectra were obtained by accumulation of 8 scans, with a resolution of 4 cm^{-1} , at $400\text{--}4000\text{ cm}^{-1}$.¹⁹

4.1.2.8.2. Thermal Gravimetric Analysis (TGA)

The thermogravimetric analyzer used in this study was a TGA Q500. A nitrogen atmosphere was used. The temperature range and heating rate were $30\text{--}600^\circ\text{C}$ and $5^\circ\text{C}/\text{min}$, followed by isothermal heating at 600°C .²⁰

4.1.2.8.3. Differential Scanning Calorimeter (DSC)

A differential scanning calorimeter DSC Q100 was used with a Hermetic pan (T 090127). Samples were subjected to 10°C/min to 105°C for 10 minutes and jump to 40°C and the again heated a 2 °C/min temperature ramp from 40 to 240 °C followed by isothermal heating at 240 °C for 10 min. An empty pan was used as the reference.²¹

4.1.2.8.4. Scanning Electron Microscope (SEM)

Morphological characterization of modified corn starch /chitosan additive-treated pulp hand sheets was performed on images acquired using a scanning electron microscope (SEM), Hitachi S-3200N.¹⁴

4.1.2.8.5. Contact Angle

Dynamic contact angle measurements were performed with a Phoenix 300 Contact Angle Analyzer (Seo Co., Ltd., Korea) on modified corn starch /chitosan-treated pulp hand sheets. Deionized water was used as the probe fluid.¹⁶

4.1.3. Results and Discussion

4.1.3.1 Characterization of modified corn starch

The carboxyl content of the corn starch increased from 0.0 meq/100 g to 380 meq/100 g. To further clarify the changes that occurred after the surface modification, the DS (degree of substitution) and percent esterification were explicitly employed and determined by titration. For this study, the monomer formula weight and number of hydroxyls per starch monomer

unit that were used in the calculations were 162 Da and 3. Thus, the degree of substitution and percent esterification were calculated to be 0.28 and 42%. The intrinsic viscosities of the 1 M CED dissolved corn starch and corn starch–DTPA were determined at 25 °C with an Ubbelohde-type viscometer to ascertain molecular weight.¹⁷ Depending on the specific viscosity measured, typical molecular weights of corn starch and corn starch–DTPA were found to be 12.96×10^4 and 16.84×10^4 Da, respectively.

FT-IR Analysis

The ATR spectra of the corn starch (A) and corn starch–DTPA/chitosan are shown in Figure 4.1.3. The spectrum of the corn starch shows a prominent peak at 3306.43 cm^{-1} which arises from the hydroxyl groups, whereas there is no peak over the region of $1720\text{--}1800 \text{ cm}^{-1}$, reflecting that there are no carbonyl groups on the corn starch. However, when the corn starch reacted with the DTPA, peaks appeared at approximately 1740 cm^{-1} that was attributable to the carbonyl group of the ester functionality. Also, the peak at 3414 cm^{-1} decreases qualitatively, indicating the conversion of hydroxyl to esters.¹⁴

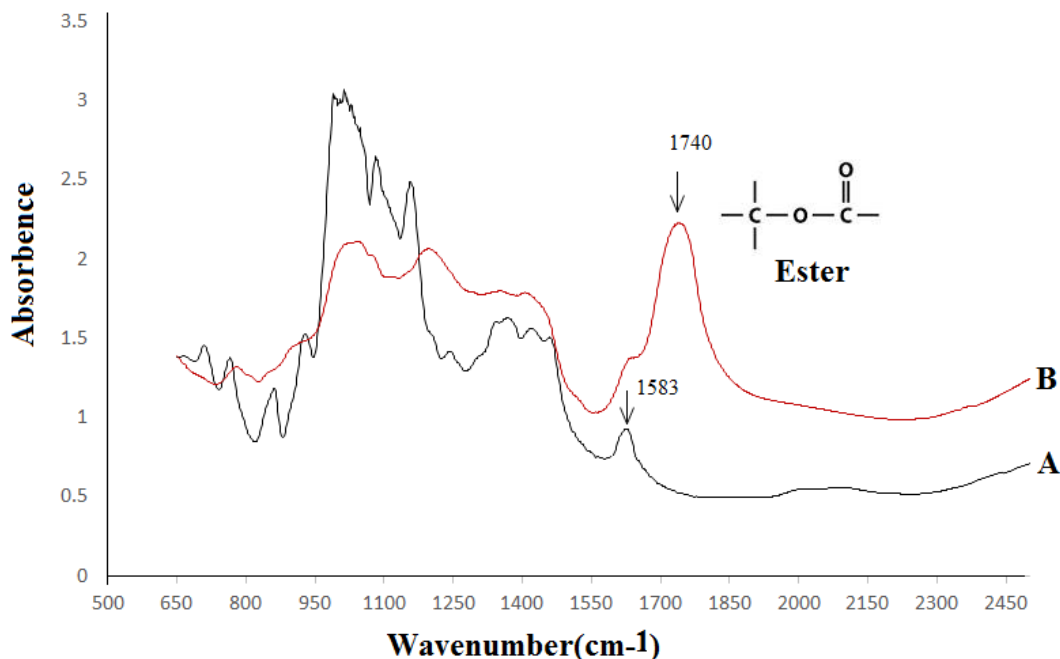


Figure 4.1.3. FT-IR spectra of corn starch (A), corn starch–DTPA/chitosan (B). As shown in the spectrum, the 1740 cm⁻¹ band can be attributed to the ester carbonyl stretch.

Thermal Behavior

The thermogravimetric behavior of the corn starch derivatives was evaluated with a 5 °C/min heating ramp under nitrogen and shown in Figure 4.1.4. For several samples, a weight loss below and around 100 °C was attributed to water evaporation.²² However, the weight loss above 100 °C was caused by the thermal decomposition of the corn starch /derivatives themselves.²³ DTPA had a single sharp decomposition peak at 280.26 °C, whereas the corn starch have a single weight loss peak at 305 °C; however, all derivatives of the corn starch have a decrease in the maximum weight loss temperature and a concomitant significantly higher residual mass after heating to 600 °C. This may be explained by the fact that the corn

starch surface-modifying agents have a lower decomposition temperature, that the layer of this material is on the surface of the corn starch, and that the materials derived from the esterification have a lower temperature of degradation as previously shown for starch citrate and xylan citrate.¹⁶⁻¹⁷

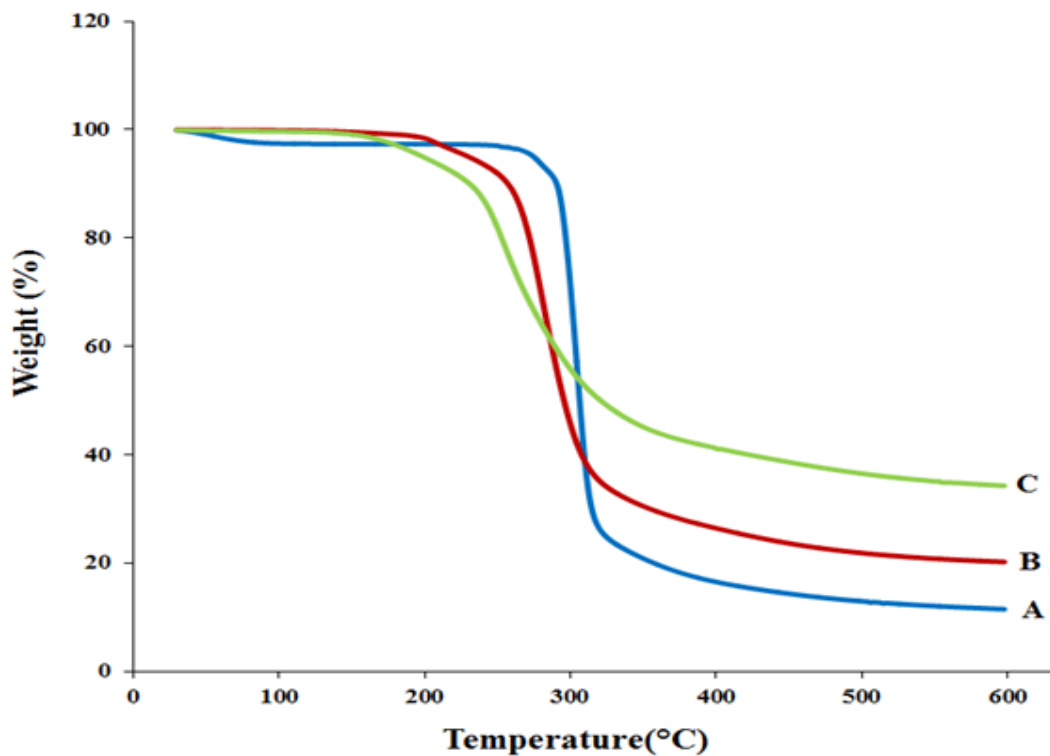


Figure 4.1.4: TGA of corn starch (A), corn starch-DTPA (B) and corn starch-DTPA/chitosan(C).

The thermal behavior obtained from a differential scanning calorimetric analysis of the corn starch derivatives was evaluated with 10°C/min to 105°C for 10 minutes and jump to 40°C and the again heated a 2 °C/min temperature ramp from 40 to 240 °C followed by isothermal

heating at 240 °C for 10 min under nitrogen as shown in Figure 4.1.5. DTPA displays a very sharp melting point at 199.2°C, whereas for the corn starch an endothermic peak was observed at 160 °C. The melting points all increased for the reaction products as illustrated in Figure 5. The increase in the melting points may be from changes in chemical composition due to increased hydrogen bonding and plasticization as well as the more robust molecular organization obtained from the esterification reaction.¹⁶

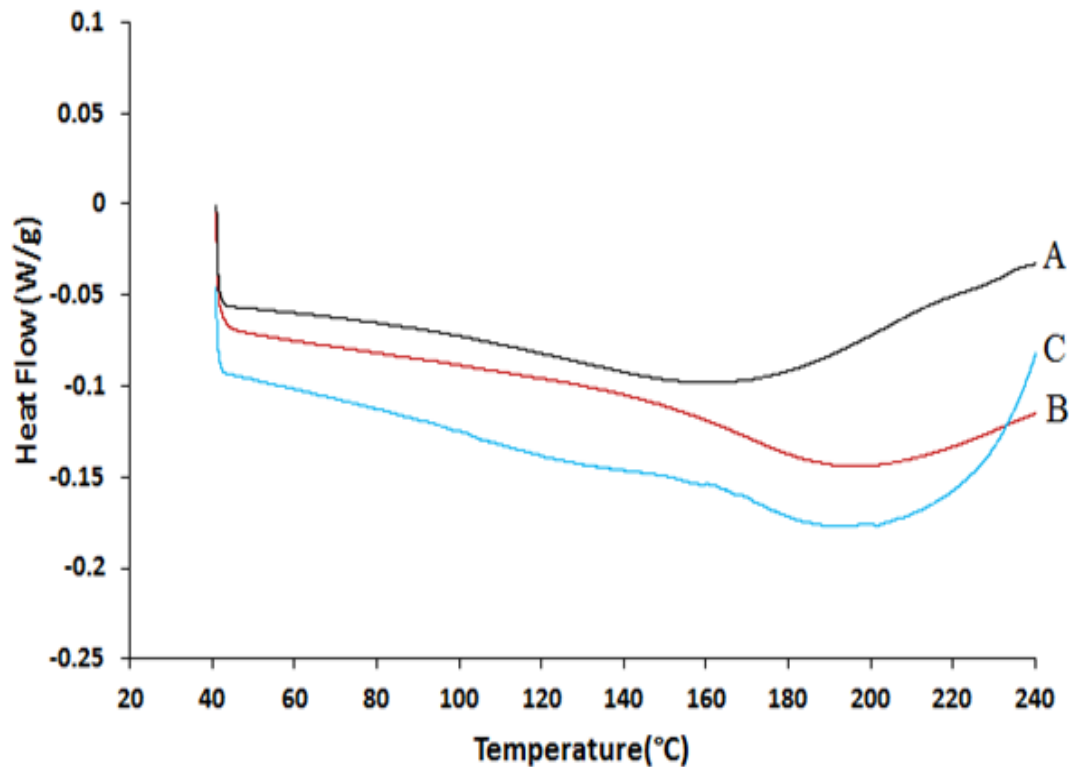


Figure 4.1.5: DSC of corn starch (A), corn starch-DTPA (B) and corn starch-DTPA/chitosan(C).

4.1.3.2. Application of Modified Corn Starch/Chitosan Additives Effect of Corn Starch Derivatives on Pulp Paper Strength Properties.

Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need to have sufficient resistance in applications that require packaging, wrapping, or sealing. In general, such gross resistance can be attributed at the molecular level to the adequate development of hydrogen bonds. Also, it depends on the quantity and area of bonding sites. In recycling, fibers irreversibly damage, and this damage can affect final paper resistance properties. Figure 4.1.6 shows the tensile strength of OCC recycled pulp hand sheet that results after the addition of corn starch derivatives.

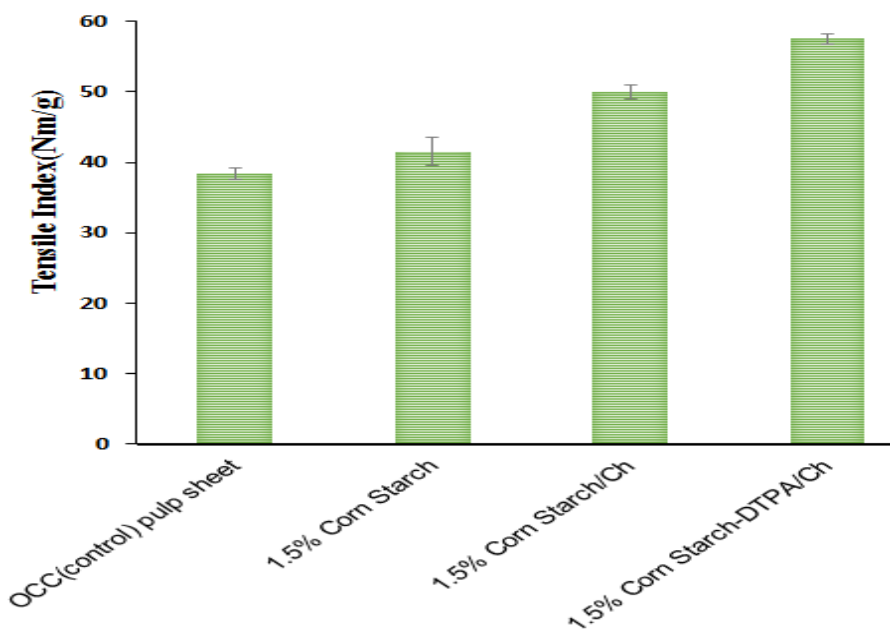


Figure 4.1.6: Effect of corn starch derivatives on the tensile strength of OCC recycle pulp samples.

The control for these studies was the base OCC recycled pulp which is a collection of fibers and broken fibers or fines (CSF = 400). In tandem, 1.5 % corn starch derivatives (based on the mass of dried pulp) were also mixed with the OCC pulp slurry separately. The tensile index of the corn starch and its derivative-treated OCC pulp samples such as corn starch/chitosan and corn starch-DTPA/chitosan were found to be 8.2, 30 and 49.9% higher than the control sample. Similarly the bursting index and STFI index were increased 15, 33.4 and 48.75%, respectively, and 11, 29.1 and 49.5% respectively compare to control sample (Fig. 4.1.7 & 4.1.8). In addition, the tear index of corn starch/chitosan additive and corn starch-DTPA/chitosan additive-treated OCC pulp sheet was decreased but corn starch treated OCC pulp sheet slightly increased compare to control sample (Fig.4.1.9).

The inter-fiber bonding strength of OCC, corn starch/chitosan additive and corn starch-DTPA/chitosan additive-treated OCC pulp sheet were measured by an Internal Bond Tester (Scott). The inter-fiber bonding strength was increased 102% for corn starch/chitosan additive-treated OCC pulp sheet sample and 176% for corn starch-DTPA/chitosan additive-treated OCC pulp sheet sample compare to control OCC pulp sheet. This may be because of corn starch–DTPA/chitosan polyelectrolyte complex became bonded (amide bond)²³ and had the opportunity to bond more liberally to the fiber hydroxyl groups; the free carboxyl groups of corn starch –DTPA also contributed to inter-fiber bonding and thus increased the paper strength.²⁴⁻²⁵ However, the density of the corn starch–DTPA/chitosan-treated sample increased approximately 25% which is also one of the causes for the increases in the strength.²⁶

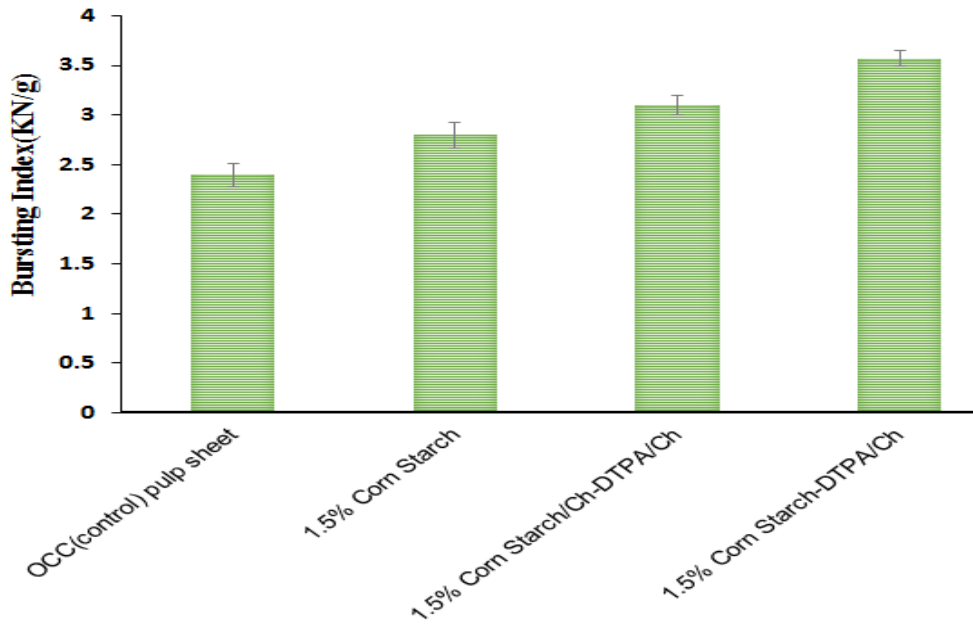


Figure 4.1.7: Effect of corn starch derivatives on the burst strength of OCC recycle pulp samples.

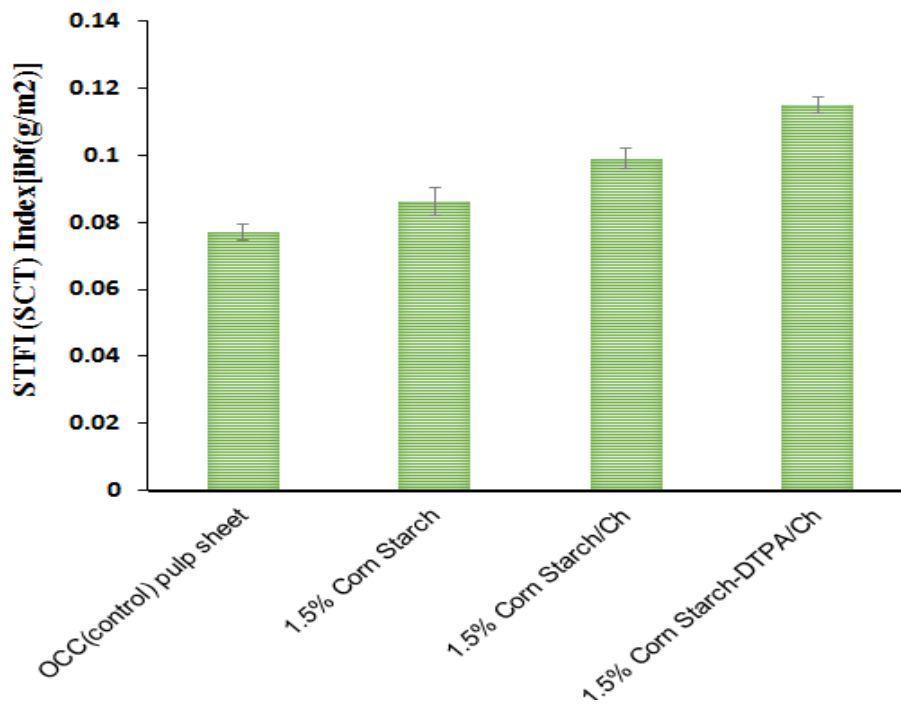


Figure 4.1.8: Effect of corn starch derivatives on the STFI index of OCC recycle pulp samples.

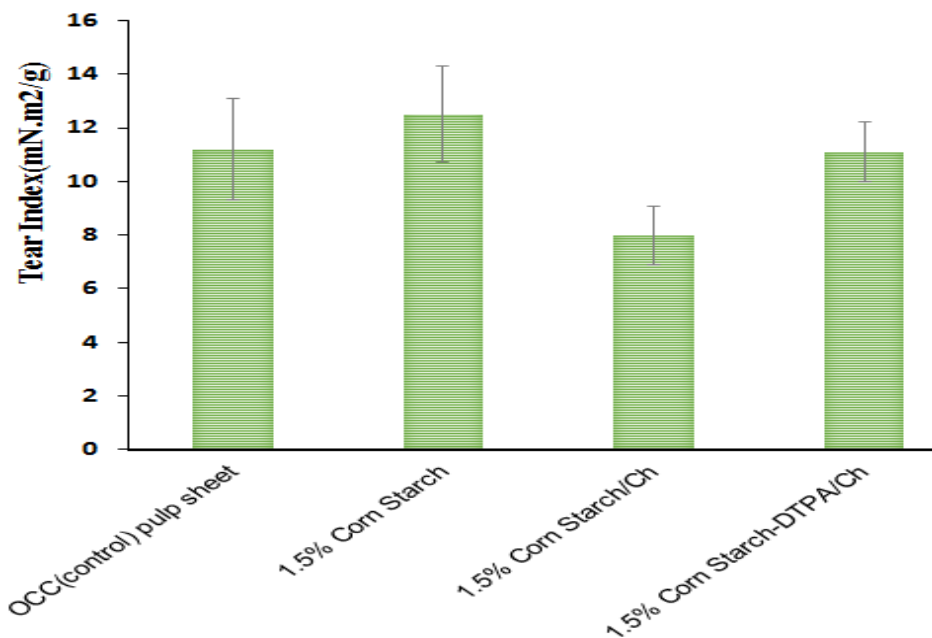


Figure 4.1.9: Effect of corn starch derivatives on the tear index of OCC recycle pulp.

4.1.3.3. Bond Formation between modified corn starch additives with OCC Recycle Pulp.

The basic groups ($-NH_2$) on every ring in corn starch–DTPA–chitosan derivatives develop positive charges when they are in a sufficiently acidic medium and may thus form ionic or covalent bonds with the negatively charged cellulosic in paper fibers during the paper making process.²⁷ In addition, the DTPA in corn starch–DTPA–chitosan derivatives contains a number of free carboxyl groups which can also engage in ionic bonds with the fiber surface of pulp and also increase the relative bonded area between fibers. The combined interactive effects attributable to the carboxyl and amine groups for increasing bonding between fibers during sheet formation also contributed to an increase in tensile strength.²⁸

Figure 4.1.10 indicates that a high residual char value was observed in the corn starch–DTPA–chitosan-treated pulp sheet compared to the control pulp sheet after heating at 600 °C (Figure 4.1.8) which is due to corn starch–DTPA–chitosan crosslinking to the pulp fiber.

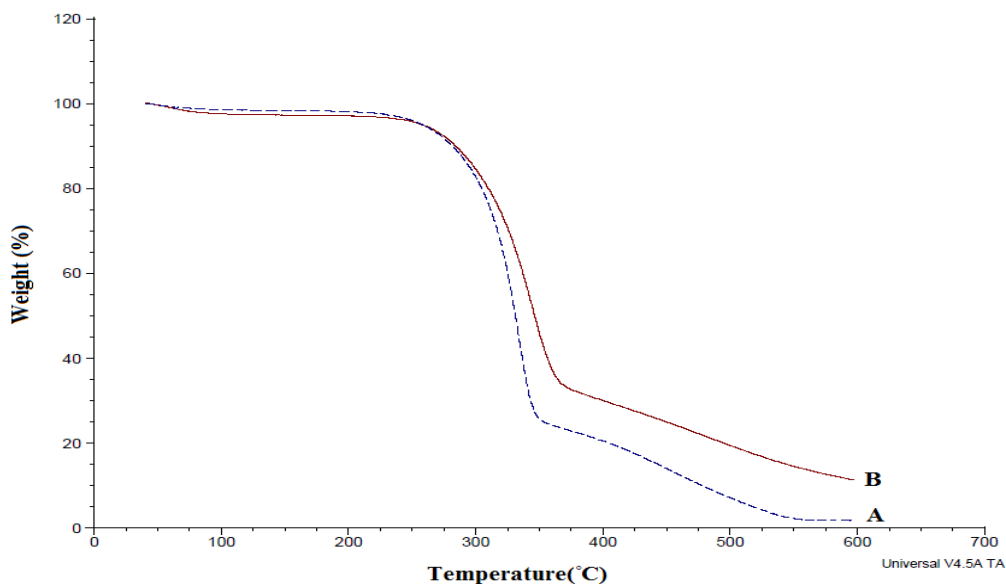


Figure 4.1.10: Thermo-gravimetric analysis of OCC pulp sheet (A) and corn starch-DTPA-chitosan treated OCC pulp sheet (B).

Scanning electron microscopy images of OCC recycle pulp samples and corn starch-DTPA/chitosan derivatives-treated OCC recycle pulp samples are shown in Figure 4.1.11. The OCC pulp sample control shows a continuous smooth pore structure with plate-like solid pore walls, but the corn starch-DTPA/chitosan derivatives-treated OCC pulp sample SEM images reveal a rougher surface with the appearance of smaller irregular fragments on the fiber's surface. It may be that these are aggregations of corn starch additive and associated fines/fibrils

that increase the bonded area among the OCC pulp fibers to make more compact fiber assemblies.

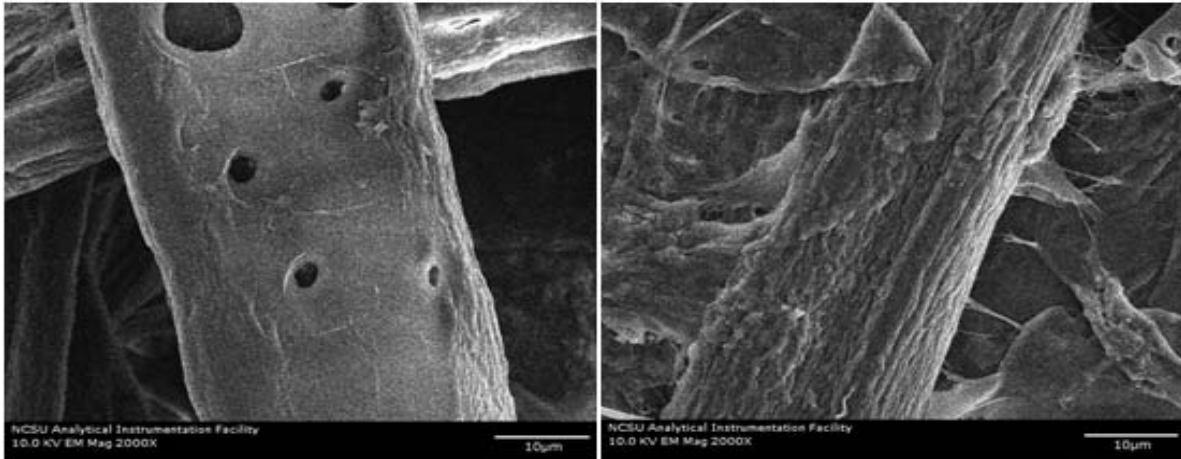


Figure 4.1.11: SEM photomicrograph of OCC recycle pulp sample (left) and corn starch-DTPA/chitosan derivative-treated OCC pulp samples (right).

4.1.3.4. Dynamic Contact Angle of Modified Corn starch/Chitosan-treated Pulp Sheet

The dynamic contact angle with DI water at 20 seconds was determined to be 45° for OCC pulp sheet (control). The water angle significantly dropped 4.5° for approximately 200 seconds (Fig. 4.1.12). In contrast, the dynamic contact angles with DI water at 20 seconds for corn starch-DTPA-chitosan-treated OCC pulp sheet was 102° and the contact angle dropped approximately 80° for approximately 400 seconds and then dropped to 75° approximately 2200 seconds and finally dropped 45° for approximately 2800 seconds. This reflects the significantly decreased water absorbency of the corn starch-DTPA-chitosan-treated OCC pulp sheet relative to the control pulp sheet. This may explained that the OCC furnish has a very

irregular surface and is extremely hydrophilic showing nearly no surface contact angle measurement in the typical contact angle time frame. Modified corn starch/chitosan additive, chitosan, is strongly hydrophobic and also produces a sticky gel under acidic pH (wet) that is adopts a plastic-like character under dry conditions. Thus, when we generate a pulp sheet with the additive, under the pressing time, it spreads very evenly over the rough surface, covering it very uniformly to produce a paper surface that was very smooth and also possessing increased gloss. Thus, because the additive-treated sheet surface was hydrophobic due to the plastic-like chitosan under dry conditions, the contact angle increased somewhat.

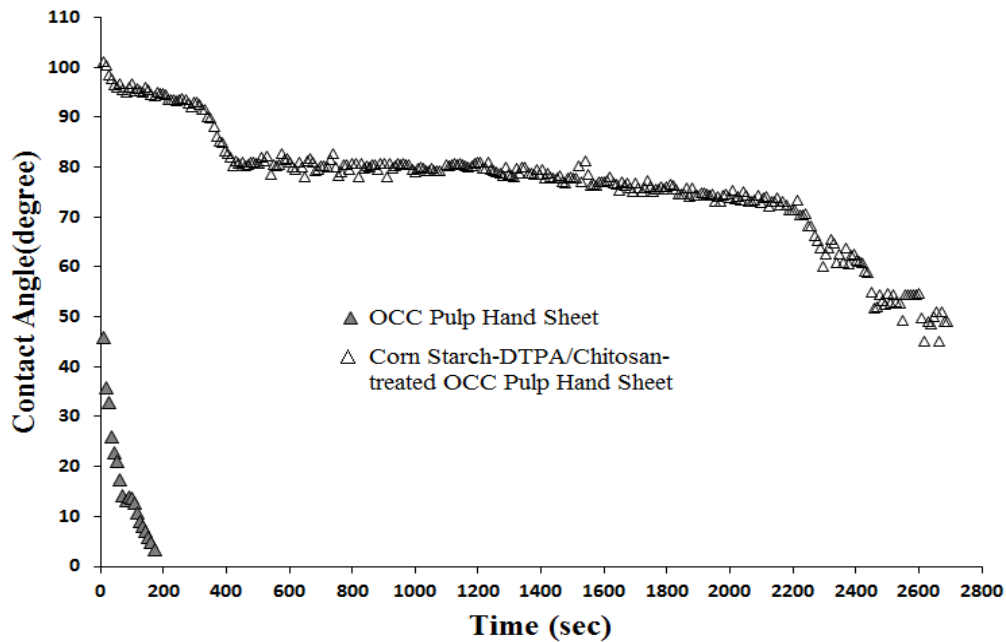


Figure 4.1.12. Contact angle of OCC pulp hand sheet (\blacktriangle) and Soy flour-DTPA/chitosan-treated OCC pulp hand sheet (\triangle).

4.1.4. Conclusions

Corn starch was modified with diethylenetriamine pentaacetic acid in the presence of sodium hypophosphite (SHP) to increase their ability to better bond recycled fibers during paper formation. It was found that the carboxyl group content, degree of esterification, and degree of substitution of diethylenetriamine pentaacetic acid with corn starch significantly increased relative to the unmodified corn starch. The modified corn starch was later coupled with chitosan. Approximately 1.5 % of corn starch and their derivatives such as corn starch/chitosan and corn starch-DTPA/chitosan were blended with OCC recycle pulp separately prior to making a sample. The tensile, burst and STFI index increased 8.2, 30 and 49.9%, and 15, 33.4 and 48.75%, and 11, 29.1 and 49.5% respectively, and the inter-fiber bonding strength of corn starch-DTPA/chitosan-treated pulp sheet was increased 176%, while there was also a significant increase in gloss (2 times) and decrease in roughness (20%) and tear index compared to the control sample. The increased strength is an agreement with increased bonding between the corn starch derivative and pulp fibers.

4.1.5. References

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CHAPTER 5

Nano-Based Carbohydrate Additive to Increase the Dry Strength of Recycled Paper Furnish.

This chapter presents extraction of starch nano particle and cellulose nanocrystals, modification of starch nano particles and cellulose nanocrystals with modifying agents in the presence of a catalyst and further complexed with chitosan, the characterization of modified starch nano particles and modified cellulose nanocrystals additives. It also focuses on the characterization of the modified starch nano particles and modified cellulose nanocrystals additives-treated recycled paper furnish (OCC) by examining the inter-fiber bonding strength and mechanical properties. Finally, it also explores the preparation of hydrophobic cellulose nanocrystals with fluorine based modifying agents for hydrophobic paper packaging.

Three article has been published from this chapter

1. Abdus Salam Lucian A Lucia, Hasan Jameel. Synthesis, Characterization, and Evaluation of Chitosan-Crosslinked Starch Nanoparticles on the Physical Properties of Recycled Paper Furnish. *ACS Applied Materials & Interfaces*. 2013, 5 (21), pp. 11029–11037.
2. Abdus Salam, Lucian A Lucia, Hasan Jameel. A Novel Cellulose Nanocrystals-Based Approach to Improve the Mechanical Properties of Recycled Paper Stock. *ACS Sustainable Chem. Eng.* 2013, 1 (12), pp 1584–1592.
3. Abdus Salam, Lucian A. Lucia, Hasan Jameel. Fluorine-based surface decorated cellulose nanocrystals as potential hydrophobic and oleophobic materials. *Cellulose*, DOI: 10.1007/s10570-014-0507-9.

Synthesis, Characterization, and Evaluation of Chitosan-Complexed Starch Nanoparticles on the Physical Properties of Recycled Paper Furnish

Abdus Salam, Lucian A Lucia, Hasan Jameel

Abstract

The objectives of the current research were to synthesize and characterize chitosan-complexed starch nanoparticles and examine their effect on the physical performance of recycled pulp, specifically old corrugated containerboard (OCC). This new approach provides a uniquely renewable and useful approach to enhance mechanical properties of pulp while maintaining environmental compatibility, industrial compatibility, and paper qualities. The starch nanoparticles used for the research were prepared from cooked cornstarch gel with ethanol and reacted with diethylenetriamine pentaacetic acid (DTPA) in the presence of sodium hypophosphite. Thereupon, the DTPA-modified starch nanoparticles (SNs) were complexed with chitosan as part of a general chemical strategy to improve their incorporation into an OCC matrix and increase inter-fiber bonding. Spectral characterization of the SNs was done using TGA, DSC, FT-IR, and SEM to analyze their composition and structure. Approximately 2% chitosan-complexed starch nanoparticle derivatives by mass (SNX/C) of OCC-based slurry were thoroughly mixed before manufacturing a two-dimensional sheet for physical testing. The tensile and burst strength of the modified OCC pulp sheet increased 50 and 49%, respectively, albeit having a decreased tear strength compared to the control sample. However, when the OCC pulp sheet was coated with a 1% SNX/C by mass solution, the tensile and burst strength increased 120 and 70%, respectively, while also providing significantly increased gloss, decreased roughness, and tear strength. Because the mechanical

properties are the most critical property facing the recyclability of OCCs, the tremendous gains afforded by the starch nanoparticle–DTPA–chitosan proposed give the system enormous potential applicability as a viable dry strength agent for paper substrates.

Keywords: *starch nanoparticles; chitosan; complexation; OCC pulp; mechanical properties*

5.1.1. Introduction

Starch is a carbohydrate-based polymer that is widely abundant and readily available in a number of commercial forms. It typically occurs as semi-crystalline granules composed of amylopectin and amylose.¹ Its multihydroxyl chemical make-up offers a number of derivatization opportunities for the chemical community, in addition to also being the primary feedstock for cyclodextrin manufacture. The low cost, commercial availability, and chemical derivatization opportunities of starch in the market not surprisingly attract a number of researchers attempting to develop new functional starch derivatives for industrial applications. Chemical modification of a paper surface in the pulp and paper arena is currently a common practice for improving printing quality, surface gloss, surface sizing, and calendaring. Typically and especially for printing- and writing-grade papers, starch is used for surface sizing, with the main goal of improving paper surface resistance (to uneven penetration and flow of inks/liquid media) and printability.² Recycling is a very visible and highly important conceptual framework in any effort to address environmental concerns, reduce expanding landfills, and reduce the need for virgin fiber manufacture with the concomitant expenditure of energy and resources. Hence, it is a highly sustainable approach that demands increased research efforts for future success. For old corrugated containerboard (OCC) paper, a major

component of the recycled market, the market is primarily concerned with improving mechanical strength because of the compromised nature of the fibers utilized. OCC pulp is a category of pulp fibers which have previously passed through at least two recycling processes. As a result, its fibers are much more degraded (shorter and/or thinner) and weaker than the original fibers. The bonding between these shorter fibers is significantly weaker which leads to very poor quality in terms of paper strength, such as burst strength, tear strength, and tensile strength. OCC also carries a significant amount of anionic trash which causes strength agents to lose their efficiency.³⁻⁴

Approximately 70 million tons of paper and paperboard are used per year in the United State (2011 MSW Characterization Reports). The utilization rate of waste fiber (OCC) for recycled containerboard in 1963 was reported to be 21.1% in the US, whereas in 2001 it was 67% with a concomitant recovery rate of approximately 70%.⁵ Recently, the American Forest & Paper Association (AF&PA) released a 2011 recovery rate for Old Corrugated Containers (24.1 million tons recovered) which has reached a new high of 91.2%. Therefore, much research in this area attempts to improve the strength of OCC because waste fibers are typically mechanically inferior to their virgin equivalents. Early research work identified several types of chemical treatments that yielded measurable improvements in the bonding strength of recycled sheets.⁶⁻⁷ A few innovative studies have shown that chemical derivatization of fiber surfaces can sometimes prevent strength losses from occurring,⁸⁻⁹ while refining and chemical treatments improved the mechanical properties of OCC pulp.³ The papermaking industry is currently using existing commercial dry strength agents such as cationic starch, polyacrylamide, and glyoxylate polyacrylamide to address potential improvements in the

strength of OCC, but strength improvement is still very low relative to that of virgin pulp despite the current efforts.¹⁰⁻¹¹

Meanwhile, nontraditional approaches for strength improvements in such materials as OCC are available. For example, nanomaterials offer a promising alternative to tackling the issue of low OCC strength because of the nanometric size effect compared to conventional bulk fillers even at low filler content. Nanofillers have strong reinforcing effects, and studies have also shown their positive impact in barrier packaging. However, for decades studies have been conducted with nonrenewable inorganic fillers and a petroleum-based matrix for a number of applications including packaging, a high value sector of the pulp market.¹² Increasing environmental concerns have led to, for example, developing new flexible barrier bio-based packaging materials and investigating the potential uses of renewable resources for such applications.¹²

The present study therefore focuses on the application of a novel nanomaterial system for improving the critically important mechanical properties of OCC: starch nanoparticles (versus bulk cationized starch, a traditional commercial product) that have been modified with diethylenetriamine pentaacetic acid in the presence of sodium hypophosphate (SHP) and

later complexed with chitosan. The chemical modification of OCC pulp fibers currently presented a means for preparing materials with unique properties that can increase the ultimate value and utility of these biopolymers. Additionally, it is suggested that the stronger bonding afforded by the current system will allow enhanced wet web formation at the paper machine and after mechanical pressing and steam drying allow for improved paper runnability (less

opportunity for paper breaks). The present research will therefore focus on their characterization and provide a review of their application in paper furnishes.

5.1.2. Experimental Methods

5.1.2.1. Materials

The OCC pulp was furnished by AzkoNobel Pulp and Performance Chemicals, Marietta, GA. Corn starch (S) was supplied by Cargill Incorporated, Minneapolis, MN. Chitosan (C), CAS no. 9012-76-4, was purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphate (SHP), CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2, and diethylenetriamine pentaacetic acid (X), CAS no. 67-43-6. Thyl alcohol denatured and acetic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water as the medium.

5.1.2.2. Extraction of Starch Nanoparticles (SNs)

Corn starch (8 g) was added into 150 mL of distilled water. The mixture was heated at 90°C with constant stirring for 1 h for the complete gelatinization of corn starch, and then 150 mL of ethanol was added dropwise to the solution of gelatinized starch solution with constant stirring. The resultant nanoparticle suspensions were cooled to room temperature; another 150 mL of ethanol was added drop-wise for 50 min with constant stirring. The suspensions were centrifuged at 5300 rpm for 20 min, and the settled SNs were washed using ethanol to remove the water. After complete washing, the SNs were dried at 50 °C to remove ethanol.¹³

5.1.2.3. Chemical Modifications of the Starch Nanoparticle (SN)

Into 20 mL of sodium hydroxide solution (pH 11) in a 50 mL Petri Dish were dissolved 10 g of diethylenetriamine pentaacetic acid (X) and 2 g of SHP. Starch nanoparticles (SNs, 10 g) were combined with diethylenetriamine pentaacetic acid (X) solution and manually mixed vigorously with a glass rod. The mixture was placed in an air oven at 130 °C for 4 h. Reaction products were washed with water and filtered several times to remove unreacted materials. The product obtained was modified starch nanoparticles (SNXs) that were air dried at 50 °C in an air oven overnight.¹⁴

The proposed reaction scheme of interest is shown in Figure 5.1.1.

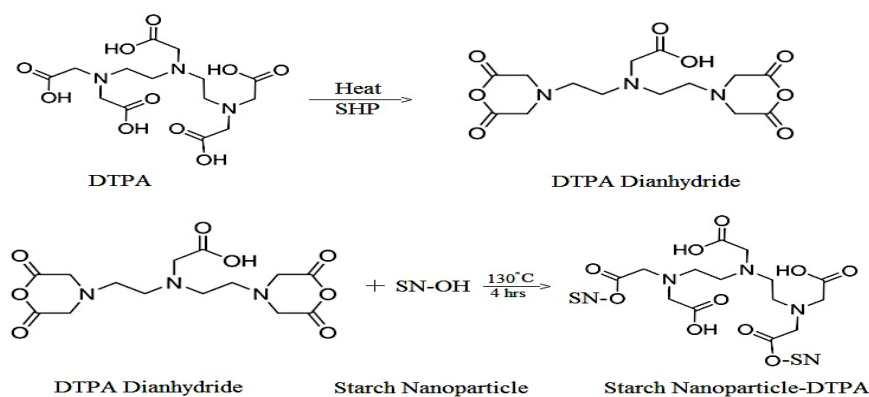


Figure 5.1.1. Esterification reaction of starch nanoparticles with DTPA.

5.1.2.4. Polyelectrolyte Complexation

Chitosan (C, 1 g) was dissolved into 50 mL of 1.5 % acetic acid solution. Modified starch nanoparticles (1 g) were also dissolved with 50 mL of water and then added to a 50 mL chitosan solution in a 250 mL round-bottom flask. The reaction mixture was stirred using a magnetic stirrer at 80 °C for 90 min.¹⁵ The proposed reaction scheme is shown in Figure 5.1.2.

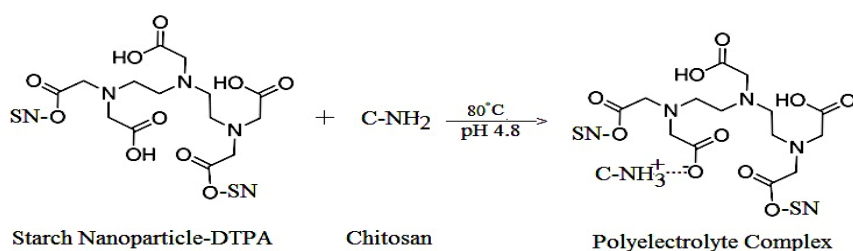


Figure 5.1.2. Polyelectrolyte complexation of starch nanoparticle-DTPA with chitosan.

5.1.2.5. Preparation of the OCC Pulp Sheet

An amount of 0.6 g of the additive was properly mixed with 10 L of the OCC pulp slurry (0.3% consistency) in a plastic bucket and then stirred (400 rpm) for 10 min. The additive mixed pulp slurry temperature was 30 °C with pH 5.4–5.8. The sheet was prepared using a 600 mL pulp slurry (1.8 g of OCC having a freeness of 400 CSF, an empirical measure of the total volume of water not absorbed in a sample, i.e., higher value, less adsorption) with or without additives in a sheet molder machine. The pulp slurry was also diluted with 10 L of white water into the sheet molder (diluted pulp slurry pH was 6.3–6.8) to produce a uniform

sheet. The sheet was dried in a condition room and subsequently cured at 105 °C for 1.0 h.

5.1.2.6. Coating of OCC

The OCC sheet was immersed into a 1% SNX/C solution and passed through a laboratory sizing press machine. The sheets were then dried in a condition room and then cured at 105 °C for 1 h for further characterization.

5.1.2.7. Testing Methods

5.1.2.7.1 Determination of Carboxyl Content

A known amount of starch nanoparticle derivative was dissolved in 0.1 N NaOH and hydrolyzed for one hour. The remaining excess amount of NaOH was determined by titration with 0.1 N HCl using phenolphthalein as an indicator,¹⁶ and the carboxyl content in milliequivalents of acidity per 100 g was calculated as follows:

$$\text{Carboxyl Content (meq)} = \frac{(V_2 - V_1) \times N \times 100}{W}$$

N = Normality of HCl

V_2 = Volume of HCl without sample

V_1 = Volume of HCl with sample

W = Weight of Sample

5.1.2.7.2. Determination of Degree of Esterification and Degree of Substitution

The starch nanoparticle derivative was dissolved in DMSO in a conical flask for 10 h, and then excess 0.1 N NaOH was added to the solution to saponify the ester over 2 h. The excess NaOH was determined by titration with 0.1 N HCl¹⁷⁻¹⁸ to determine the percent esterification and the degree of substitution shown below:

$$\text{Degree of Esterification (\%)} = \frac{6.005(V_2 - V_1) \times N}{W}$$

N = Normality of HCl

V_2 = Volume of HCl without sample

V_1 = Volume of HCl with sample

$$\text{Degree of Substitution} = \frac{162 \times A\%}{100M - (m - 1)A\%}$$

$A\%$ = Degree of esterification

W = Weight of sample

M = Molecular weight of crosslinking agent

m = Molecular weight of the crosslinking part of crosslinking agent

5.1.2.7.3. Gloss Testing

The gloss of OCC pulp hand sheet was tested with a GLOSSMETER tester according to the TAPPI T 480 test method.

5.1.2.7.4. Roughness Testing

The roughness of the OCC pulp hand sheet was tested with an L&W roughness tester according to the TAPPI T 538 test method.

5.1.2.7.5. Tensile Strength

The tensile of OCC pulp hand sheet strength was tested with an ALWETRON TH1 tester according to the TAPPI T 220 test method.

5.1.2.7.6. Burst Strength

The burst strength of OCC pulp hand sheet was tested with a MULLEN tester according to the TAPPI T 810 test method.

5.1.2.7.7. Tear Strength

The tear strength of the OCC pulp hand sheet was tested with an L & W tester according to the ASTM D 689 test method.

5.1.2.8. Characterization

5.1.2.8.1. ATR Analysis

IR spectra of all starch-based nanoparticle samples were recorded with a Perkin Elmer FT-IR spectrophotometer. All the spectra were obtained by accumulation of 8 scans, with a resolution of 4 cm^{-1} , at $400\text{--}4000\text{ cm}^{-1}$.¹⁹

5.1.2.8.2. Thermal Gravimetric Analysis (TGA)

The thermogravimetric analyzer used in this study was a TGA Q500. A nitrogen atmosphere was used. The temperature range and heating rate were $30\text{--}600^\circ\text{C}$ and $5^\circ\text{C}/\text{min}$, followed by isothermal heating at 600°C .²⁰

5.1.2.8.3. Differential Scanning Calorimeter (DSC)

A differential scanning calorimeter DSC Q100 was used with a Hermetic pan (T 090127). Samples were subjected to a $2^\circ\text{C}/\text{min}$ temperature ramp from 30 to 200°C followed by isothermal heating at 200°C for 15 min . An empty pan was used as the reference.²¹

5.1.2.8.4. Scanning Electron Microscope (SEM)

Morphological characterization of modified starch nanoparticle/chitosan derivative-treated OCC pulp hand sheets was performed on images acquired using a scanning electron microscope (SEM), Hitachi S-3200N.¹⁴

5.1.2.8.5. Contact Angle

Dynamic contact angle measurements were performed with a Phoenix 300 Contact Angle Analyzer (Seo Co., Ltd., Korea) on starch derivative/chitosan-treated OCC pulp hand sheets. Deionized water was used as the probe fluid.¹⁶

5.1.3. Results and Discussion

5.1.3.1. Characterization of Starch Nanoparticles

Morphology and Surface Chemical Changes

The SEM image of extracted starch nanoparticles had the form of coagulates that displayed a particle size length and width of 386.52 and 222.38 nm, respectively (Figure 5.1.3). In general, starch nanoparticles possess a surface covered with reactive hydroxyl groups that allow for surface decoration (for a specific functionality) using the appropriate chemical reaction strategy. The reaction pathway that was chosen for the particular functionality (mechanical strength improvement of OCC) in this work has already been shown in Figures 5.1.1 and 5.1.2.

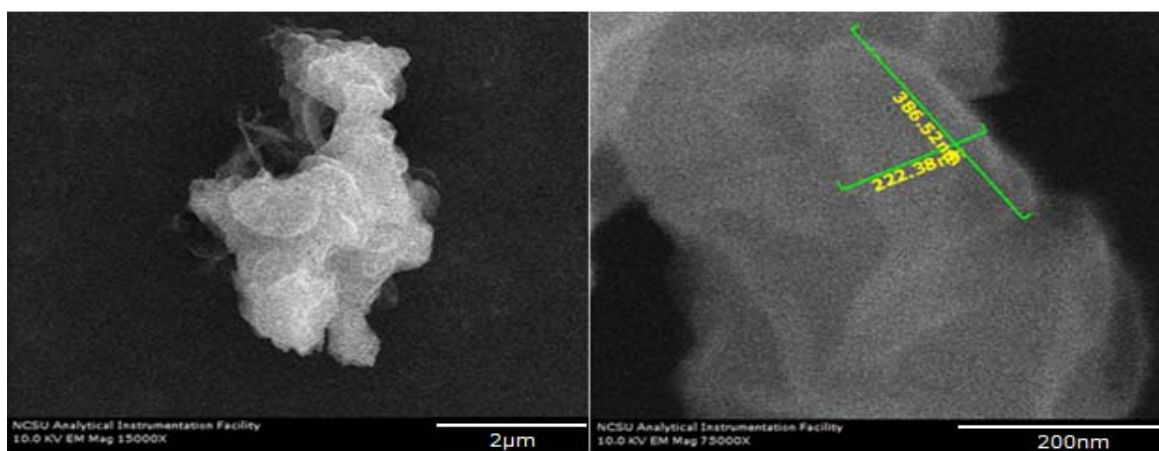


Figure 5.1.3. SEM photomicrographs of coagulated starch nanoparticles (The images have length scales of 2 microns (left) and 200 nanometer (right), respectively).

The carboxyl content of the starch nanoparticles increased from 0.0 meq/100 g to 452 meq/100 g. To further clarify the changes that occurred after the surface modification, the DS (degree of substitution) and percent esterification were explicitly employed and determined by titration. For this study, the monomer formula weight and number of hydroxyls per starch monomer unit that were used in the calculations were 162 Da and 3. Thus, the degree of substitution and percent esterification were calculated to be 0.2 and 38%. The intrinsic viscosities of the 1 M CED dissolved starch nanoparticle and starch nanoparticle–DTPA were determined at 25 °C with an Ubbelohde-type viscometer to ascertain molecular weight.¹⁷ Depending on the specific viscosity measured, typical molecular weights of starch nanoparticles and starch nanoparticle–DTPA were found to be 10 190 and 14 623 Da, respectively.

Thermal Behavior

The thermogravimetric behavior of the starch nanoparticle derivatives was evaluated with a 5 °C/min heating ramp under nitrogen and shown in Table 5.1.1. For several samples, a weight loss below and around 100 °C was attributed to water evaporation.²² However, the weight loss above 100 °C was caused by the thermal decomposition of the starch nanoparticles/derivatives themselves.²³ DTPA had a single sharp decomposition peak at 280.26 °C, whereas the starch nanoparticles have a single weight loss peak at 300.12 °C; however, all derivatives of the starch nanoparticle have a decrease in the maximum weight loss temperature and a concomitant significantly higher residual mass after heating to 600 °C. This may be explained by the fact that the starch surface-modifying agents have a lower decomposition temperature, that the layer of this material is on the surface of the starch nanoparticles, and that the materials derived from the esterification have a lower temperature of degradation as previously shown for starch citrate and xylan citrate.¹⁶⁻¹⁷ From this past work, it was shown that citric acid can be bonded to xylan (another polysaccharide), a compound containing multiple carboxylic acid groups, in a similar respect to DTPA. In addition, agents such as citric acid or DTPA both possess maximum degradation temperatures that are lower than that of the substrate (SN, chitosan).¹⁶

Table 5.1.1. Thermal analysis of starch nanoparticles and derivatives.

Sample	TGA maximum (DTG) degradation temp., (°C)	Residual char at 600°C, (%)	DSC melting point, (°C)
DTPA	280.26	25.10	199.2
SN	300.12	10.4	117.0
SNX	283.26	27.9	170.5
SNX/C	285.85	30.5	175.3
Chitosan	290.0	26.0	269.0

The thermal behavior obtained from a differential scanning calorimetric analysis of the starch nanoparticle derivatives was evaluated with a 2 °C/min heating ramp up to 200 °C under nitrogen as shown in Table 5.1.1. DTPA displays a very sharp melting point at 199.2°C, whereas for the starch nanoparticles an endothermic peak was observed at 117.0 °C. The melting points all increased for the reaction products as illustrated in Table 5.1.1. The increase in the melting points may be from changes in chemical composition due to increased hydrogen bonding and plasticization as well as the more robust molecular organization obtained from the esterification reaction.¹⁶

ATR Analysis

The ATR spectra of the starch nanoparticles (A) and starch nanoparticle–DTPA/chitosan are shown in Figure 5.1.4. The spectrum of the starch nanoparticle shows a prominent peak at 3306.43 cm⁻¹ which arises from the hydroxyl groups, whereas there is no peak over the region of 1700–1800 cm⁻¹, reflecting that there are no carbonyl groups on the starch nanoparticles. However, when the starch nanoparticles reacted with the DTPA and further complexed with

chitosan, peaks appeared at approximately 1732.39 cm^{-1} that were attributable to the carbonyl group of the ester functionality and at 1638.38 cm^{-1} when chitosan was reacted with the starch nanoparticle–DTPA derivatives that were attributable to the carbonyl groups in the amide bond of starch nanoparticle–DTPA derivatives. Thus, the appearance of amide bands increased after the starch nanoparticle–DTPA derivatives were reacted with chitosan first by a complexation reaction that was then followed by an amide reaction (arising from the pressure/heat of the sheet formation), strongly pointing to the conclusion that starch nanoparticle–DTPA was linked to chitosan via a coupling reaction between the amino groups of chitosan and the carboxylic groups of starch nanoparticle–DTPA derivatives.¹⁴

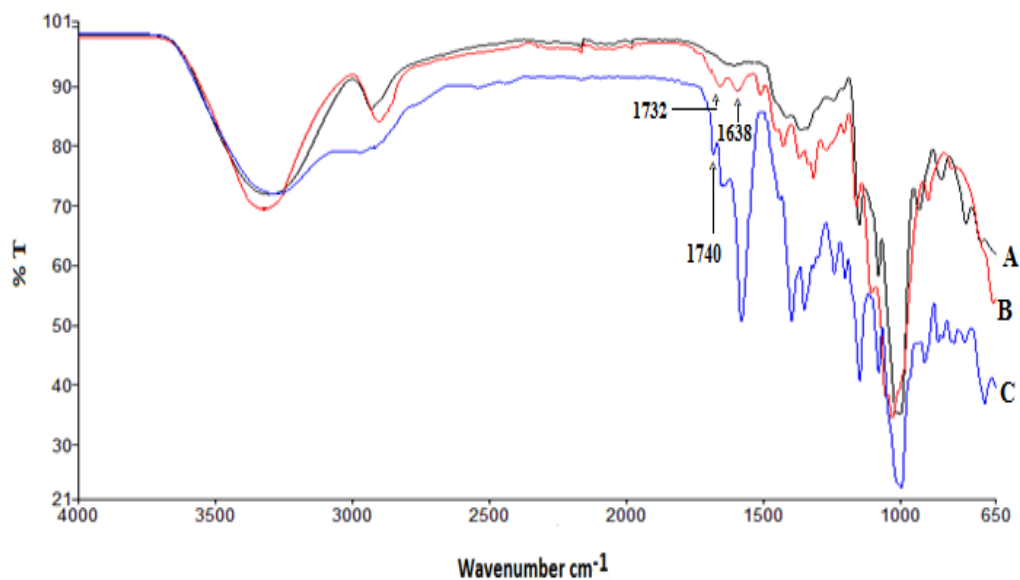


Figure 5.1.4. ATR spectra of starch nanoparticle (A), starch nanoparticle-DTPA-chitosan (B) and starch nanoparticle-DTPA(C). As shown in the spectrum, the 1732 cm^{-1} band can be attributed to the ester carbonyl stretch (from the DTPA attachment), whereas the 1638 cm^{-1} band can be attributed to the carbonyl stretch in the amide bond of starch nanoparticle-DTPA derivatives.

5.1.3.2. Starch Nanoparticle Derivatives Applications

5.1.3.2.1. Effect of Starch Nanoparticle Derivatives on OCC Pulp Paper Strength Properties

Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need to have sufficient resistance in applications that require packaging, wrapping, or sealing. In general, such gross resistance can be attributed at the molecular level to the adequate development of hydrogen bonds. Also, it depends on the quantity and area of bonding sites. In recycling, fibers irreversibly damage, and this damage can affect final paper resistance properties. Figure 5.1.5 shows the tensile strength of OCC recycled pulp hand sheet that results after the addition of either virgin (nonrecycled) pulp or starch nanoparticle derivatives.

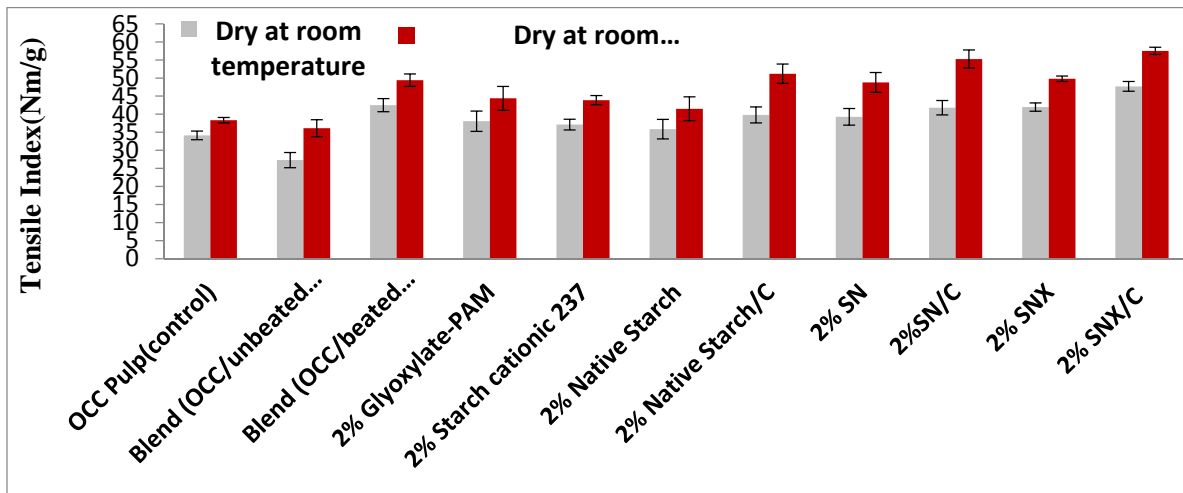


Figure 5.1.5. Effect of starch nanoparticle derivatives on the tensile strength of OCC recycle pulp samples.

Virgin pulp in theory has a much higher mechanical resistance because the fibers have not been damaged from previous use. The control for these studies was the base OCC recycled pulp which is a collection of fibers and broken fibers or fines (CSF = 400). Defibrillated or nondefibrillated virgin soft wood kraft pulp (revolutions = 5000, CSF = 530) was blended with OCC recycle pulp (50:50) to increase the ultimate strength properties. In tandem, 2% starch nanoparticle derivatives (based on the mass of dried pulp) were also mixed with the OCC pulp slurry separately. As a result, the nondefibrillated virgin pulp sample had a decreased tensile index, but the defibrillated virgin pulp blend sample had a significantly increased tensile index compared to the control sample (Figure 5.1.5). This may happen due to a significant decrease in the fiber size and an increase in the bonded area at the high revolutions (for defibrillation of fibers) introduced to the virgin pulp. The tensile index of the starch nanoparticle (SN) and its derivative-treated OCC pulp samples such as SNX, SN/C, and SNX/C were found to be 27, 30, 44, and 50% higher than the control sample. However, the inter-fiber bonding strength and STFI index were tested only for SNX/C-treated pulp hand sheet. The inter-fiber bonding strength and STFI index were increased 200 and 46.1% respectively compare to control sample. The result was also significantly higher than what has been found for commercial dry strength additives such as glyoxylate polyacrylamide, cationic starch, and native corn starch. This may be because of the very high surface area/volume ratio (very small size) of the starch nanoparticles and the resultant strong bonding that is generated among the OCC pulp fibers through the high quantity of carboxyl and amino groups on the nanoparticles. During the formation of the sheets, i.e., the drying and curing (heating) of hand sheets, the starch nanoparticles and its derivatives can deform into very thin films and distribute within the

fibers/fibrils/fines. Consequently, more hydrogen bonds can be formed among the fibers (including the fines) and starch nanoparticle derivatives via the increased generation of contact areas. Additionally, the starch nanoparticles–DTPA/chitosan polyelectrolyte complex became bonded (amide bond)²³ and had the opportunity to bond more liberally to the fiber hydroxyl groups; the free carboxyl groups of starch nanoparticle–DTPA also contributed to inter-fiber bonding and thus increased the paper strength.²⁴⁻²⁵ However, the density of the starch nanoparticles–DTPA/chitosan-treated sample increased approximately 30% which is also one of the causes for the increases in the strength.²⁶

In contrast, the tensile index of 2% SN/C and SNX/C derivative-treated OCC pulp samples was also more improved than defibrillated virgin pulp blends (Figure 5.1.5). Similarly, a burst index of SN, SNX, SN/C, and SNX/C treated samples increased 22, 24, 37, and 49%, respectively, compared to the control sample, and all the test cases provided better results compared to the commercial dry strength additive (Figure 5.1.6). It is also observed from Figure 5.1.7 that the tear index of SN, SNX, SN/C, and SNX/C treated OCC pulp samples was less than the control sample but slightly higher than the commercial glyoxylate polyacrylamide-treated sample.

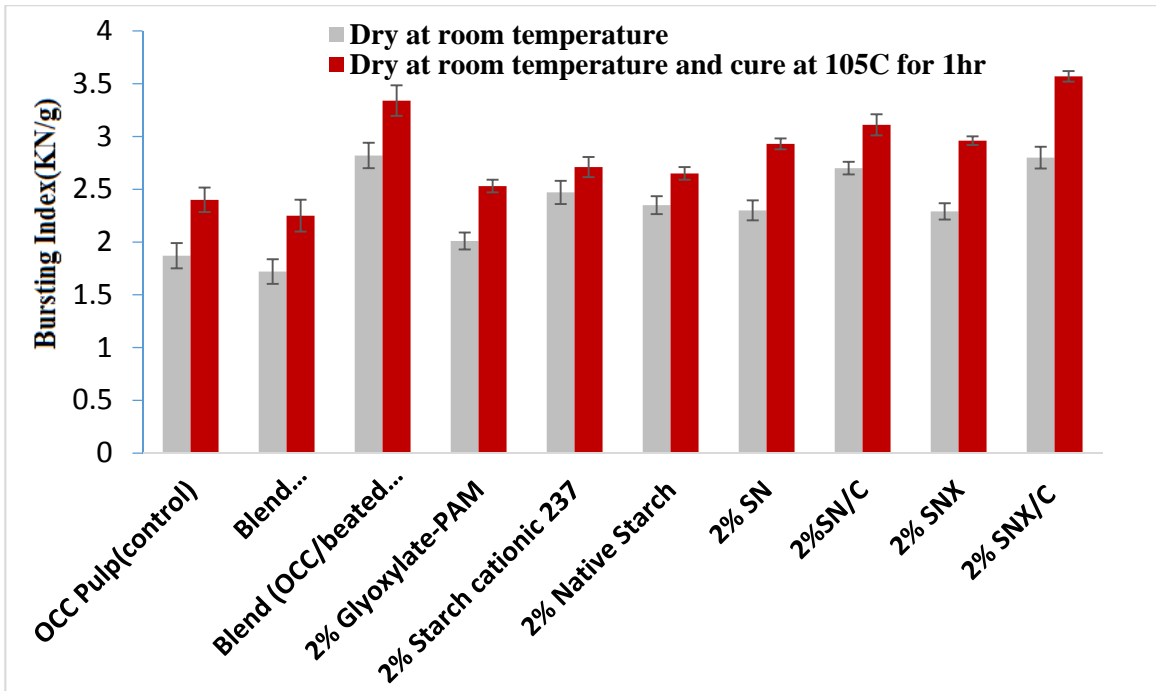


Figure 5.1.6. Effect of starch nanoparticle derivatives on the burst strength of OCC recycle pulp samples.

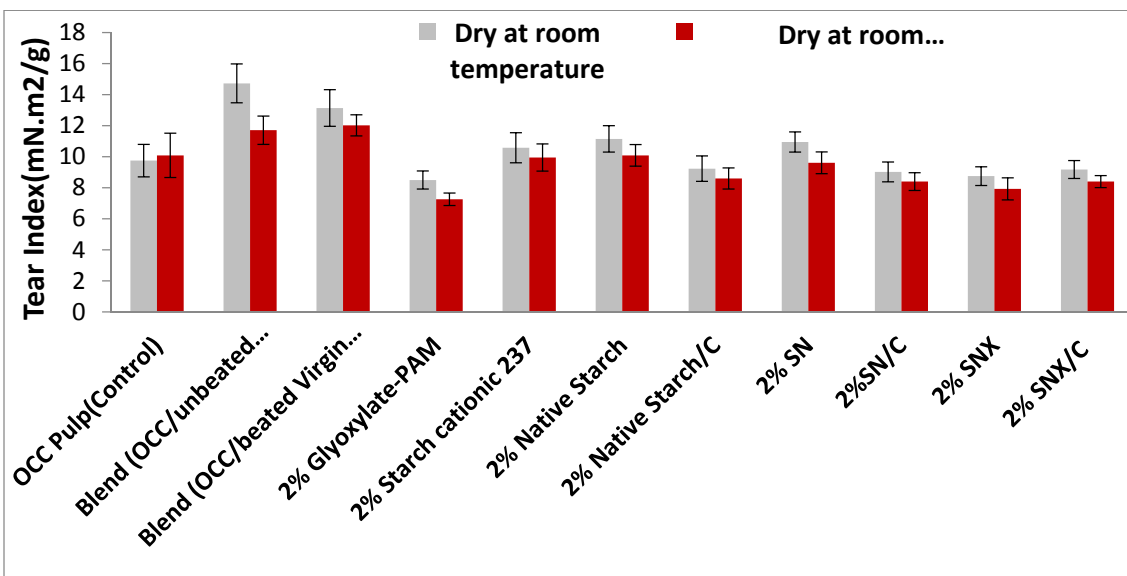


Figure 5.1.7. Effect of starch nanoparticle derivatives on the tear strength of OCC recycle pulp samples.

5.1.3.3. Bond Formation with OCC Recycle Pulp

The basic groups ($-NH_2$) on every ring in starch nanoparticle–DTPA–chitosan derivatives develop positive charges when they are in a sufficiently acidic medium and may thus form ionic or covalent bonds with the negatively charged cellulose in paper fibers during the paper making process.²⁷ In addition, the DTPA in starch nanoparticle–DTPA–chitosan derivatives contains a number of free carboxyl groups which can also engage in ionic bonds with the fiber surface of pulp and also increase the relative bonded area between fibers. The combined interactive effects attributable to the carboxyl and amine groups for increasing bonding between fibers during sheet formation also contributed to an increase in tensile strength.²⁸

It can also be observed from Figure 5.1.8 that the starch nanoparticle–DTPA–chitosan derivatives-treated pulp sheet has a large band at 3400 cm^{-1} compared to the control pulp sheet. This large band can be attributed to the hydrogen bonding interactions arising among the hydroxyl groups within the chitosan, starch nanoparticles, and DTPA moieties. However, a large new peak observed at 1632 cm^{-1} is present from the polyelectrolyte complex of starch nanoparticle–DTPA–chitosan derivatives that is attributed to an amide linkage when the pulp sheet was dried at high temperature.²³ In addition, a high residual char (4.5%) value was observed in the starch nanoparticle–DTPA–chitosan-treated pulp sheet compared to the control pulp sheet (1.7%) after heating at $600\text{ }^\circ\text{C}$ (Figure 5.1.9) which is due to starch nanoparticle–DTPA–chitosan crosslinking to the pulp fiber.

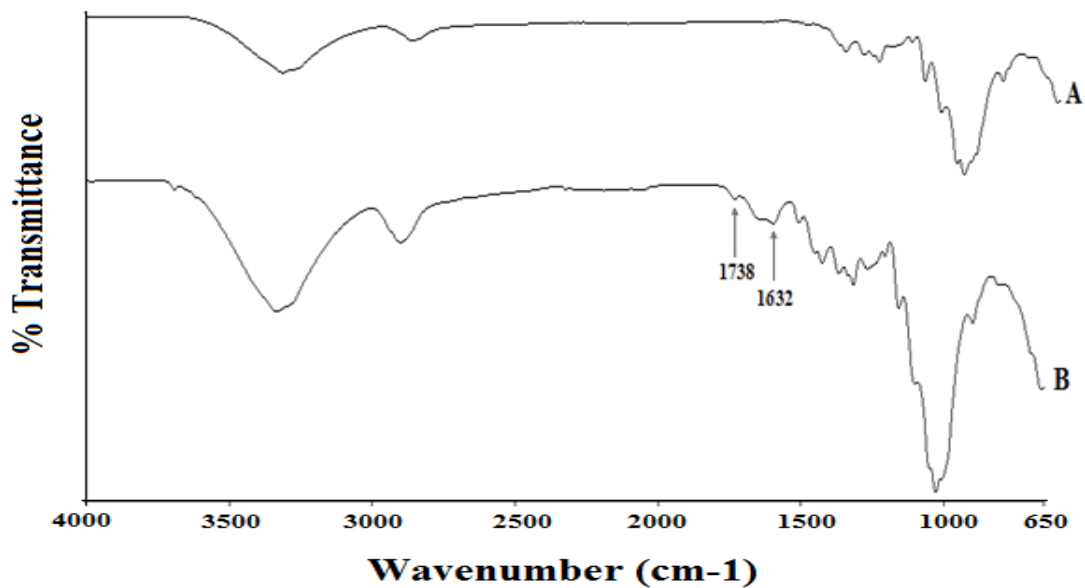


Figure 5.1.8. ATR spectra of control pulp sheet (A) and starch nanoparticle-DTPA-chitosan-pulp sheet (B).

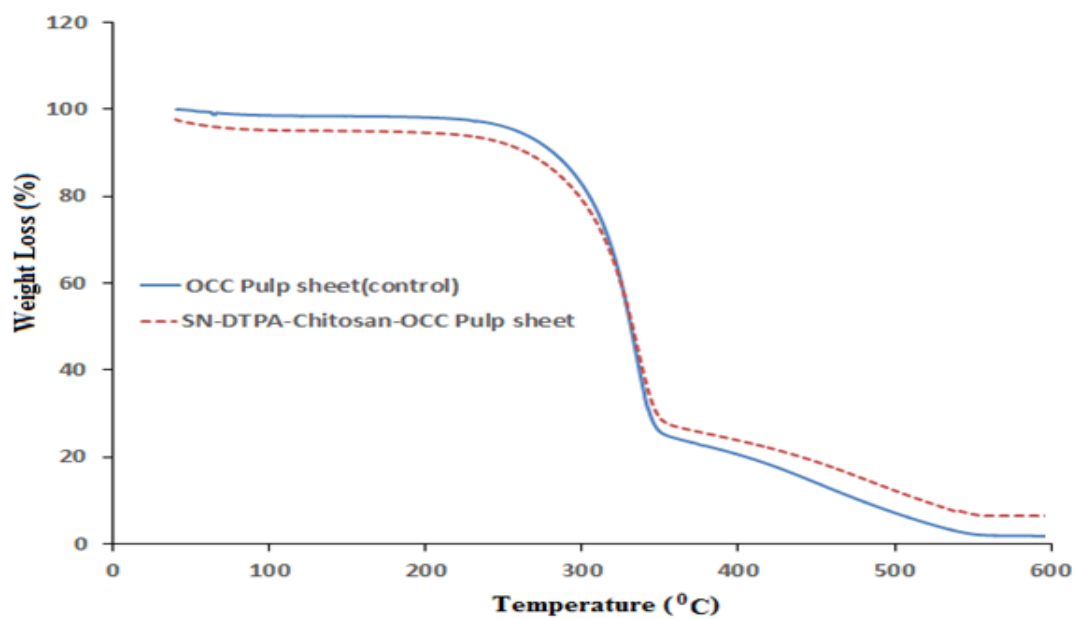


Figure 5.1.9. Thermo-gravimetric analysis of OCC pulp sheet (—) and starch particle-DTPA-chitosan treated OCC pulp sheet (---).

Scanning electron microscopy images of OCC recycle pulp samples and SNX/C derivatives-treated OCC recycle pulp samples are shown in Figure 5.1.10. The OCC pulp sample control shows a continuous smooth pore structure with plate-like solid pore walls, but the SNX/C derivative-treated OCC pulp sample SEM images reveal a rougher surface with the appearance of smaller irregular fragments on the fiber's surface. It may be that these are aggregations of starch nanoparticles and associated fines/fibrils that increase the bonded area among the OCC pulp fibers to make more compact fiber assemblies.

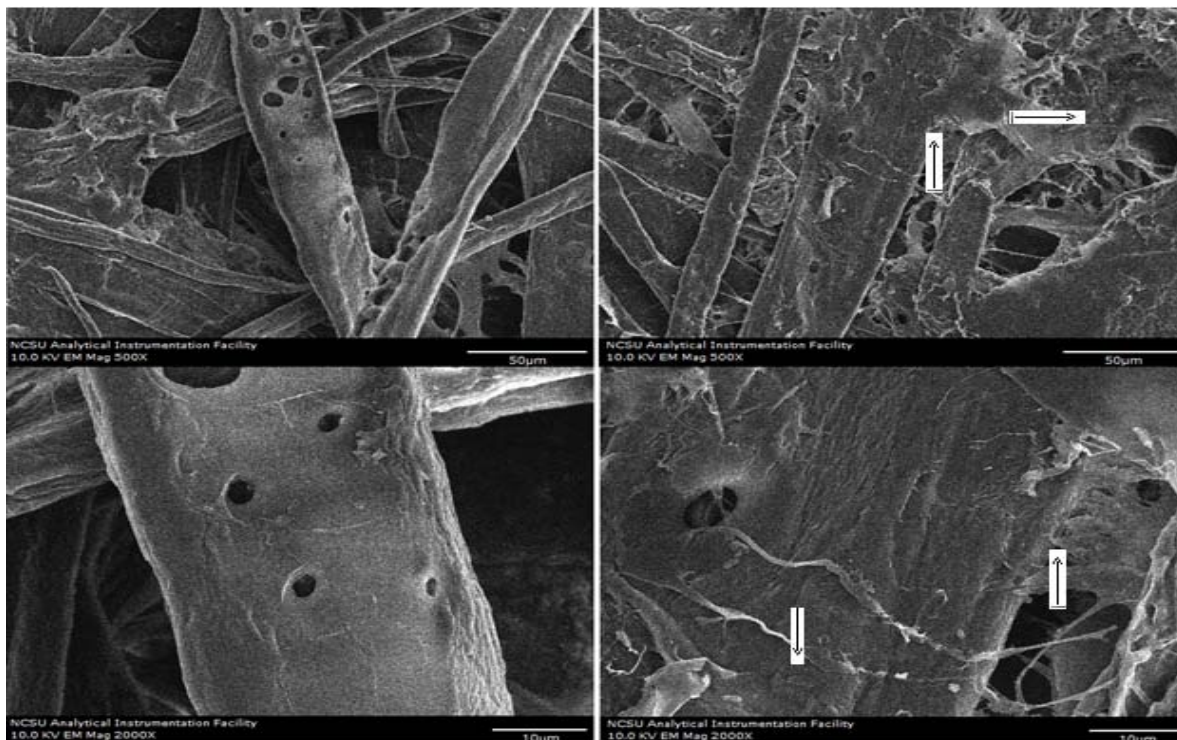


Figure 5.1.10. SEM photomicrograph of OCC recycle pulp sample (left) and 2% SNX/C derivative-treated OCC pulp samples (right). Top and bottom images have length scales of 50 and 10 microns, respectively. The arrows on the right images point to the smaller fiber fragments and fibrils that partially account for the enhanced mechanical properties.

5.1.3.4. Effect of Starch Nanoparticle Derivatives Coating on OCC Pulp Hand Sheet

A summary of the tensile and other properties of 1% starch nanoparticle derivatives-coated OCC pulp samples is shown in Table 5.1.2. The OCC pulp hand sheet was immersed into 1% of SN, SN/C, and SNX/C derivative solution separately and then passed through a laboratory sizing press machine. The hand sheets were then dried at room temperature and cured at 105 °C for 1 h. The tensile and burst index of SN-, SN/C-, and SNX/C-treated samples increased 19.4, 62.5, and 120% and 17.2, 61, and 70.1%, respectively, compared to the control sample. This may happen due to (1) bond formation between the hydroxyl group of the pulp fibers and the -COOH, -NH₂, and -OH groups of the SNX/C additive and (2) increased density of the SNX/C-treated pulp sheet compared to the control sample.²⁶ It is also observed from Table 2 that the SNX/C coating-treated sample gloss increased about four times, and tear strength and roughness significantly decreased. The contact angle of starch nanoparticle derivatives, e.g., SN/C- and SNX/C-treated samples, increased significantly, but the starch nanoparticle (SN)-treated sample decreased compared to the control. This may be explained by the fact that the starch nanoparticle is extremely hydrophilic thus showing not surprisingly a very low surface contact angle measurement in the typical contact angle time frame. However, SN/C and SNX/C additives contain chitosan, which is strongly hydrophobic and also produces a sticky gel under acidic pH (wet) that adopts a plastic-like character under dry conditions. Thus, when a pulp sheet is generated with the additive, under the pressing time, it spreads very evenly over the rough surface, covering it very uniformly to produce a paper surface that is very smooth and also possesses increased gloss (Table 5.1.2). Thus, because the additive-treated sheet surface was hydrophobic due to the plastic-like chitosan under the dry

conditions, the contact angle increased somewhat. In this study, we did not attempt to provide a systematic analysis of the gelation phenomenon because the study focused on the industrially relevant conditions without their optimization. It is possible that the coverage based on the chitosan gelation could influence its spreading and final paper properties.

Table 5.1.2. Results of starch nanoparticle derivative-based coating on OCC pulp samples

OCC starch nanoparticle derivatives	Tensile			Brightness Index	Gloss	Roughness	Contact Angle (20 sec)
	Tensile Index (Nm/g)	Burst Index (KN/g)	Tear Index (mN.m ² /g)				
-	38.35	2.44	9.28	20.91	10.43	11.14	80
SN	45.80	2.86	7.30	20.56	11.50	10.27	50
SN/C	62.30	3.92	5.93	18.50	36.20	9.40	95
SNX/C	84.38	4.15	4.81	18.20	53.10	9.0	100

(Conditions: 1% starch nanoparticle derivative solution, coated with laboratory paper machine, and cured at 105°C for 1hr).

It is important to note, additionally, that the starch nanoparticle–DTPA–chitosan may possess strong antimicrobial activity based on preliminary work in this lab (unpublished results) that may protect the OCC pulp sheet from fouling and thus avoid the use of any biocide.

5.1.4. Conclusions

Starch nanoparticles (SNs) were modified with diethylenetriamine pentaacetic acid (X) in the presence of sodium hypophosphite (SHP) to increase their ability to better bond recycled fibers during paper formation. It was found that the carboxyl group content, degree of esterification,

and degree of substitution of diethylenetriamine pentaacetic acid with starch nanoparticles significantly increased relative to the unmodified starch nanoparticle. The modified starch nanoparticle (SNX) was later coupled with chitosan (C). Approximately 2% of starch nanoparticles (SNs) and their derivatives such as SNX, SN/C, and SNX/C were blended with OCC recycle pulp separately prior to making a sample. The tensile and burst index increased 27, 30, 44, and 50% and 22, 24, 37, and 49%, respectively, compared to the control samples. It was also significantly higher than what is typically found for commercial dry strength agents and blended OCC pulp. In addition, when the OCC pulp hand sheet was coated with a 1% starch nanoparticle derivative (SNX/C) solution, the tensile and burst index increased 120 and 70%, respectively, while there was also a significant increase in gloss and decrease in roughness and tear index compared to the control sample. The increased strength is an agreement with increased bonding between the starch nanoparticle derivative and pulp fibers.

The authors declare no competing financial interest.

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A Novel Cellulose Nanocrystals-Based Approach to Improve the Mechanical Properties of Recycled Paper

Abdus Salam, Lucian A Lucia, Hasan Jameel

ABSTRACT

The ability to introduce cellulose nanocrystals (CNs) into any of a number of single-component or composite applications is currently limited because they are difficult to efficiently isolate and in certain cases difficult to maintain homogeneously disperse. The current research introduces a novel purification technique and composite application for modified cellulose nanocrystals derivatives by using them as an additive for dry strength in recycled paper OCC (Old Corrugated Containerboard). More specifically, the present work illustrates a way to easily isolate CNs by extracting them through a traditional mineral acid hydrolysis followed up by washing them several times with ethanol. The extracted cellulose nanocrystals did not flocculate and were completely homogeneously dispersed in water. Additionally, it was found that the incorporation of carboxylic acid functionalities onto the CNs by reaction with diethylenetriamine pentaacetic acid (DTPA) followed by crosslinking with chitosan and introduction into the OCC greatly improved its tensile and other mechanical properties. The tensile and burst strength of the modified OCC pulp sheet increased 40.3 and 46%, respectively, with significantly increased gloss, decreased roughness, and tear strength as compared to the control sample. Spectral characterization of the CNs and their derivatives was accomplished using TGA, DSC, FT-IR, and SEM.

Keywords: Cellulose nanocrystals (CNs), chitosan, crosslinking, OCC pulp, mechanical

properties.

5.2.1. INTRODUCTION

Cellulose is arguably the most important biopolymer on the planet because not only is it the most abundant biomaterial available (as produced by all plants and many microorganisms including algae, plankton, and bacteria), it is renewable, biodegradable, biocompatible, non-hypoallergenic, readily derivatived, extremely strong, and eco-friendly. No other natural or synthetic polymer comes close to matching its highly functional mechanical and chemical properties. It is a carbohydrate polymer made up of repeating β -D-glucopyranose units that is characterized by three hydroxyl groups per anhydroglucose unit that is able to impart a high degree of functionality to the biomacromolecule.¹

The materials based on cellulose and its derivatives have been used for more than 150 years in a wide variety of applications, such as food, paper, biomaterials, and pharmaceuticals.² Typically, printing and writing grade paper is a prime example; starch is used for its surface fluid resistance characteristics (sizing) with the main goal of improving paper surface resistance and printability.³ In recycled paper applications, the primary concern is addressing low mechanical properties (bonding/ because of the strength losses occurring after one or more uses. Research has shown that strength loss is more important in the case of refined pulp for papermaking, compared to the production of dry-lap pulp, which is unrefined.⁴ The utilization rate of waste fiber for recycled containerboard (Old Corrugated Containerboard or OCC) in 1963 was reported to be 21.1% in the US, whereas in 2001 it was 67% with a concomitant recovery rate of approximately 70%.⁴ In 2011, the American Forest & Paper Association

(AF&PA) released a recovery rate for OCC which reached a high of 91.2 percent. Therefore, any further research in this area must focus on improvements in the strength of OCC to validate current and future recovery rates. Early research identified several types of chemical treatments that yielded measurable improvements in the bonding strength of recycled paper.⁵⁻
⁶ A few innovative studies have shown that chemical derivatization or the appropriate chemical treatment of fiber surfaces may prevent strength losses from occurring.⁷⁻⁸ The papermaking industry is currently using commercial dry strength agents such as cationic starch, polyacrylamide, and glyoxylate polyacrylamide as the primary agents to improve the mechanical properties of recycled OCC, but strength improvements are still low relative to that of virgin pulp (original, non-recycled paper).⁹⁻¹⁰

Meanwhile, numerous advancements in materials science and engineering research have targeted the use of nanomaterials to offer heretofore unattainable benefits. Nanomaterials offer a promising alternative to tackling the issue of low OCC strength because of a concept known as the nanometric size effect as it relates to conventional bulk fillers even at low filler content. Nanometric materials have quite high reinforcing effects and studies have also shown their positive impact in barrier packaging. However, for decades, studies have been conducted with nonrenewable inorganic fillers and a petroleum-based matrix for a number of applications including packaging, a high value sector of the pulp market. Increasing environmental concerns have lead to, for example, developing new flexible barrier bio-based packaging materials and investigating the potential uses of renewable resources for such applications.¹⁰ Recently, nanoparticles made of cellulose (cellulose nanocrystals, or CNs) have become an extremely important class of nanomaterials because of their strength-reinforcing effects.

Acid hydrolysis of cellulose is an effective method to remove the amorphous regions of cellulose fibers and obtain CNs. Sulfuric acid and mineral (hydrochloric) acid have been the chief methods used to produce cellulose nanocrystals from cellulosic biopolymers.¹²

The present study focuses on the characterization and application of a novel cellulose-based nanomaterial for improving the mechanical properties of OCC; more specifically, cellulose nanocrystals have been modified with diethylenetriamine pentaacetic acid (DTPA) in the presence of sodium hypophosphate (SHP) and later crosslinked with chitosan and applied to an OCC recycled paper stock for the express purpose of improving its mechanical properties by taking advantage of both chemical crosslinking and hydrogen bonding to the OCC fiber surface. The present research will focus on the CNs characterization and provide a review of their application in OCC strength improvement.

5.2.2. EXPERIMENTAL SECTION

5.2.2.1. Materials

The OCC pulp was furnished by AzkoNobel Pulp and Performance Chemicals, Marietta, GA. Whatman filter paper from Whatman International Ltd, Maidstone, England. Chitosan (Ch) CAS no. 9012-76-4 was purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphate (SHP), CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2 and diethylenetriamine pentaacetic acid (DTPA), CAS no. 67-43-6. Ethyl alcohol (denatured) and acetic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water as the medium.

5.2.2.2. Preparation of Cellulose Nanocrystals (CNs)

The cellulose nanocrystals (CNs) was prepared from pure cellulose (Whatman paper #4) by acid hydrolysis using HCl (3 N) at 90°C for 2 h under continuous agitation to obtain cellulosic nanocrystals. The suspension was centrifuged at 5300 rpm for 15 min. to concentrate the CNs and remove the excess aqueous acid. The resultant precipitate was rinsed and re-centrifuged until a constant neutral pH was achieved. After a neutral pH was achieved, the solid aggregate was washed with ethanol two times and re-centrifuged. The CN suspension was dried in air under a hood and then stored under a vacuum desiccator until required for further application.¹³ In addition, it was found that water-washed and subsequently dried CNs readily flocculated into aggregates, but upon using an alcohol wash with subsequent drying, they did not aggregate and were easily dispersible in water (Fig.5.2.1).



Figure 5.2.1. Photographic images of water-washed cellulose nanocrystals (left image), alcohol-washed cellulose nanocrystals (center image), and alcohol-washed cellulose nanocrystals dispersed in water (right image).

5.2.2.3. Chemical Modifications of CNs

Approximately five (5.0) g of diethylenetriamine pentaacetic acid (DTPA) and one (1.0) g of

SHP were dissolved in 20 ml alkali solution (pH 12) in a fifty (50) ml Petri dish. Five (5) g of CNs were combined in a DTPA solution and manually mixed vigorously with a glass rod. The mixture was placed in an air oven at 130°C for 4 hours. Reaction products were washed with distilled water and filtered several times to remove unreacted materials. The product referred to as CNs-DTPA was air dried at 50°C in an air oven overnight.¹⁴ The proposed reaction scheme is shown in Figure 5.2.2.

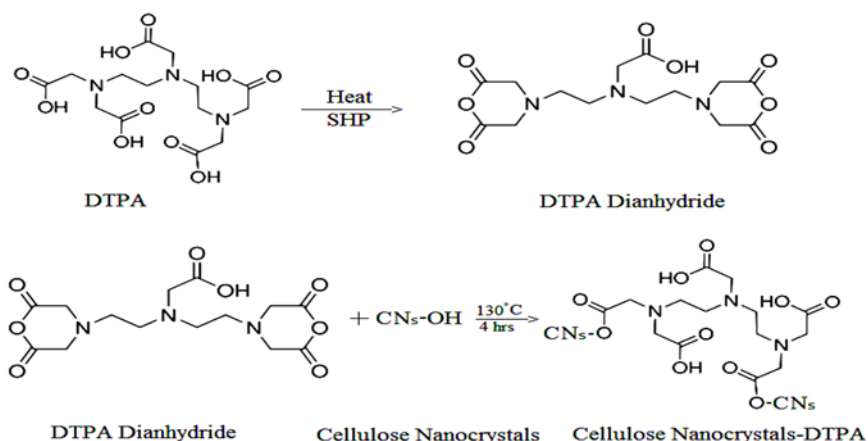


Figure 5.2.2. Esterification reaction of CNs with DTPA.

Polyelectrolyte Complexation Reaction

Chitosan (Ch, 1g) was dissolved into 50 ml of 1.5 % acetic acid solution. DTPA-modified cellulose nanocrystals (CNs-DTPA, 1g) were also dispersed with 50 ml of water and then added to a 50 ml chitosan solution in a 250 ml round bottom flask. The reaction mixture was stirred using a magnetic stirrer at 80°C for 90 minutes.¹³ The proposed reaction scheme based

on literature precedent is shown in Figure 5.2.3.

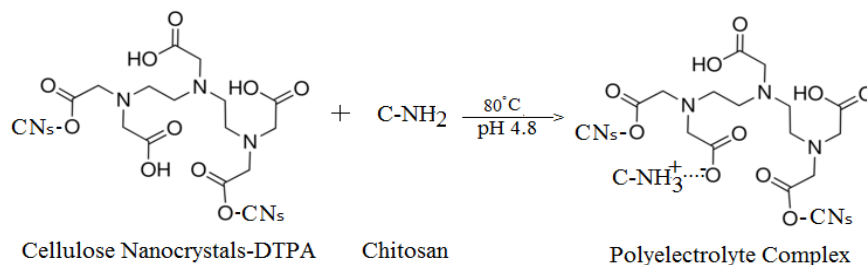


Figure 5.2.3. Polyelectrolyte complexation of cellulose nanocrystals-DTPA with chitosan.

5.2.2.4. Preparation of OCC Paper Stock

The stock was prepared using a 600 ml pulp slurry (1.8 g OCC having a freeness of 400 CSF) in a sheet molder machine. The pulp slurry was also diluted with 10 L of white water into the sheet molder to produce a uniform sheet. The sheet was dried in a conditioning room and thereafter cured at 105°C for 1.0 hour.

5.2.2.5. Testing Methods

Determination of Carboxyl Content

A known amount of the CNs derivative was dispersed in 0.1 N NaOH and neutralized for one hour. The remaining excess amount of NaOH was determined by titration with 0.1 N HCl using phenolphthalein as an indicator¹⁵ and the carboxyl content in milliequivalents of acidity per 100 grams was calculated as follows:

$$\text{Carboxyl Content (meq)} = \frac{(V_2 - V_1) \times N \times 100}{W}$$

Where,

N = Normality of HCl

V_2 = Volume of HCl without sample

V_1 = Volume of HCl with sample

W = Weight of Sample

Determination of Degree of Esterification and Degree of Substitution

The CNs derivative was dispersed in DMSO in a conical flask for 10 hr., and then excess 0.1N NaOH was added to the solution to saponify the ester over two hours. The excess NaOH was determined by titration with 0.1N HCl¹⁶⁻¹⁷ to determine the percent esterification and the degree of substitution:

$$\text{Degree of Esterification (\%)} = \frac{6.005(V_2 - V_1) \times N}{W}$$

Where,

N = Normality of HCl

V_2 = Volume of HCl without sample

V_1 = Volume of HCl with sample

$$\text{Degree of Substitution} = \frac{162 \times A\%}{100M - (m - 1)A\%}$$

Where,

$A \%$ = Degree of Esterification

W = Weight of sample

M = Molecular weight of crosslinking agent

Gloss Testing

The gloss of OCC pulp hand sheet was tested with a GLOSSMETER tester according to TAPPI T 480 method.

Roughness Testing

The roughness of OCC pulp hand sheet was tested with an L & W roughness tester according to TAPPI T 538 method.

Tensile Index

The tensile Index of OCC pulp hand sheet strength was tested with an ALWETRON TH1 tester according to TAPPI T 220 method. Tensile index is defined as the tensile strength (N/m) and the basic weight (g/m^2) of the paper. For example, the tensile index of paper is determined in units of $(\text{N/m})/(\text{g/m}^2) = \text{Nm/g}$. Where tensile strength is defined as the breaking force (load) per standard width of the paper.

Burst Strength

The burst strength of OCC pulp hand sheet was tested with a MULLEN tester according to TAPPI T 810 method.

Tear Strength

The tear strength of OCC pulp hand sheet was tested with an L & W tester according to ASTM D 689 method.

5.2.2.6. Characterization

FTIR Analysis

The FTIR spectra were recorded on a NEXUS 670 FTIR spectrophotometer using a KBr disc containing 2% finely ground samples. All the spectra were obtained by accumulation of 64 scans at a resolution of 4 cm^{-1} over a range of 400–4000 cm^{-1} .¹⁸

Thermal Gravimetric Analysis (TGA)

The thermogravimetric analyzer used in this study was a TGA Q500. A nitrogen atmosphere was used. The temperature range and heating rate were 30–600°C and 5°C/min, followed by isothermal heating at 600°C.¹⁹

Differential Scanning Calorimeter (DSC)

A differential scanning calorimeter DSC Q100 was used with a Hermetic pan (T 090127). Samples were subjected to a 2°C/min temperature ramp from 30–200°C followed by isothermal heating at 200°C for 15 min. An empty pan was used as the reference.²⁰

Scanning Electron Microscope (SEM)

Morphological characterization of modified CNs-DTPA-chitosan derivative-treated OCC

pulp hand sheets was obtained using a scanning electron microscope (SEM), Hitachi S-3200N.¹⁴

Contact Angle

Dynamic contact angle measurements were performed with a Phoenix 300 Contact Angle Analyzer (Seo Co., Ltd., Korea) on CNs-DTPA-chitosan-treated OCC pulp hand sheets. Deionized water was used as the probe fluid.¹⁵

5.2.3. RESULTS AND DISCUSSION

5.2.3.1 Characterization of Cellulose Nanocrystals (CNs)

Morphology and Surface Chemical Changes:

The SEM image of water-washed extracted CNs displayed a coagulated-like distribution with nanoparticles having a length and width of 256.5 nm and 242.6 nm, respectively (Fig. 5.2.4). In general, CNs possess a surface covered with reactive hydroxyl groups that allow for facile surface decoration for a specific end via the appropriate chemical reaction strategy. The reaction pathways that were chosen for the particular surface functionalization in this work are shown in Figures 5.2.2 and 5.2.3.

The carboxyl content of the CNs increased from a minimal 62 meq./100 g in the control to over six times (375 meq./100 g) in the test sample. To further clarify the changes that occurred after the surface modification, the DS (degree of substitution) and percent esterification were explicitly investigated and determined by titration. For this study, the monomer formula

weight and number of hydroxyls per starch monomer unit that were used in the calculations were 162 Da and 3, respectively. Thus, the degree of substitution and percent esterification were calculated to be 0.25 and 37.2%. The intrinsic viscosities of 1M CED-dissolved CNs and CNs-DTPA systems were determined at 25°C with an Ubbelohde-type viscometer to determine molecular weight.¹⁵ Depending on the specific viscosity measured, typical molecular weights of CNs and CNs-DTPA were found to be 19,200 Da and 22,800 Da, respectively.

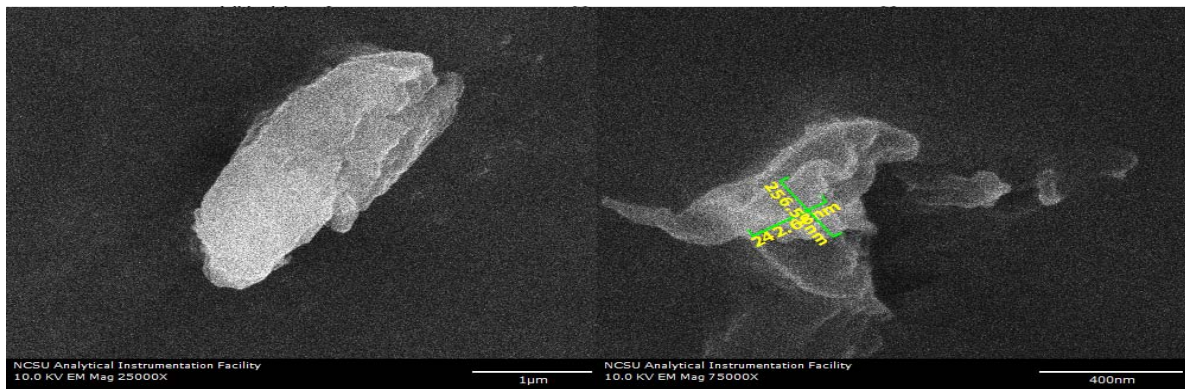


Figure 5.2.4. SEM photomicrographs of flocculated (aggregated) CNs (The images have length scales of 1 microns (left) and 400 nanometer (right), respectively).

Thermal Behavior

The thermogravimetric behavior of the CNs derivatives was evaluated over a 5°C/minute heating ramp under nitrogen and are shown in Table 5.2.1. For several samples, a weight loss below and around 100°C was attributed to water evaporation.²¹ However, the weight loss above 100°C was due to the thermal decomposition of the CNs/derivatives themselves.²⁰

DTPA had a single sharp decomposition peak at 280.26°C, whereas the CNs have a single weight loss peak at 334.56°C; however, all derivatives of CNs have a decrease in maximum weight loss temperature and concomitant significantly higher residual mass after heating to 600°C. This may be explained by the fact that the cellulose nanocrystals surface-modifying agents have a lower decomposition temperature; this layer is on the surface of the CNs, and these materials attached via ester bonds have a lower temperature of degradation.¹⁵

The thermal behavior obtained from a differential scanning calorimetric analysis of the CNs derivatives was evaluated with a 2°C/minute heating ramp up to 200°C under nitrogen as shown in Table 5.2.1. DTPA displays a very sharp melting point at 199.2°C, whereas an endothermic peak was observed at 94.0°C for the CNs. The melting points all increased for the reaction products as illustrated in Table 5.2.1. The increase in the melting points may be owing to the chemical architectural robustness arising from increased hydrogen bonding and plasticization as well as the higher molecular organization obtained from crosslinking.¹⁵

Table 5.2.1. Thermal analyses of CNs and CNs derivatives.

Sample	TGA maximum (DTG) degradation temp. (°C)	Residual char at 600°C, (%)	DSC melting point (°C)
DTPA Salt	280	25.10	199.2
CNs	334	7.0	94.0
CNs-DTPA	320	14.0	98.5
CNs-DTPA/Ch	325	30.0	113.0
Ch	290	26.0	269.0

FT-IR Analysis

The FT-IR spectra of the CNs and CNs-DTPA/chitosan are shown in Figure 5.2.5. The spectrum of CNs shows a prominent peak at 3400 cm^{-1} which arises from the hydroxyl groups, although the carbonyl region does not clearly show a carbonyl stretch, likely due to its low levels (65 meq./100 g) and being swamped out by the remaining stronger signals in the spectrum. However, when the CNs were reacted with DTPA, and were further crosslinked with chitosan, a peak appeared at approximately 1733 cm^{-1} that is attributable to the carbonyl group. In addition, another new peak was observed at 1640 cm^{-1} when chitosan crosslinked with CNs-DTPA derivatives. This peak is attributable to the characteristic stretching band of carbonyl groups in the amide bond of CNs-DTPA derivatives.²³ However, the intensity of this amide band increased after the CNs-DTPA-Ch derivative was dried at 105°C after incorporation into an OCC pulp matrix, strongly pointing to the conclusion that at high temperature the polyelectrolyte complex originating from the interaction between the carboxyl group of CNs-DTPA and amino group of chitosan was converted to amide bond (Fig.5.2.9).²²

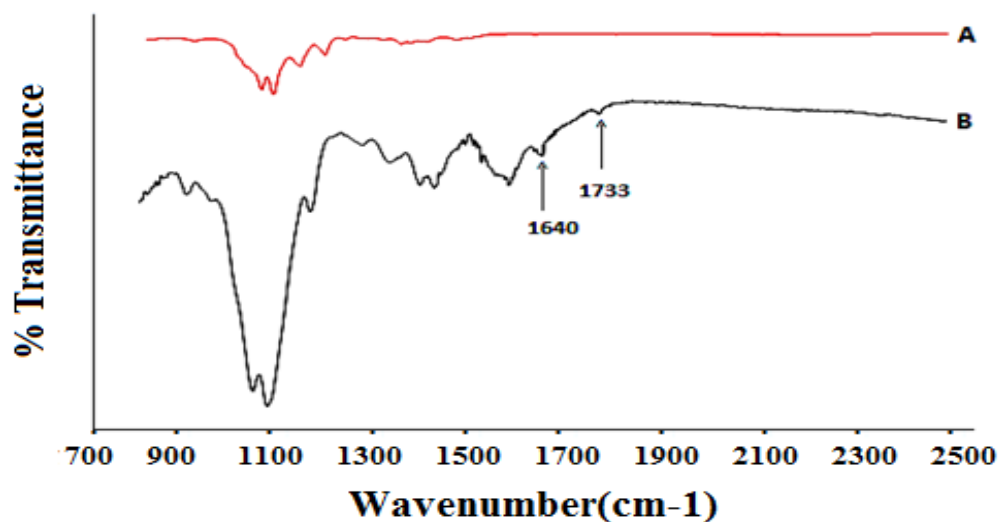


Figure 5.2.5. FT-IR spectra of CNs (A) and CNs-DTPA/chitosan. The 1733 cm^{-1} band can be attributed to the ester carbonyl stretch (from the DTPA attachment), whereas the 1640 cm^{-1} band of carbonyl groups in an amide bond of CNs-DTPA derivatives.

5.2.3.2. Cellulose Nanocrystals Derivatives Application for OCC Strength Improvement

Effect of Cellulose Nanocrystals Derivatives on OCC Pulp Paper Strength Properties

Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need to have sufficient resistance in applications that require packaging, wrapping, or sealing. In general, such gross resistance can be attributed at the molecular level to the adequate development of hydrogen bonds. Also, it depends on the quantity and area of bonding sites. In recycling, fibers irreversibly damage and this damage can affect final paper resistance properties. Figure 5.2.6 shows the tensile index of OCC recycled pulp hand sheet that results after the addition of either virgin (non-recycled) pulp or cellulosic nanoparticle derivatives. Virgin pulp in theory has a much higher mechanical resistance because the fibers have not been damaged from prior use. The control for these studies was the base OCC

recycled pulp (CSF = 400, a measure of the adsorption of water, i.e., higher value, less adsorption). The earlier researcher reported that the range of tensile index (Nm/g) for OCC pulp sheet is 20-35.²⁴ Defibrillated or non-defibrillated virgin softwood kraft pulp (revolutions = 5000, CSF = 530) was blended with OCC recycle pulp (50:50) to increase strength properties. In tandem, 2% CNs derivatives (based on the mass of dried pulp) were also mixed with the OCC pulp slurry separately. As a result, the non-defibrillated virgin pulp sample had a decreased tensile index, but the defibrillated virgin pulp blend sample had a significantly increased tensile index compared to the control sample (Fig. 5.2.6). This may happen due to a significant decrease in the fiber size and an increase in the bonded area at the high revolutions (to defibrillate) introduced to the virgin pulp. The tensile index of 2% CNs and its derivatives-treated OCC pulp samples such as CNs-DTPA, CNs-Ch and CNs-DTPA-Ch were found to be 20.5, 20.3, 37.6, and 40.3% higher than the control sample. However, the inter-fiber bonding strength and STFI index were tested only for CNs-DTPA-Ch-treated pulp hand sheet. The inter-fiber bonding strength and STFI index were increased 38.5 and 152% respectively compare to control sample. The result was also significantly higher than what has been found for commercial dry strength additives such as glyoxylate polyacrylamide, cationic starch, and native cornstarch. This may be because of the very high surface area/volume ratio (very small size) of the CNs and the concomitant stronger bonding that is generated with the OCC pulp fibers through the high quantity of carboxyl and amino groups in the nanoparticles.²⁵⁻²⁶ However, the density of CNs-DTPA-Ch treated sample was increased about 25% which is also one of the causes to increase the strength.²⁷

In contrast, the tensile index of 2% CNs-Ch and CNs-DTPA-Ch derivatives-treated OCC pulp

samples was also better than defibrillated virgin pulp blends (Fig.5.2.6). Similarly, the burst strength of CNs, CNs-DTPA, CNs-Ch and CNs-DTPA-Ch-treated samples increased 11, 10.8, 35, and 46% compared to the control sample and all the cases provided better results compared to the commercial dry strength additive (Fig.5.2.7). It is also observed from Figure 5.2.8 that the tear strength of CNs, CNs-DTPA, CNs-Ch and CNs-DTPA-Ch-treated OCC pulp samples were lower than the control sample, but slightly higher than commercial glyoxylate polyacrylamide-treated sample. However, CNs-DTPA-Ch-treated pulp sheet gloss increased more than two times and the roughness significantly decreased. This may happen due to increased density of CNs-DTPA-Ch-treated pulp sheet compare to control sample.²⁷

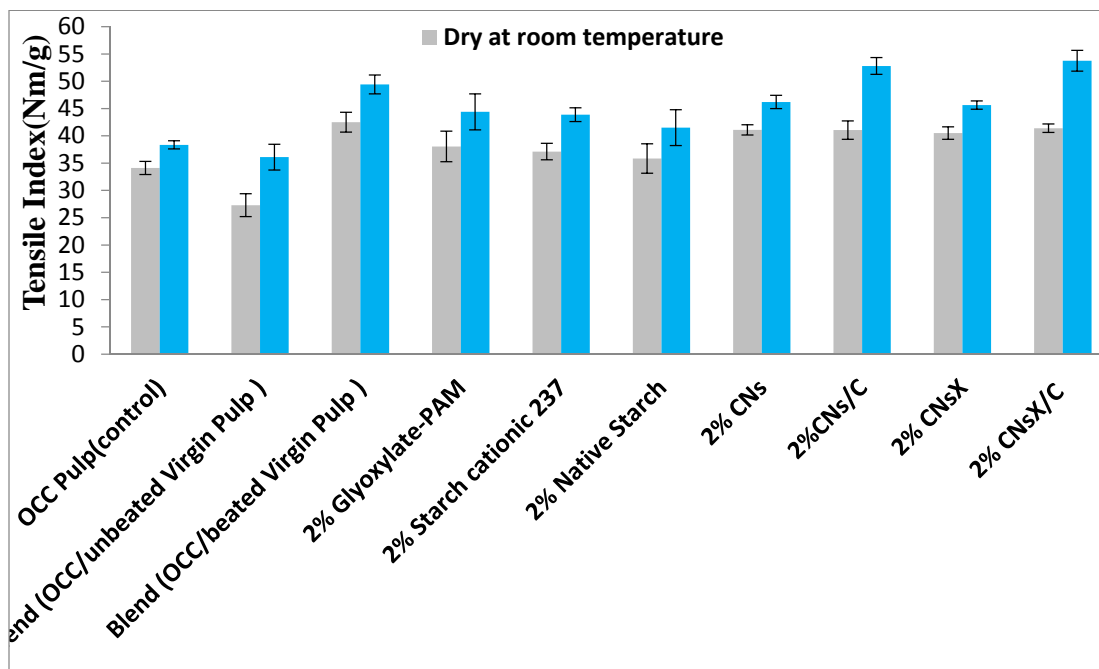


Figure 5.2.6. Tensile strength of CNs derivative-treated OCC recycle pulp hand sheets.

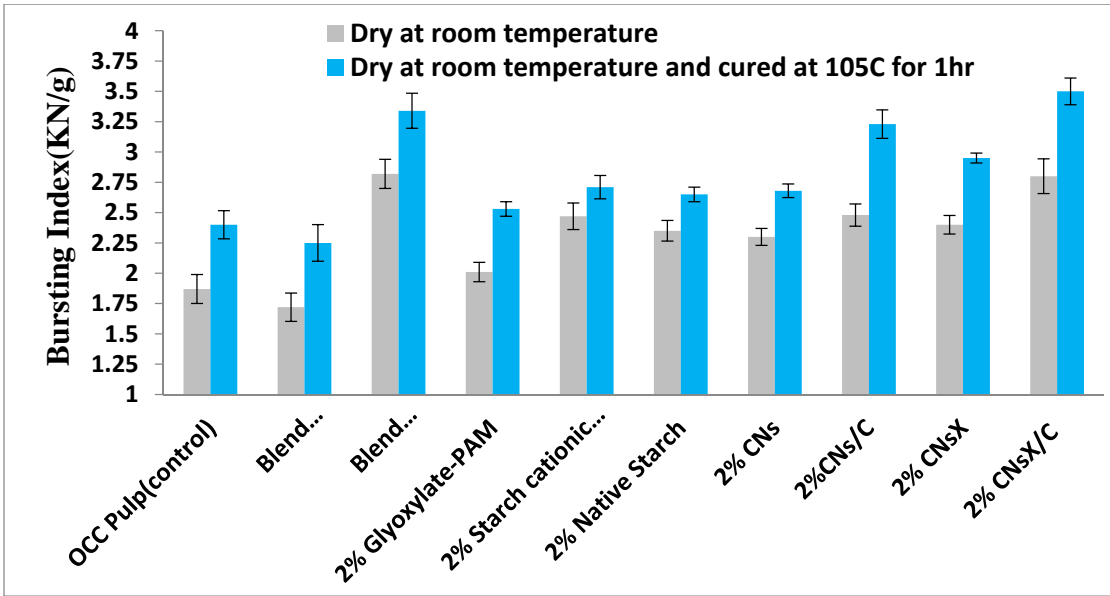


Figure 5.2.7. Bursting strength of CNS derivative-treated OCC recycle pulp hand sheets.

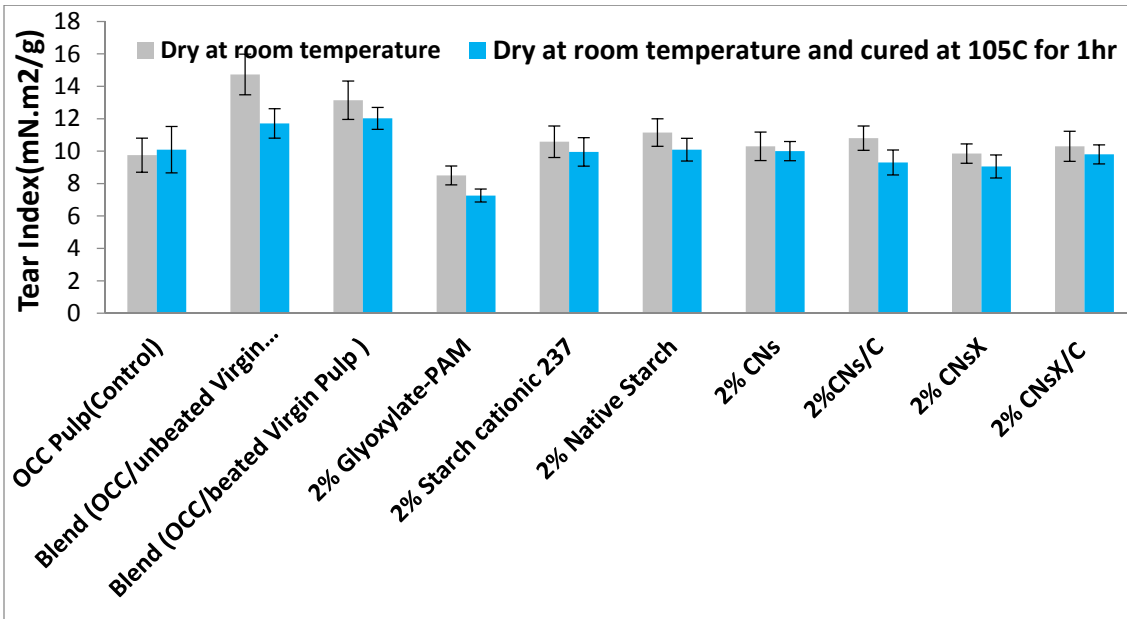


Figure 5.2.8. Tear strength of cellulose nanocrystals derivative-treated OCC recycle pulp hand sheets.

5.2.3.3. Bond Formation with OCC Recycle Pulp

The basic groups (-NH₂) on every ring in chitosan-DTPA-CNs derivatives develop positive charges when they are in a sufficiently acidic medium and may thus form ionic or covalent bonds with the negatively charged cellulose in paper fibers during the paper making process.²⁸ In addition, the DTPA in chitosan-DTPA-CNs derivatives contains a number of free carboxyl groups which can also engage in ionic bonds with the fiber surface of pulp and also increase the relative bonded area between fibers. The combined interactive effects attributable to the carboxyl and amine groups for increasing bonding between fibers during sheet formation also contributed an increase in tensile strength.²⁹

It can also be observed from Figure 5.2.9 that the chitosan-DTPA-CNs derivatives-treated pulp sheet has a large band at 3400 cm⁻¹ compared to control pulp sheet. This large band can be attributed to the hydrogen bonding interactions arising among the hydroxyl groups within the chitosan, CNs,³⁰ and DTPA moieties. However, a large new peak observed at 1640 cm⁻¹ is present from the polyelectrolyte complex of chitosan-DTPA-CNs derivatives that has been converted to an amide linkage when the pulp sheet is dried at high temperature.²² In addition, a high residual char (5.8 %) value was observed in the chitosan-DTPA-CNs-treated pulp sheet compare to the control pulp sheet (1.7%) after heating at 600°C (Fig.5.2.10) which is attributed to chitosan-DTPA-CNs crosslinks to the pulp fiber.

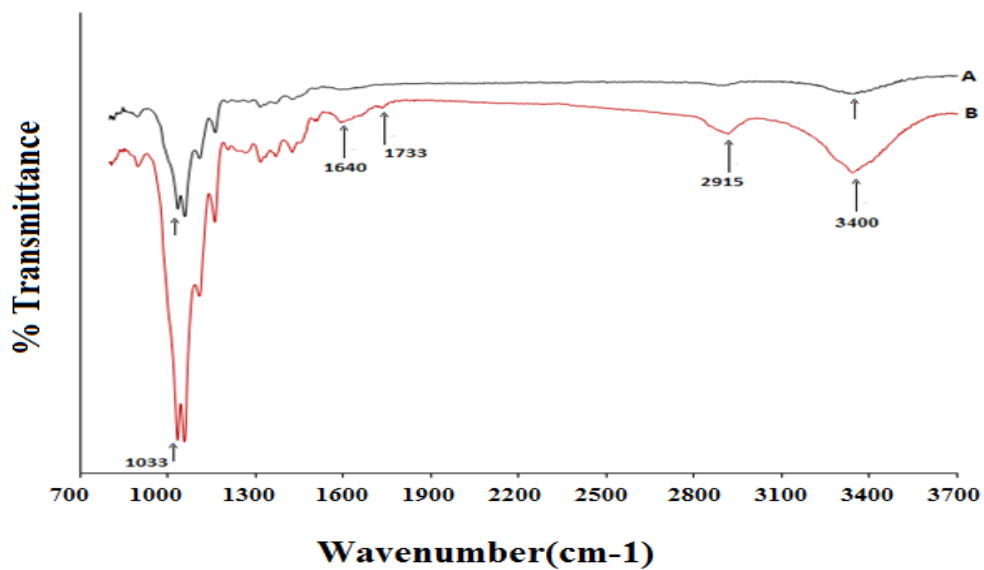


Figure 5.2.9. ATR spectra of pulp sheet (A) and cellulose nanocrystals-DTPA/chitosan-pulp sheet.

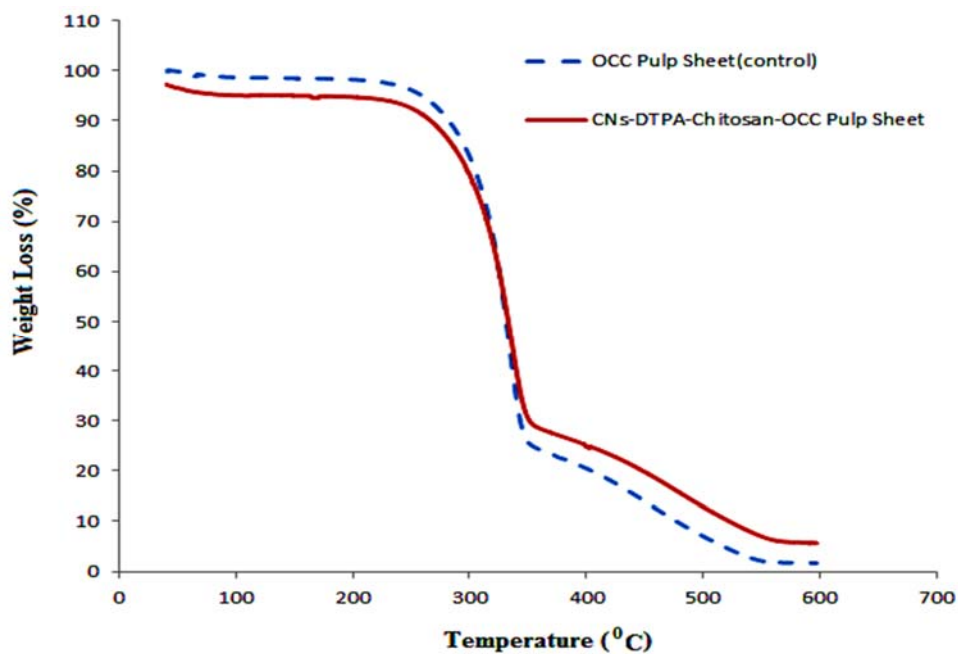


Figure 5.2.10. Thermo-gravimetric analysis of OCC pulp sheet and cellulose nanocrystals-DTPA/chitosan treated OCC pulp sheet.

Scanning electron microscopy of OCC recycle pulp samples and CNsX/C derivatives-treated OCC recycle pulp samples are shown in Figure 5.2.11. The OCC pulp sample control shows a continuous irregular pore structure with plate like solid pore walls, but the CNs-DTPA-Ch-treated OCC pulp sample SEM images reveal a smoother surface with the appearance of depositions on the fibers surface. It may be that the depositions arise from the phenomenon of crosslinking on the OCC pulp fibers.

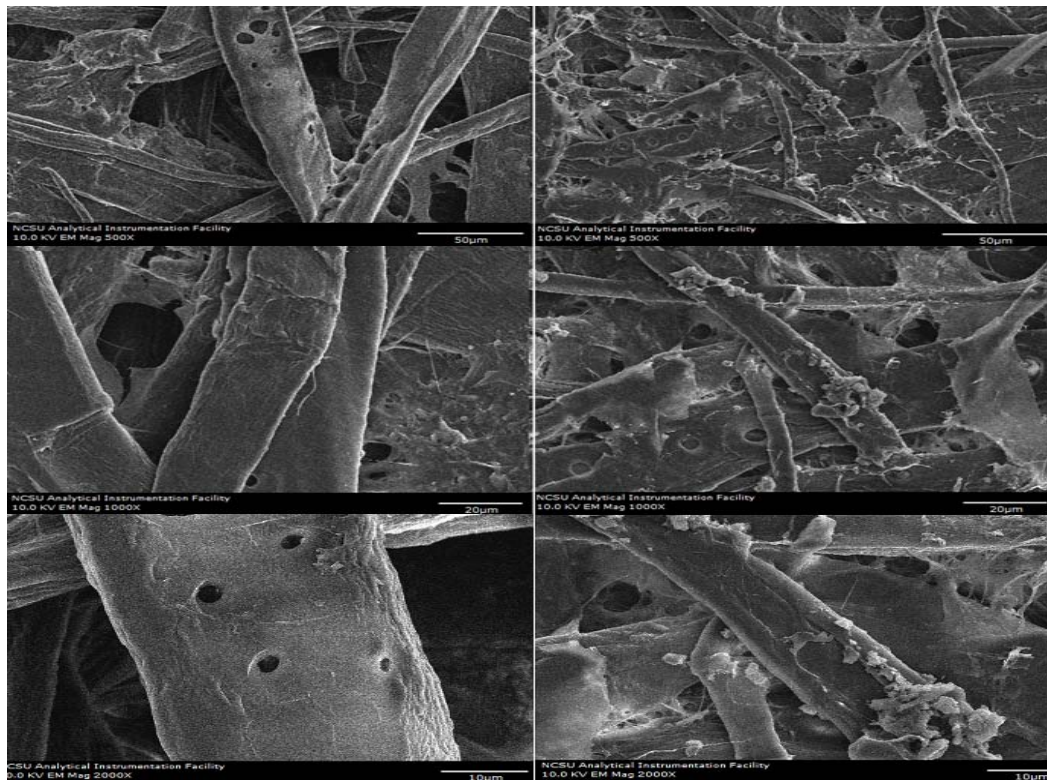


Figure 5.2.11. SEM image of OCC recycle pulp hand sheet (three left photomicroimages) and 2% CNs/Ch derivative treated OCC pulp hand sheet (three right photomicroimages). Top, middle and bottom images have length scales of 50, 20, and 10 micrometers, respectively.

5.2.3.4. Contact Angle

The dynamic contact angle with DI water at 9 seconds was determined to be 90° for OCC pulp sheet (control). The water angle significantly dropped 15° for approximately 180 seconds (Fig. 5.2.12). In contrast, the dynamic contact angles with DI water at 9 seconds for CNs-DTPA-Ch-treated OCC pulp sheet was 108° and the contact angle dropped approximately 85° for approximately 1875 seconds and then finally dropped 50° for approximately 2700 seconds. This reflects the significantly decreased water absorbency of the CNs-DTPA-Ch-treated OCC pulp sheet relative to the control pulp sheet. This may be explained that the OCC furnish has a very irregular surface and is extremely hydrophilic showing nearly no surface contact angle measurement in the typical contact angle time frame. Our additive, chitosan, is strongly hydrophobic and also produces a sticky gel under acidic pH (wet) that adopts a plastic-like character under dry conditions. Thus, when we generate a pulp sheet with the additive, under the pressing time, it spreads very evenly over the rough surface, covering it very uniformly to produce a paper surface that was very smooth and also possessing increased gloss (Fig.5.2.12). Thus, because the additive-treated sheet surface was hydrophobic due to the plastic-like chitosan under dry conditions, the contact angle increased somewhat.

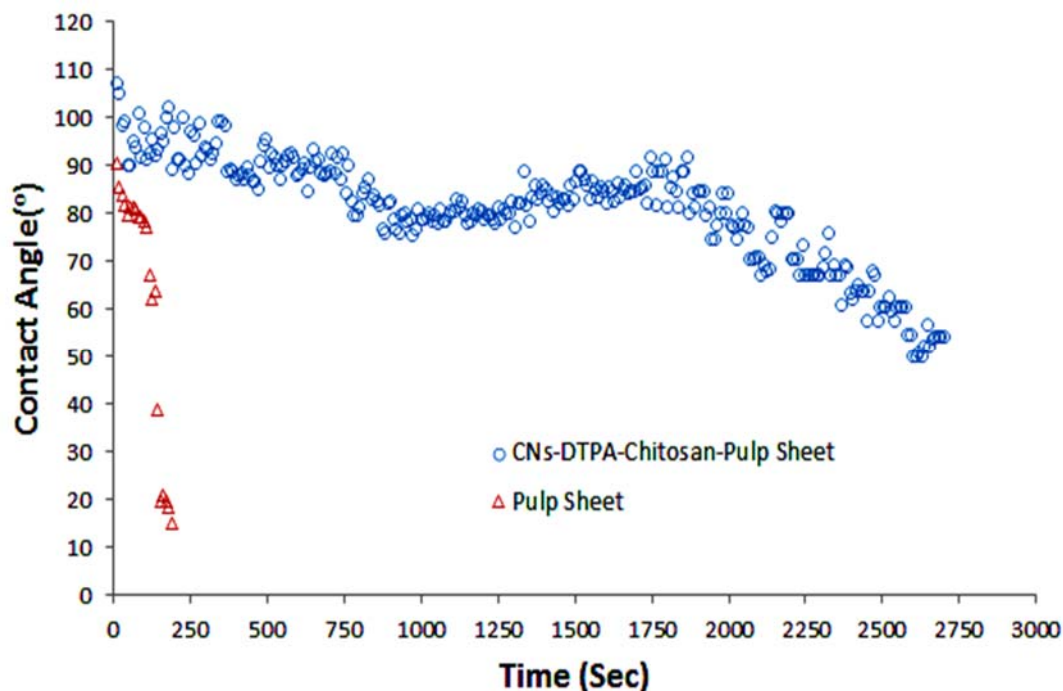


Figure 5.2.12. Contact angle of OCC pulp sheet (Δ) and CNS-DTPA/chitosan-treated OCC pulp sheet (O).

ACKNOWLEDGEMENTS

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Fluorine-Based Surface Decorated Cellulose Nanocrystals as Potential Hydrophobic and Oleophobic Materials

Abdus Salam, Lucian A. Lucia, and Hasan Jameel

Abstract

The objective of this research was to provide the first account of a simple preparation of surface fluorinated bulk cellulose nanocrystals and a characterization of their physical and chemical properties. The surface fluorinated, or polyfluorinated cellulose nanocrystals were first generated by reacting bulk cellulose with hydrochloric acid in an aqueous medium to yield cellulose nanocrystals that were subsequently purified and reacted with pentafluorobenzoyl chloride in presence of pyridine. The degree of substitution (DS, out of a possible 3.0 hydroxyl groups/anhydroglucopyranose residue) of the polyfluorinated cellulose nanocrystals was 0.77. It was found that the dispersion of cellulose nanocrystals within an organic solvent was significantly improved following surface fluorination. Dynamic contact angle, FT-IR, NMR, TGA, DSC, XRD and XPS were used to confirm the fluorinated character of the reactant products. The polyfluorinated cellulose nanocrystals obtained and characterized demonstrated excellent hydrophobic and oleophobic properties providing a non-traditional and highly attractive conceptual paradigm for a variety of low surface energy applications.

Key words: *Cellulose nanocrystals, Polyfluorination, Dispersibility, Hydrophobicity, Oleophobicity.*

5.3.1. Introduction

Recently, there has been an increasing demand for water and oil resistant products due to the continuously growing packaging markets for food items such as bakery products, pet foods, instant and fast foods (Deisenroth et al. 1998). These products are generally packed in paper-based materials and packaging that requires resistance against staining that results from oil/fat migration from the product (Ham-Pichavant et al. 2005). A recently growing trend in the development of advanced materials has been to incorporate nanomaterials as a type of filler into a bulk matrix to significantly improve select physical, chemical, and/or optical properties (Samir et al. 2005). One of the most important biologically relevant and nearly universally bio-compatible nanomaterials is nanocellulose, a novel material that is exclusively derived from cellulose, a biopolymer that has been gaining significant attention because it is the most abundant renewable (plant- and animal-based) biopolymer on the planet (George et al. 2010). Acid hydrolysis of cellulose is an effective method to remove discontinuous (structurally amorphous) regions and thus obtain highly ordered cellulose nanocrystals, a species of material that is virtually unlike its original source because of its extremely unique physico-chemical properties. Sulfuric acid and hydrochloric acid are among the most widely used acidolytic methodologies to produce cellulose nanocrystals from bulk cellulose (Habibi et al. 2010). Utilizing cellulose nanocrystals as a reinforcing phase for developing new nanocomposite materials has recently been the subject of a numerous investigations, in which

several of those efforts have focused on transforming hydrophilic cellulose nanocrystals into hydrophobic polymeric matrices (Dufresne 2010). The challenge in the latter work is the extremely high hydrophilicity and surface energy of the cellulose nanocrystals; their incorporation into hydrophobic matrices, therefore, requires a compatibilization procedure or step that typically can be achieved by a modification of their surface functionalities.

In general, surface-fluorinated materials are among the most non-interactive and lowest surface energy materials known. Fluorocarbons, for example, substantially surpass hydrocarbons in terms of thermal, chemical and biological inertness, reduced surface energy, hydrophobicity, and oleophobicity (Kissa 2001; Rojas et al. 2002; Schoenroth et al. 1967; Schwartz 1981). The ability to attain improved hydrophobicity such as oil and water repellency in a material may be adequately addressed by the pursuit of surface fluorination. Fluorinated compounds have exhibited extremely tunable and attractive surface energy properties by reducing matrix/matrix interactions and engaging the matrix/solvent medium to a greater degree. Therefore, the ability to promote a hydrophobic matrix/solute interaction is one of the primary reasons for the current interest to prepare and characterize surface fluorinated cellulose nanocrystals.

5.3.2. Experimental

5.3.2.1 Materials:

Whatman #4 filter paper was supplied by Whatman International Ltd, Maidstone, England. The Whatman #4 filter paper was used as the starting bulk cellulose substrate for the

production of cellulose nanocrystals (CNs). Chemicals of reagent grade utilized were hydrochloric acid, pentafluorobenzoyl chloride (CAS registry number 2251-50-5), pyridine, toluene, CH₂Cl₂, and ethanol from Fisher Scientific, Fair Lawn, New Jersey, USA.

5.3.2.2. Preparation of Cellulose Nanocrystals (CNs):

The CNs were prepared from pure cellulose (Whatman paper #4) by acid hydrolysis using HCl (3 N) with a solid-to-liquor ratio of 1:50 at 90°C for 2 h under continuous agitation to obtain cellulosic nanocrystals. The suspension was centrifuged at 5300 rpm for 15 min. to concentrate the CNs and remove the excess aqueous acid. The resultant precipitate was rinsed and re-centrifuged eight time to achieve neutral pH. After a neutral pH was achieved, the solid aggregate was washed with ethanol two times (each time with 30 ml) and re-centrifuged. The CNs suspension was dried in air under a hood and then stored under a vacuum desiccator until required for further application (Jin et al. 2010; Lirong et al. 2013).

5.3.2.3. Preparation of Polyfluorinated Cellulose Nanocrystals (PCNs):

Pentafluorobenzoyl chloride (850mg) was placed in a 25 mL round-bottom flask, to which dry toluene (8 mL), pyridine (290mg), and finally cellulose nanocrystals (200 mg) were added under a nitrogen atmosphere (Zhang et al. 2002). Reactions were conducted under magnetic stirring at 80°C for 2 hours. The polyfluorinated products were centrifuged at 5300 rpm for 15 min. to concentrate the polyfluorinated products and remove the excess solvent. The resultant precipitate was washed and re-centrifuged ten time with toluene (5 times, each time 30ml), CH₂Cl₂ (3 times, each time 30ml), and ethanol (2 times, each time 30ml), and dried in

air under a hood and then stored under a vacuum desiccator until required for further application (Hasan Sadeghifar et al. 2011). Shown below is a simplification of the reaction scheme used to generate the polyfluorinated nanocrystals (Fig.5.3.1).

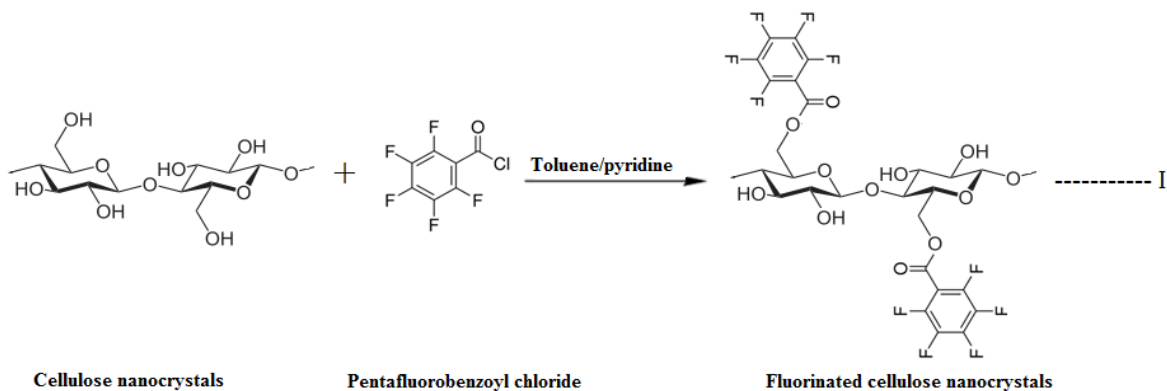


Figure 5.3.1. A representation of the surface decoration of cellulose nanocrystals by fluorinated residues.

5.3.2.4. Characterization:

5.3.2.4.1. Determination of Degree of Substitution:

The degree of substitution (DS) of the polyfluorinated cellulose nanocrystals was calculated from fluorine elemental analysis data (F %) by using following eq. (Vaca-Garcia et al. 2001).

$$\text{Degree of Substitution (DS)} = \frac{162 \times \text{F}\%}{100M - (m-1) \text{F}\%}$$

Where F% = percent of fluorine in the polyfluorinated cellulose nanocrystals

M = Molecular weight of total fluorine in the fluorinating agent (that has 5 fluorine atoms)

m = Molecular weight of the cross linker part of pentafluorobenzoyl chloride

5.3.2.4.2. X-Ray Photoelectron Spectroscopy (XPS):

The surface chemical composition of the polyfluorinated cellulose nanocrystals samples was determined with XPS. The measurements were performed using a XPS/UVS – SPECS system with hemispherical analyzer PHOIBOS 150. The monochromatic Al $K\alpha$ excitation was 1486.7 eV and X-Ray incidence angle is $\sim 30^\circ$ from surface and X-ray source to analyzer $\sim 60^\circ$. The energy calibration was established by referencing to adventitious C (C1s line at 285.0 eV binding energy). The base pressure in the analysis chamber was in the 10^{-10} mbar range (Freire et al. 2006).

5.3.2.4.3. ATR Analysis:

IR Spectra were recorded of polyfluorinated cellulose nanocrystals samples with a Perkin Elmer FT-IR spectrophotometer. All the spectra were obtained by accumulation of 8 scans, with a resolution of 4 cm^{-1} , at $400\text{--}4000\text{ cm}^{-1}$ (Salam et al. 2010).

5.3.2.4.4. NMR Analysis:

Cross polarized magic angle spinning nuclear magnetic resonance (CP: MAS NMR) spectra were obtained for polyfluorinated cellulose nanocrystals sample using a Bruker 500 instrument operating at 75.4 MHz for ^{13}C . The samples were packed in two 3.2 mm rotors and

spun at 4000 Hz (Salam et al. 2010).

5.3.2.4.5. Thermal Gravimetric Analysis (TGA):

Thermogravimetric behavior was studied using a TGA Q500 under nitrogen from 30–600°C at a temperature ramp of 5°C/min, followed by isothermal heating at 600°C for 2 min. The differential of the weight loss (differential thermogram, DTG) was observed and the maximum in the DTG was reported (Salam et al. 2010).

5.3.2.4.6. Differential Scanning Calorimetry (DSC):

A differential scanning calorimeter DSCQ100 was used with a Hermetic pan (T 090127). Samples were subjected to a 2°C/min temperature ramp from 30–200°C, followed by isothermal heating at 200°C for 2 min. An empty pan was used as a reference (Salam et al. 2010).

5.3.2.4.7. Dynamic Contact Angles:

Dynamic contact angle measurements were performed with a Phoenix 300 Contact Angle Analyzer on a polyfluorinated cellulose nanocrystals film. Deionized water was used as the probe fluid (Salam et al. 2011).

5.3.2.4.8. X-ray Diffraction:

The crystallinity index (CI) was measured by an X-ray diffraction diffractometer. The X-ray diffraction patterns with CU KR radiation (λ 1.5406Å) at 40KV and 30mA were recorded in the range of (2 θ) 5-40° with an X-ray diffraction diffractometer (Zhang et al. 2005). The

crystallinity index (CI) was determined according to eq. 1:

$$CI = 100[I_{002} - I_{am}]/I_{002} \dots\dots\dots 1$$

Where I_{002} is the intensity of the principal cellulose peak at $2\theta = 22.7^\circ$ and I_{am} is the intensity attributed to amorphous cellulose given at $2\theta = 18^\circ$.

5.3.2.4.9. Elemental Analysis:

The fluorine percentage of polyfluorinated cellulose nanocrystals was determined by oxygen flask combustion and the standard addition method using an ion specific electrode (ISE).

5.3.2.4.10. Oil Resistance Test

The oil resistance test was carried out according to AATCC Test Method 118-1997.

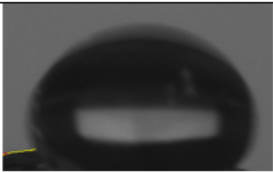
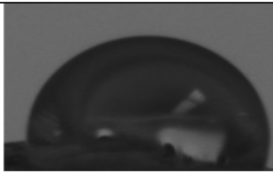
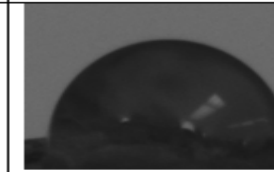

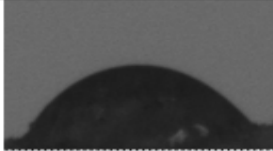
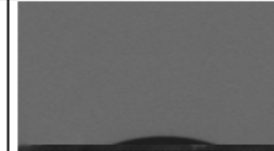



5.3.3. Results and Discussion

The degree of substitution (DS) of pentafluorobenzoyl group incorporation of the nanocrystals were determined by elemental analysis. For this study, the monomer formula weight of glucose monomer unit or anhydroglucose (MW = 162) was used with the number of hydroxyls per glucose monomer unit equal to three. DS is expressed as the average number of moles of substituent per anhydroglucose unit. The degree of substitution (DS) for polyfluorinated cellulose nanocrystals was found to be 0.77, whereas for polyfluorinated cellulose it was 0.32. It was observed that the dispersion of cellulose nanocrystals in an organic solvent (acetone) was significantly improved when cellulose nanocrystals were modified with pentafluorobenzoyl chloride. This effect is what is normally observed when cellulose

nanocrystals are generated from a hydrosulfuric acid acidolysis of bulk cellulose (Jin et al. 2010). In this particular case, the dispersion effect is likely due to strong fluorine-fluorine repulsions amongst surface fluorine-decorated nanocrystals (Gousse et al. 2002; Lucia et al. 2003).

It is expected that polyfluorinated cellulose nanocrystals, as most polyfluorinated materials, would display decreased water affinity relative to their non-polyfluorinated state. Work in the biomedical field with hemodialytic membranes has already shown that a plasma surface fluorine etching induces significant surface energy changes that reduce adhesion of hydrophilic blood components (Poncin-Epaillard et al. 1992). A significant decrease in water absorption is also shown for fluorinated cellulose nanocrystals relative to cellulose nanocrystals (see Table 5.3.1 and Figure 5.3.2) as a result of higher fluorine content.

Table 5.3.1. Dynamic contact angle of polyfluorinated cellulose nanocrystals, polyfluorinated cellulose (pulp) and filter paper (cellulose).

Sample	Picture capture at 10.0 sec	Picture capture at 200.0 sec	Picture capture at 1200.0 sec
Polyfluorinated cellulose nanocrystals			
Polyfluorinated cellulose (pulp)			
Cellulose nanocrystals			

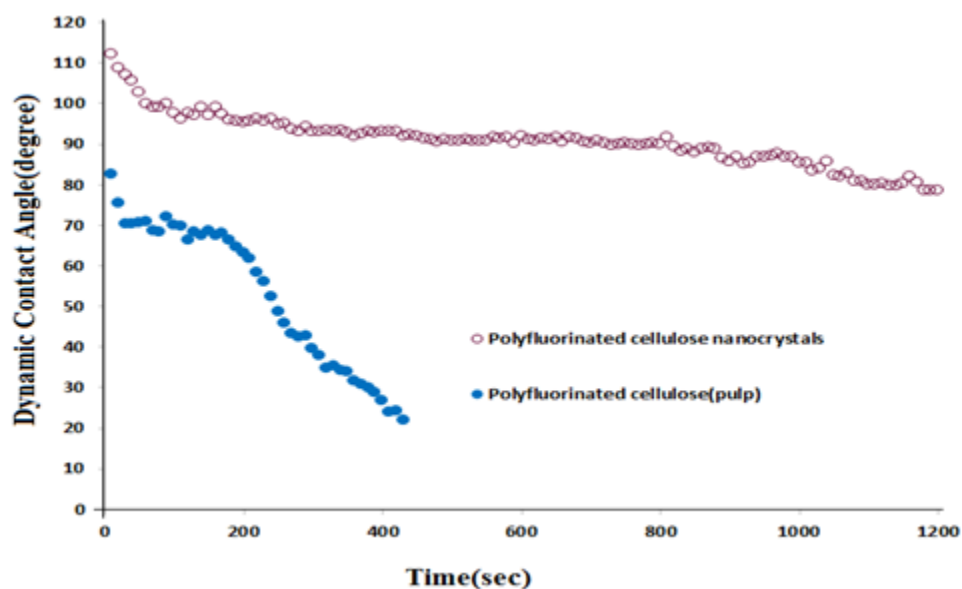


Figure 5.3.2. Dynamic contact angle of (●) polyfluorinated cellulose nanocrystals (○) and polyfluorinated cellulose (pulp).

The contact angles (CAs) with water at 10.0 sec were determined to be 112° for polyfluorinated cellulose nanocrystals whereas they were 0° for the control (neat cellulose nanocrystals) (Figure 5.3.2). The observed increases of the contact angle for the polyfluorinated cellulose nanocrystals relative to the cellulose nanocrystals indicates a significant decrease in the wettability of the modified materials, in agreement with the contact angle images in Table 5.3.1. Tuning of the overall hydrophobic properties of the final substrate may be possible by the overall surface incorporation of fluorine-based residues. The current surface energy attained is only indicative of the overall state of fluorination at the nanocrystal surface which has not been optimized in the current study. A slow, protracted drop in the CA indicates that there are accessible (exposed) hydrophilic regions (hydroxyl groups) in the highly wettable nanocrystals that have not been derivatized by the fluorination

treatment. This has been already demonstrated to be the case by incomplete incorporation of perfluorobenzoyl groups onto the surface. It is likely as shown in Figure 5.3.1 that the sterically bulky aromatic nuclei upon which the pendant fluorine groups reside do not pack facially and thus interfere to some degree with the ability of neighboring (exposed) hydroxyl groups to be derivatized. Interestingly, what is noteworthy is that there exists a pronounced difference in the surface energies between the fluorinated nanocrystals and the fluorinated bulk cellulose. The surface energy of the hydrophobized crystals is much lower than the cellulosic material. This difference may be related to differences in efficiency of reaction between the very high area and individualized nanocrystals versus the bulky, fibrous, and less defined cellulosic material. The nanocrystals have a very defined surface region whereas the cellulosic material is much more amorphous, has many more concavities, and less defined from a topochemistry perspective. Such a difference may allow for more surface coverage on the nanocrystals relative to the bulk cellulose. In addition, oil resistance of polyfluorinated cellulose nanocrystals was characterized and shown to be the highest on a standard relative scale measurement for oil resistance (see Experimental, 8/8). Such an observation is clearly indicative of the general, non-interactive nature of the fluorine residues toward the oil molecules and thus amplify inter-oil molecular interactions resulting in the witnessed repulsive (oleophobic) phenomenon (Lucia et al. 2003).

The ATR spectra of the cellulose nanocrystals and polyfluorinated cellulose nanocrystal are illustrated in Figure 5.3.3. The broad bands in the 3400 cm^{-1} region can be attributed to the O–H stretching vibrations and the peaks at 2900 cm^{-1} correspond to C–H stretching vibrations. Both the cellulose nanocrystals and fluorinated cellulose nanocrystals are cellulose β type (Lu

et al. 2010). The crystalline β characteristic peaks are present in the cellulose nanocrystals: OH stretching signal at 3270 cm^{-1} and OH out-of-plane bending signal at 710 cm^{-1} . The ATR spectrum of the polyfluorinated cellulose nanocrystals displayed a new strong band peak at approximately 1740 cm^{-1} , an absorption peak that corresponds to the stretching of the carbonyl group in the resulting benzoyl ester derivatives of the cellulose nanocrystals, although for cellulose nanocrystals the carbonyl region ($1700\text{--}1800\text{ cm}^{-1}$) does not clearly show a carbonyl stretch. The difference spectrum also showed absorption peaks at 1600 and 1450 cm^{-1} which correspond to the IR stretching vibrations of the carbon-carbon double bonds in the benzene ring of the benzoyl esterified cellulose nanocrystals (Sadeghifar et al. 2011). In addition, to strongly confirm for carbonyl peak in the polyfluorinated cellulose nanocrystals the sample was performed with ^{13}C NMR. A new peaks at $\delta = 165.896\text{ ppm}$ appeared of carbon signals of a carbonyl group of an ester. This indicates that the acetyl chloride group of pentafluorobenzoyl chloride reacted with the hydroxyl groups of CNs.

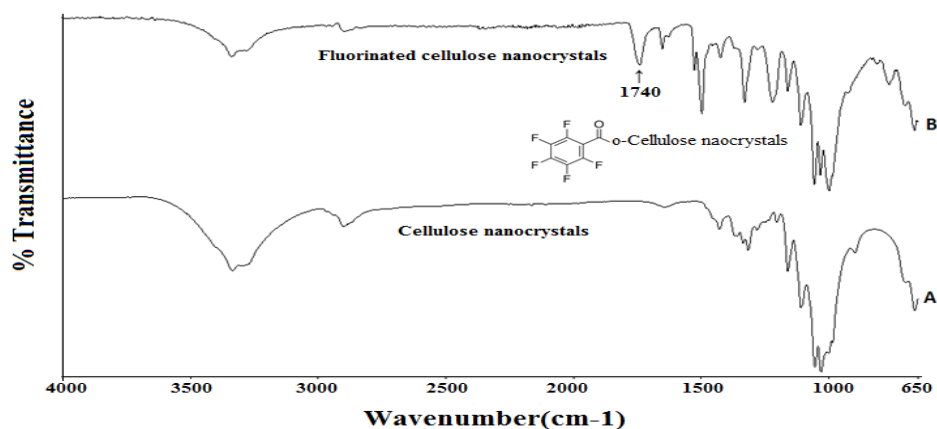


Figure 5.3.3. ATR spectra of cellulose nanocrystals (A) and polyfluorinated cellulose nanocrystals (B).

The surface chemical composition results of the polyfluorinated cellulose nanocrystals are shown in Figure 5.3.4. Pure cellulose contain two main element like carbon and oxygen when detected by XPS (Poncin-Epaillard et al. 1992). But when the polyfluorinated cellulose nanocrystals sample was performed with XPS, the sample clearly showed three main elements: carbon (51.11%), oxygen (25.37%) and fluorine (23.51%), thus confirming the occurrence of the expected esterification reaction between cellulose nanocrystals and pentafluorobenzoyl chloride (Figure 5.3.4). This results is also an agreement with the existence of the surface reaction of the cellulose nanocrystals materials (Freire et al. 2006).

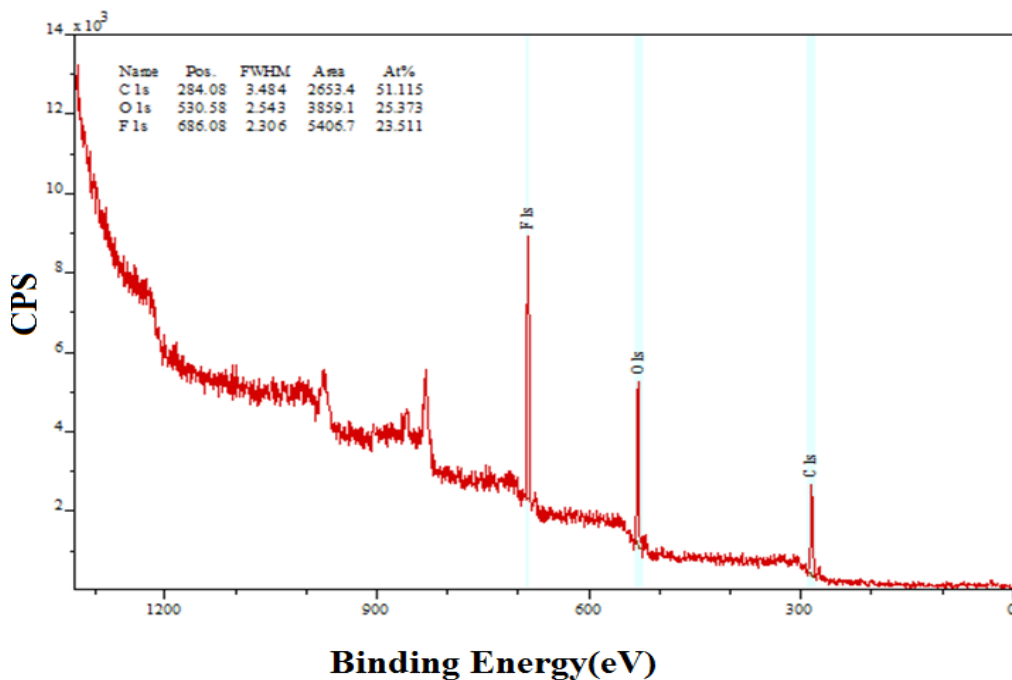


Figure 5.3.4. XPS analysis results of polyfluorinated cellulose nanocrystals.

A thermogravimetric analysis of cellulose nanocrystals and fluorinated cellulose nanocrystals was done under nitrogen atmosphere, shown in Figure 5.3.5. Weight loss below 100°C was due to water evaporation; however, the weight loss above 100°C was caused by the thermal decomposition of the cellulose nanocrystals and fluorinated cellulose nanocrystals (Salam et al. 2011). Cellulose nanocrystals have a single weight loss peak at 329.96°C, whereas polyfluorinated cellulose nanocrystals have a significant decrease in maximum weight loss temperature (286.38°C) and a significantly higher residual mass (18.5%) after heating to 600°C. The fluorinated residues are anchored on the surfaces of the cellulose nanocrystals via ester bonds that tend to have a lower temperature of degradation (Salam et al. 2011; Shi et al. 2007). The increased residual mass of the char after heating to 600°C for the fluorinated cellulose nanocrystals products is in agreement with the distinct possibility of the modified cellulose nanocrystals undergoing surface crosslinking after degradation of the modifying groups to enhance the in-carbonization of the cellulose nanocrystals (Shi et al. 2007).

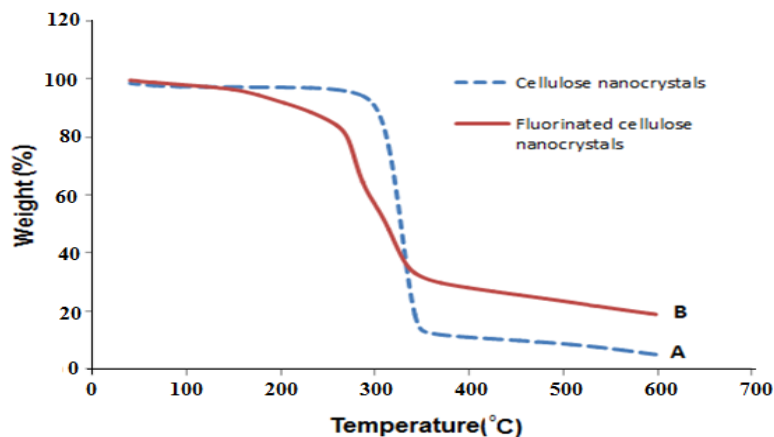


Figure 5.3.5: TGA of cellulose nanocrystals (A), and polyfluorinated cellulose nanocrystals (B).

Additionally, further thermal behavior of cellulose nanocrystals and fluorinated cellulose nanocrystals was evaluated using differential scanning calorimetry (DSC) by applying a 2°C/min heating rate up to 220°C under nitrogen atmosphere (Fig. 5.3.6). Glass transition temperatures (T_g) of fluorinated cellulose nanocrystals were observed at 180°C, whereas cellulose nanocrystals did not show any glass transition temperatures (Fig. 5.3.6). The appearance of a glass transition temperature peak for fluorinated cellulose nanocrystals products may arise from changes in their chemical composition with respect to their new surface energies and plasticization, as well as changes caused in the crystalline molecular organization due to the esterification reaction between the hydroxyl group of the cellulose nanocrystals and the acetylchloride group of pentafluorobenzoyl chloride (Salam et al. 2011; Shi et al. 2007).

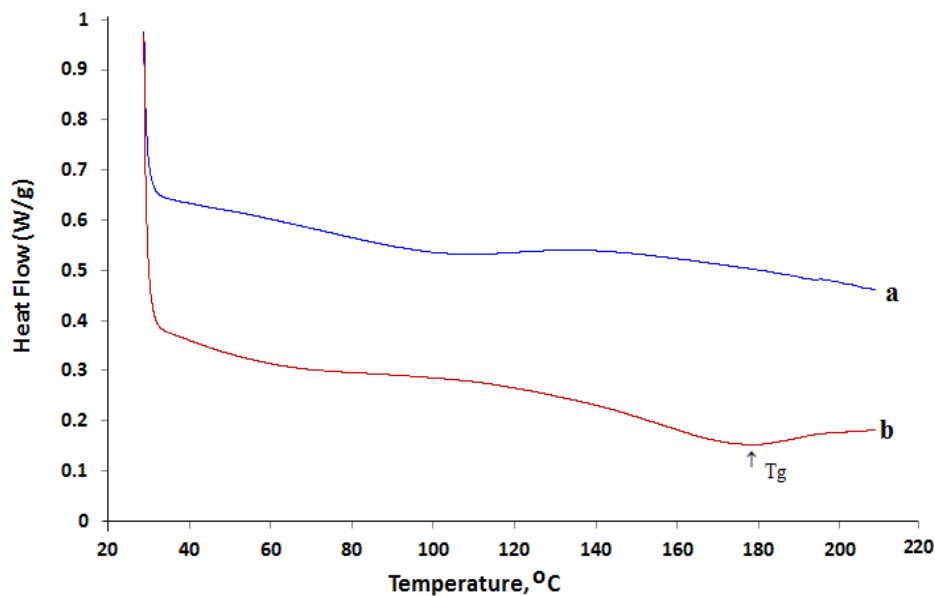


Figure 5.3.6. DSC of CNs (a), and polyfluorinated CNs (b).

X-ray diffraction of both the CNs and polyfluorinated CNs sample are shown in the Figure 5.3.7. The X-ray diffraction of polyfluorinated CNs demonstrates that they have a slightly reduced crystallinity (CI value = 82%) compared to the CI value 91% of CNs. Although it is not a surprising result, it may occur due to the surface modification of CNs with pentafluorobenzoyl chloride treatment that may either abrade the surface to a small degree or perturb the surface structural organization (Mohkami 2011).

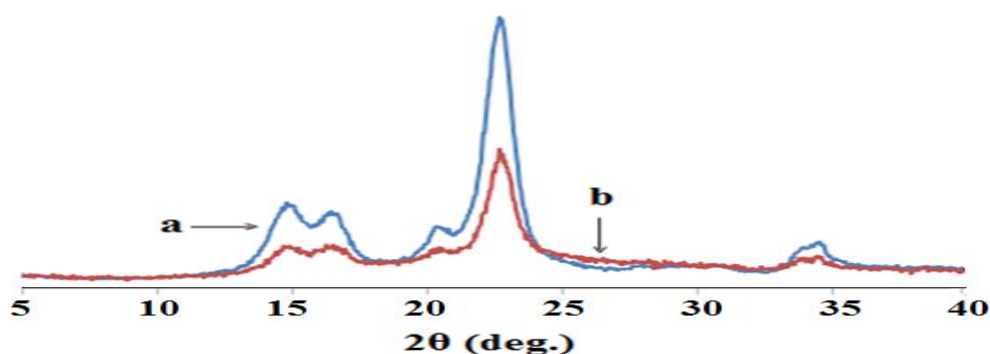


Figure 5.3.7. X-ray Diffraction of CNs (a) and polyfluorinated CNs (b).

5.3.4. Conclusions

This work provides the first detailed account of the preparation and characterization of surface-polyfluorinated cellulose nanocrystals. Hydrochloric acid was used to preparation of cellulose nanocrystals which were then modified by pentafluorobenzoyl chloride through an esterification reaction. The 1740 cm^{-1} peak observed in the ATR spectrum of polyfluorinated cellulose nanocrystals indicated the installation of the carbonyl group of pentafluorobenzoyl chloride at a hydroxyl group to yield a DS of 0.77 on the CNs. The XPS analysis of

polyfluorinated cellulose nanocrystals indicated that there was a mass fraction of 23.51% of fluorine, thus confirming the occurrence of the anticipated esterification reaction. From the TGA, it was found that the significantly decreased maximum degradation temperature (DTG) and increased residual char of fluorinated cellulose nanocrystals indicated that pyrolysis of pentafluorobenzoyl chloride lead to surface modification reactions that increased the in-carbonization of cellulose nanocrystals. The observed glass transition temperatures peak at 180°C of fluorinated cellulose nanocrystals also indicated changes in the chemical composition of cellulose nanocrystals especially with regards to covalent bonding and plasticization as well as the interference of the crystalline molecular organization resulting from the esterification reaction. The X-ray diffraction indicated that the degree of crystallinity (CI) of polyfluorinated cellulose nanocrystals was slightly decreased compare to control sample (cellulose nanocrystals) and may due to the surface modification. The dynamic contact angle for fluorinated cellulose nanocrystals were observed to be 112° and 80° at 10.0 sec and 1200.0 sec., respectively, whereas the dynamic contact angle for unfluorinated cellulose nanocrystals were observed to be 0° at 10.0 sec. (see Table 1). Additionally, the oleophobic properties of fluorinated cellulose nanocrystals were tested and the results were shown to be excellent as anticipated by the general non-interacting nature of fluorinated materials. These significantly improved contact angles and superior oleophobic properties for the polyfluorinated cellulose nanocrystals clearly indicated that they possess favorable surface energy properties that may have potential applications in a number of hydrophobic and oleophobic systems.

Acknowledgments

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CHAPTER 6

Antimicrobial Activity of Modified Polysaccharides additive Materials.

This chapter focus on the study of the decomposition of soy flour, fundamental reasons for decomposition of soy flour, and a functional understanding of why newly developed soy flour derivatives do not decompose. It provides a characterization of the antimicrobial activity of soy flour, corn starch, modified soy flour, modified corn starch, and modified soy flour or modified corn starch additive-treated OCC pulp sheets. The fundamental reasons or mechanism for how the modified soy flour or modified corn starch kills bacteria is also provided.

Antimicrobial Activity Observed in New Polysaccharide Macromolecular-Cellulosic Composites

Abdus Salam, Lucian A. Lucia, and Hasan Jameel

Abstract

Cellulosic fiber-based materials (papermaking) are generally a composite containing petroleum-based polymeric strength agents as filler. The use of soy protein flour, an attractive sustainable biomaterial, as an alternative bio-based agent for its mechanical enhancement, poses a bacterial digestion problem principally due to microbially-digestible proteins. Rank odors, papermachine fouling, and paper strength losses characterize the product. These are problems also typically faced for the packaging and shipping for foods, textiles, coating, and related commodity industries. The goal of this study was to therefore develop a sustainable soy protein flour derivative to reduce bacterial digestion in and simultaneously provide a robust cellulosic composite. More specifically, the current research goal focused on synthesizing a biochemical that enhances inter-cellulosic fiber binding and provides antimicrobial activity. The installation of carboxylic and amine groups into soy flour for increasing available binding functional groups and reducing bacterial digestion in soy flour was achieved in the present report. Diethylenetriaminepentaacetic acid (DTPA) was reacted with soy protein flour in presence of sodium hypophosphite and further reacted with chitosan to provide a new biomaterial for enhanced papersheet mechanical properties. *E. coli* was used to test the antimicrobial activity of unmodified and modified soy protein flour additive, modified cornstarch additive, and modified additive-treated recycled pulp sheets. It was found that unmodified soy flour additives began decomposing within 24 hours as evidenced by foul

odors, whereas modified soy flour additive samples did not after nearly two years of exposure. *Escherichia coli* was used to test antimicrobial activity of the cellulosic fibers. The OCC pulp sheet did not show any antimicrobial activity. Unmodified soy protein flour and cornstarch significantly increased bacterial populations compared to the control; however, modified soy protein flour and cornstarch exhibited near unit bactericidal activity.

Key words: *Soy flour, cornstarch, chitosan, decomposition, anti-microbial activity*

6.1.1. Introduction

Soy flour is made by roasting and grinding soybean. Soy flour is commercially available and contains approximately 33.7 % carbohydrate, 34.5% soy protein, 21.9% fatty acid and other components such as moisture, vitamin, mineral and biologically active or metabolic proteins such as enzyme¹. The metabolic protein (enzyme) in soy flour is vital issue to decompose of soy protein. However, soybean is also an excellent source of soy protein which is highly digestible (92-100%). The soy protein component is a long polymer chain consisting of 18 different polar and nonpolar amino acids; amongst the polar amino acids are cysteine, arginine, lysine, and histidine which can be used as a chemical "hook" to crosslink the protein and thus improve its mechanical, thermal and physical properties as well as reduce water sensitivity and hydrophilicity.¹⁻² Earlier research has related that soy proteins can be cross-linked by incorporation of aldehydes such as glyceraldehyde, formaldehyde and glutaraldehyde by employment of *Maillard* reactions.³ Crosslinked isolated soy protein has previously been used to develop biodegradable polymers that possess enhanced mechanical properties.⁴ Chitosan is an abundant naturally occurring polysaccharide which is poly β -(1-4) d-glucosamine

deacetylate form of chitin that is obtained by alkaline treatment. Chitosan has become useful polysaccharides in the biomedical area because of their biocompatible, biodegradable, and non-toxic properties⁵. Earlier researcher found that chitosan is a potential candidate for targeting antibiotic resistant microorganisms due to its antimicrobial activity and strong bactericidal effect on gram-positive and on gram-negative bacteria⁶. The mechanisms for killing bacteria is that chitosan has a positive charge due to amine group which is adsorb the electronegative substance in the cell of bacteria and flocculate them. Therefore the physical activates of bacteria is significantly disturbs and eventually died⁷. Chitosan also has an antifungal activities which molecules directly interfere to fungal growth⁸. However, a microscopic observation indicated that chitosan molecules diffuse inside hyphae interfering on the enzymes activity responsible for the fungus growth.⁹

The current research is focused on the incorporation (by organic synthesis) of carboxylic and/or amine groups into soy flour for increasing the available functional groups and reduce bacterial digestion in soy flour. DTPA was reacted with soy flour in the presence or absence of sodium hypophosphite. Thereupon, the modified soy flour was complexed with chitosan in acidic medium solution. This research also main focuses on study of bacteria decomposition of soy protein flour with or without adding modified soy protein flour, Antimicrobial activity test of modified soy protein flour and modified soy protein flour additive-treated OCC pulp sheet. Modified corn starch also will be used for comparism.

6.1.2. Experimental

6.1.2.1. Materials

Soy flour was provided by Archer Daniel Midland (ADM, Decatur, IL). Starch, was supplied by Cargill Incorporated, Minneapolis, MN. Reclaimed OCC pulp were supplied by Georgia Pacific Innovation Research Institute, Norcross, GA. Diethylenetriaminepentaacetic acid (DTPA) and chitosan, were purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphate, (SHP) CAS registry number 123333-67-5. Escherichia coli was provided by Department of Textile Engineering in NC State University. Acetic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water.

6.1.2.2. Chemical Modification of Soy Flour

In a typical protocol for the basis of the current review, diethylenetriaminepentaacetic acid (DTPA) is dissolved in 20 mL alkali in a 50mL Petri dish in the presence of 5% sodium hypophosphite (SHP). It is placed in a Petri Dish and manually mixed vigorously with a glass rod. The mixture is then placed in an air oven at 120°C for 3 hours, after which the reaction products are washed with DI water and filtered several times to remove unreacted materials. Subsequently, the modified soy flour is complexed with chitosan at 80°C for 90 minutes.¹⁰ The proposed reaction schemes are shown in **Figure 6.1.1**.

bacteria were incubated at 37 °C for 24 h, and then the numbers of the surviving colonies were counted. These results were compared to the number of bacteria colonies of the untreated control that had not been exposed to the active materials. The inhibition rate was calculated by the following equation:

$$X = \frac{A-B}{A} \times 100\%$$

Where, *A* and *B* are the number of colonies on the plates before and after inhibition.

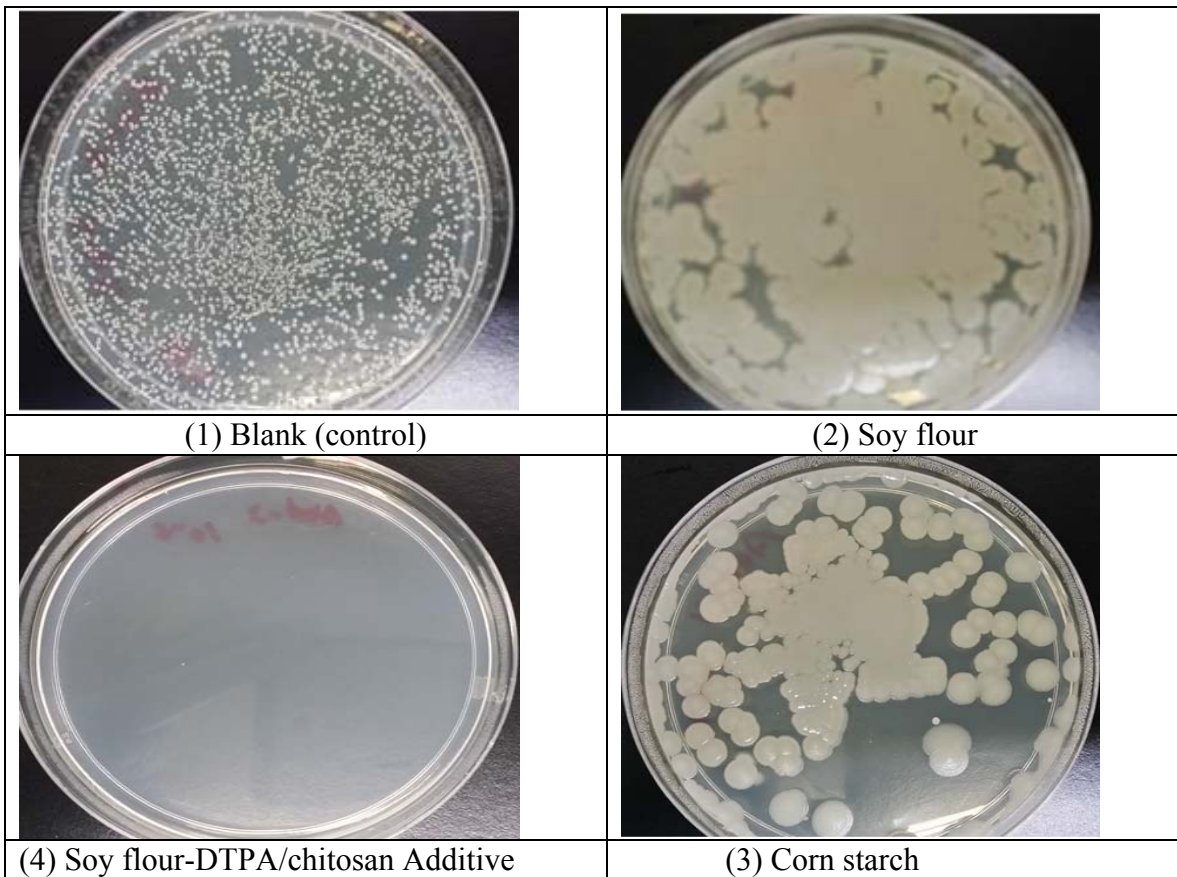
6.1.3. Results and Discussion

Decomposition of modified and unmodified soy flour additives were studied under open-air conditions for nearly two years. The unmodified soy flour additive began decomposing within 24 hours as evidenced by the detection of foul odors. This was not observed for the modified soy flour additive sample even after nearly two years (Fig.6.1.2). In addition, 0.1% modified soy flour additive was added to 1 Kg soy protein flour solution and observed the decomposition for six month by follow odors. No bad odors was observed. Antimicrobial activity of modified and unmodified soy protein flour and modified soy protein flour additive-treated recycle pulp hand sheet both were tested according to the standard antimicrobial test method AATCC 100. A microbial suspension of bacteria (*Escherichia coli*) was used to test antimicrobial activity. It is observed from the Figure 6.1.3 that the bacteria colony was significantly increased when unmodified soy protein flour was added into bacteria suspension plate. Similar results was found for unmodified corn starch. This may explained that soy protein flour obtain metabolic proteins such as enzyme and also highly nutritious cause's

bacteria growth easily rise up significantly. However, the interesting thing is that no bacteria or bacteria colony was observed when modified soy protein flour or modified corn starch was added into bacteria suspension plate (Fig. 6.1.3). It may be explained that the modified soy flour obtains positive charges from protonation of the chitosan amine group to likely play a significant role to kill the bacteria. The mechanism of the antimicrobial action is attributable to an interaction between positively charged substrate molecules (the chitosan amino residues) and negatively charged microbial cell membranes.⁷ Once the coulombic interaction occurs, there is a tendency for a flocculation event that disrupts the vital physiological activities of the microbes. In general, a significant inhibition of microbial enzymatic activity occurs that leads to their demise. In general, chitosan dissolves under acidic conditions and gains positive charges believed to play a crucial role in preventing soy protein from microbial digestion and subsequent foul odor generation. It is also observed from Figure 3 that the OCC pulp sheet did not show any antimicrobial activity even grew up more bacteria colony. However, modified soy protein flour or modified corn starch-treated OCC pulp sheet were killed about 93-97% bacteria. The bacteria killing rate was not observed 100% due to use of very low amount of additive to treat the OCC pulp sheet.



Figure 6.1.2. A simplistic and wholly unrehearsed depiction of the olfactory sensory experience resulting from exposure to unmodified soy flour (left) and modified soy flour (right).



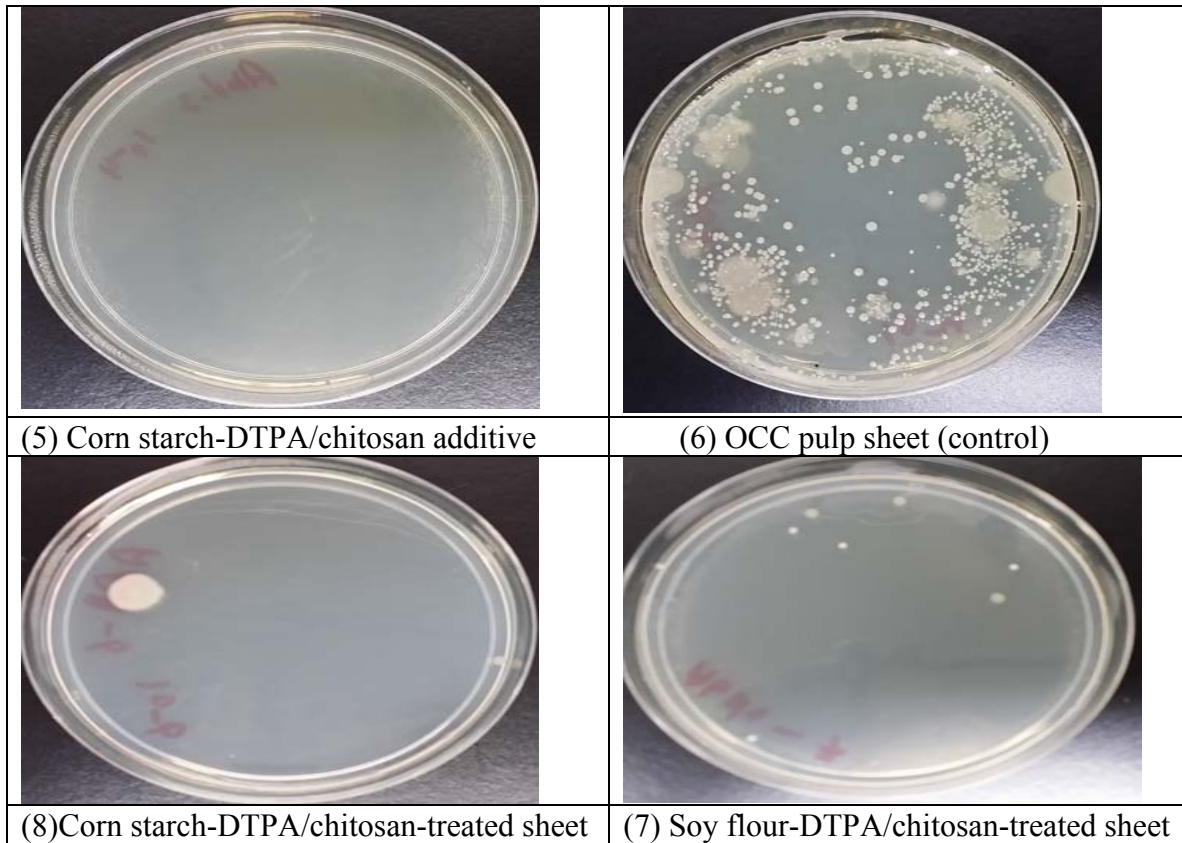


Figure 6.1.3: Antimicrobial activity of unmodified and modified polysaccharide additives.

6.1.4. Conclusion

Decomposition of modified and unmodified soy flour additives were studied under open-air conditions for nearly two years. It was found that the unmodified soy flour additive began decomposing within 24 hours as evidenced by the detection of foul odors. But, modified soy flour additive sample was not observed for the even after nearly two years. Antimicrobial activity of unmodified polysaccharide, modified polysaccharides and modified polysaccharide additive-treated recycle pulp hand sheet both were tested according to the standard antimicrobial test method AATCC 100. Soy flour and corn starch significantly increased

bacteria growth compare to control sample. But modified soy protein flour and modified corn starch were shown strongly antimicrobial activities and killed 100% bacteria. In addition, OCC pulp sheet did not show any antimicrobial activity but modified soy flour and modified corn starch-treated OCC pulp sheet were killed about 93-97% bacteria compare to control sample (OCC).

Acknowledgments

We gratefully acknowledge partial support from the United Soybean Board (Smith, Bucklin & Associates, LLC) that allowed significant portions of this work to be completed.

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 11. Antimicrobial Test-AATCC 100.

CHAPTER 7

This chapter reports the overall conclusions that are resulted from this study

7.1. Overall Conclusions

A fundamental understanding of the potential of a new class of polysaccharide (soy flour, corn starch, and carbohydrate/cellulose nanoparticles) derivatives by appropriate chemical modification has been obtained for dry strength improvements to recycled paper. These new polysaccharide dry strength additives significantly improve inter-fiber bonding between fibers and improve the antimicrobial properties of pulp or paper sheets. The novel polysaccharides derivatives enhanced pulp fiber bonding by developing extensive hydrogen and ionic bonding networks and also contributing to a chemically cross-linked network.

In the first part of this work, the preparation and study of nano materials (starch nanoparticles and cellulose nanocrystals), hydrolysis of soy protein isolate from acid, alkali and enzyme, selection of modifying agents, synthesis (modification) conditions, optimum blend ratio (modified polysaccharide/chitosan), characterization of modified polysaccharides (soy flour, corn starch, starch nanoparticles, cellulose nanocrystals and hydrolyzed isolate soy protein) derivatives were accomplished. It was found that hydrochloric acid hydrolyzed cellulose nanocrystals did not coagulate and easily dispersed in water in alcohol. The diethylenetriaminepentaacetic acid agent showed better strength performance for OCC pulp compared to other modifying agents. The optimum synthesis conditions were found to be 20% DTPA, 3 hrs, 120°C and pH 10. The optimum blend (modified polysaccharide/chitosan) ratio was found 70:30. The modified polysaccharides significantly increased carboxyl content (190-452 meq/100gm of polysaccharides), glass transition temperature, and residual char, but decreased maximum degradation temperature. An IR spectra of modified polysaccharide

indicated the modifier was esterified with hydroxyl group of polysaccharide by the presence of a peak at 1732-1748 cm^{-1} .

In the second part of this work, pulp hand sheets were examined in the presence or absence of modified polysaccharide additives to obtain optimized additive dosage and pH, drainage rate, additive retention and charge density, tensile, bursting, tear and STFI index, inter-fiber bonding strength, gloss, roughness, storage modulus, contact angle, and morphology. It was found that at the optimum additive dosage of 1.5% and pH 4 & 8, the drainage rate increased 18%, additive retention 65% and the charge of density was 230 meq/100g of additive. The physical properties showed an increase of 40-52% for tensile index, 42-48% for bursting index, 38-46% for STFI index, 78-200% for inter-fiber bonding strength, and 160-227% for gloss; however, decreases of 16-19% in roughness and 15-33% for tear index were found. The *t*-Test value for the control and additive-treated pulp sheet were significant indicating that the results were reliable. The total ester bonds formed were found by titration to be 1.82-1.90 mmol/100g after the additive-treated pulp hand sheets were cured at 110 °C for 1.0 hour. For curing temperatures between 25 °C and 90 °C, no ester bond formation occurred. The storage modulus increased about 135.9%, but the loss modulus decreased by 21%. However, the dynamic contact angle of an OCC pulp sheet hand sheet was 46° at 20 seconds and 4.5° after 380 seconds; the modified additive-treated sheet was 106° at 20 seconds and 31° after 3,700 seconds. A peak was found at 1734 cm^{-1} , while high residual char and a rougher surface with smaller irregular fragments on the fiber surfaces were observed. These latter results indicate that the modified polysaccharide additive was cross-linked with the fibers via esterification. The physical properties of the modified polysaccharide

additive-treated pulp sheets were compared with commercial dry strength additives such as cationic starch, amphoteric starch, cationic polyacrylamide, and glyxolate polyacrylamide (g-PAM) and found to be significantly higher.

In addition, polyfluorinated cellulose nanocrystals was also prepared for hydrophobic paper packaging. The results supported their ability to deliver excellent hydrophobic properties and strong water repellency.

In the final part, decomposition of soy flour and modified soy flour (open-air conditions), antimicrobial activity of soy flour and corn starch, modified soy flour and modified corn starch, modified soy flour, and modified corn starch-treated recycle OCC pulp hand sheet were investigated. It was found that the soy flour began decomposing within 24 hours as evidenced by the detection of foul odors. A rank odor for the modified soy flour was not observed after nearly two years. Soy flour and corn starch significantly increased bacteria growth compared to the control sample, whereas the modified soy protein flour and modified corn starch showed strongly antimicrobial activities as corroborated by 100% bactericidal activity. In addition, an OCC pulp sheet did not show any antimicrobial activity, but modified soy flour and modified corn starch-treated OCC pulp sheet showed between 93-97% bactericidal properties compared to a control sample (OCC).

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Antimicrobial Test-AATCC 100.

APPENDICES

Appendix A

In this appendix, a number of valuable mechanical properties were obtained which are presented in the Tables and Figures through chapters 3-6.

Table A. 1. The mechanical properties obtained from polysaccharide-based dry strength additive-treated recycled OCC pulp hand sheets characterization.

Dry Strength Additive	Tensile Index (Nm/g)	Bursting Index (KN/g)	Tear Index (mN.m2/g)
No additive(control)	37.05	2.4	10.34
Soy Flour-DTPA-Chitosan	53.7	3.4	9.5
Soy Flour-Chitosan	50.15	3.0	8.15
Soy Protein Flour-DTPA-Chitosan	52.58	3.2	8.34
Soy Protein Flour-Chitosan	49.82	3.14	8.72
Soy Protein Flour	38.05	2.35	11.76
Soy Flour	37.9	2.4	11.54
Acid Hyd. Soy Protein Flour	36.9	2.2	9.6
Acid Hyd. Soy Protein Flour-Chitosan	49.55	3.13	7.9
Acid Hyd. Soy Protein Flour-DTPA-Chitosan	54.85	3.4	10.5
Acid Hyd. Soy Protein Flour-EDTA-Chitosan	54.03	3.3	8.7
Corn Starch	40.5	2.7	12.6
Corn Starch-Chitosan	50.26	3.2	7.83
Corn Starch-DTPA-Chitosan	57.6	3.6	10.17
Starch Nanoparticle	45.78	2.8	7.85
Starch Nanoparticle-Chitosan	49.77	2.96	7.1
Starch Nanoparticle-DTPA-Chitosan	55.26	3.11	6.04
Cellulose Nanocrystals	46.2	2.7	10.2
Cellulose Nanocrystals-Chitosan	50.8	3.2	10.9
Cellulose Nanocrystals-DTPA-Chitosan	53.5	3.5	9.8