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The Synthesis, Characterization, and Application of Polysaccharide-Based Additive To Improve Wet and Dry Strength and High-Barrier Properties of Paper Products

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THE SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF POLYSACCHARIDE-BASED ADDITIVE TO IMPROVE WET AND DRY STRENGTH AND HIGH-BARRIER PROPERTIES OF PAPER PRODUCTS

Cornellius Marcello, Ph.D.

Western Michigan University, 2024

Paper products play an essential role in our daily lives owing to their low cost, environment-friendly character, renewability, and recyclability. Paper manufacturers have been using petroleum-based strength additives (cPAM, GPAM, PAE) to meet the perceived needs of customers. On the other hand, paper produced from cellulose is hydrophilic and porous, leading to shallow water and grease resistance, causing paper manufacturers to use many kinds of coating materials such as poly-fluoroalkyl substances (PFAS) and synthetic plastic to improve water resistance, especially for food packaging paper products like cups, plates, food boxes, and packaging. However, PFAS are identified as likely carcinogenic to humans causing cancer, and petroleum-based synthetic polymers (strength and coating additives) are non-biodegradable, creating microplastic in drinking water which is considerably a significant health and environmental concern.

The goal of this Ph.D. thesis work is to develop a biodegradable bio-based paper strength agent (wet and dry) to replace the petroleum-based paper wet strengthening agents like polyamide epichlorohydrin (PAE) and glyoxylate polyacrylamide (GPAM), especially for the application of hygienic paper products. Furthermore, a bio-based coating material was formulated from the above bio-based paper strength agent by the addition of a hydrophobic agent to replace PFAS and petroleum-based non-biodegradable synthetic coating materials like polyethylene. The research results showed that synthesized bio-based paper strength additive significantly increased the wet and dry strength of paper products that are like commercial GPAM and PAE. Additionally, the synthesized bio-based coating materials casted film displayed very high strength and flexibility. The biobased coating-coated paper showed significantly increased water barrier properties, in which the goal is to close the gap to polyethylene-laminated paper bowl products.

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by

Cornellius Marcello

A dissertation submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
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1. INTRODUCTION

In this modern electronic age, the world appears to be trending toward a paperless society. However, there is still a long way to go before we can replace our dependence on paper products. Paper products such as plates, cups, napkin, toilet paper, office paper, tissue towels, and packaging/shipping boxes are used daily in significant quantities. In 2021, the global consumption of paper and paperboard totaled 408 million metric tons, with packaging having the largest share of paper production ***(Suzano, 2022).*** In the United States alone, around 70 million metric tons of paper and paperboard were produced last year ***(FAO, 2022).*** It is well-known that the environmental effects of the production of the paper include deforestation, the use of high amounts of energy and water, water and pollution, and landfill waste problems. With the need to conserve the forest and to meet the demand for paper, the industry has put a lot of effort into recycling. According to the AFANDA (American Forest & Paper Association), the recycling rate of paper climbed to 68%, and the recycling rate for old corrugated cardboard (OCC) will be 91% in 2021 ***(AFANDA, 2022).*** Ideally, consumers and businesses would send all their paper waste to a recycling plant to create an endless loop of reuse. Unfortunately, paper cannot be endlessly recycled. This is because the paper is made of cellulosic fibers. These fibers degrade each time they go through the recycling process. Cellulose fibers can change significantly when they are formed into a wet web of paper and subsequently are subjected to processes such as pressing, drying, printing, storage, repulping, and deinking ***(Hubbe, A. M.; Venditti, A. R.; & Rojas J. O., 2007).*** The drying process is accompanied by a partially irreversible closure of small pores in the fiber wall and increased resistance to swelling during rewetting ***(Hubbe, A. M.; Venditti, A. R.; & Rojas J. O., 2007)*** (Figure 1)**.**

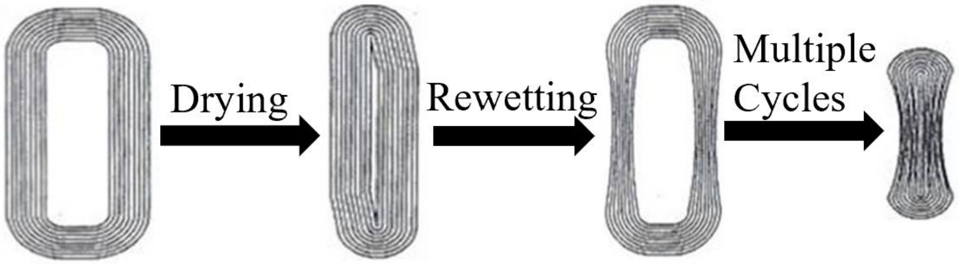


Figure 1*: Resistance to swelling due to repeated drying & rewetting cycles of cellulose fibers. (G.H.D. Tonoli, 2015)*

Additionally, the repeated drying and rewetting of the fibers result in the loss of swelling capacity of the fiber walls and results in a change in the fiber wall structure of the fibers (Figure 2).

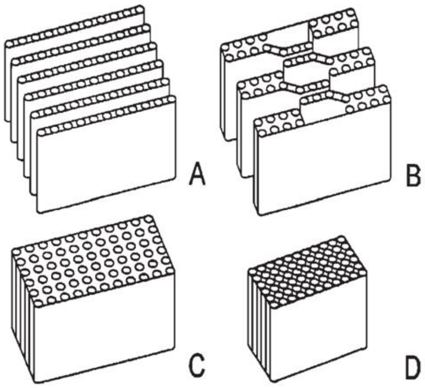


Figure 2*: Change in fiber wall structure due to drying and rewetting cycles of recycling.*

(Weise & Paulapuro, 1996)

This is also known as the hornification of fibers. This results in the stiffening of the fibers, which reduces their ability to form inter-fiber bonds ***(Scallan, A. M.; & Laivins, G.V., 2018).*** Inter-fiber bonding consists primarily of hydrogen bonds between the surface carbohydrate macromolecules of neighboring fibers. The extent of inter-fiber bonding depends on key factors such as the polysaccharide molecules, the presence of surface functional groups such as hydroxyl, carbonyl, and carboxyl, and the extent of surface contact between the fibers ***(Minor, L. J.; &***

Atalla, H. R., 1992). The loss of mechanical strength properties such as burst and tensile strength is often associated with the reduced extent of inter-fiber bonding.

Therefore, researchers are attempting to improve the mechanical properties of recycled paper, but we are still far from attaining the properties of virgin pulp ***(Mohammad, N. et. al., 2011).*** A few efforts have shown a chemical modification of fiber may prevent strength losses from occurring ***(Gruber, E.; & Weigert, J., 1998)***. For example, a chitosan-complex starch nanoparticle was made to improve the physical properties of recycled pulp ***(Salam, A.; Lucia, L; Jameel, H., 2018)***, while mechanical and chemical treatments may improve the strength properties of OCC pulp sheet ***(Laivins, J. V.; & Scallan, A. M., 1996)***. The difference between the above-developed bio-based paper strength additives and commercial petroleum-based paper strength additives (GPAM and PAE) is that these bio-based paper additives only improved the dry strength of paper products, but GPAM and PAE improved both wet and dry strengths.

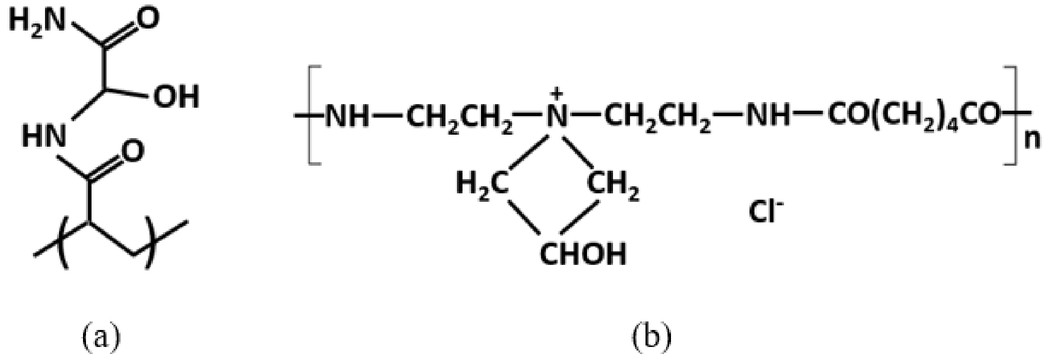


Figure 3: Chemical structure of (a) GPAM and (b) PAE.

Petroleum-based paper strength agents such as glyoxylate polyacrylamide (GPAM) and polyamide epichlorohydrin (PAE) shown in Figure 3, are widely used to improve paper products' wet and dry strength properties ***(Yuan, Z.Y.; & Hu, H., 2012)*** ***(Obokata, T.; & Isogai, A., 2007).*** The widespread use of petroleum-based non-biodegradable and water-soluble paper-strength agents in the papermaking industry has raised environmental and health concerns and prompted efforts toward developing alternatives ***(Corre, D. L.; Bras, J.; Dufresne, A., 2010).***

Another petroleum-based product that has become part of our daily lives is plastics. Petroleum-based plastics are artificial organic polymers obtained from natural gas or oil. Industrialization resulted in rapidly increasing rate of plastic production, from 1.7 million metric tons in 1950 to 322 million metric tons in 2015 ***(PlasticsEurope, 2021).*** This number rises to 335, 348, and 359 million metric tons in the consecutive years ***(PlasticsEurope, 2021).*** Even though plastics can be fragmented, they cannot naturally break down due to their profound stability. Even degradable plastic materials can last for many years to break down and are usually highly dependent on environmental circumstances such as temperature, oxygen, and UV light exposure ***(Hopewell, J.; Dvorak, R.; Kosior, E., 2009).*** Plastics are usually categorized depending on their sizes. Larger-sized plastic materials ranging from 2.5cm to 1.0m, usually refer to as microplastic, include items such containers, bottles, and plastic toys ***(Cole, M.; et al, 2011).***

Mesoplastics are large virgin plastic resin pellets, usually in the 5-10mm range ***(Isobe; et al, n.d).*** Microplastics are small plastic fragments, smaller than 5mm, derived from the breakdown of macroplastics ***(Cole, M.; et al, 2011).*** In this research, we are targeting to provide a possible alternative for the microplastics that are causing environmental and human health issues through commodity products and packaging materials. Researchers have found that regularly used plastic packaging materials are microplastics to our food and drinks in various ways ***(Ekta, B. J.; et al, 2021)***. This has become an increasingly concerning issue because everyone, including infants to oldsters, directly consumes microplastics with or without their knowledge.

Therefore, this research work attempts to develop new bio-based paper strength and coating additives that will improve the wet and dry strength and provide high barrier coating properties for paper products. In the present investigation, polysaccharides (starch and chitosan) will be used as the bio-based raw materials. The corn starch will be modified with 2-chloroacetamide ($ClCH_2$-$CONH_2$) in the presence of sodium hydroxide in an aqueous medium. The reaction conditions such as the effect of chloro-acetamide concentration, reaction time and temperature, and the materials-to-liquor ratio will be optimized based on the percent of acetamide groups (-$CONH_2$) that will be incorporated into the starch molecule (see Figure 4) ***(Li, S.; et al, 2011)***.

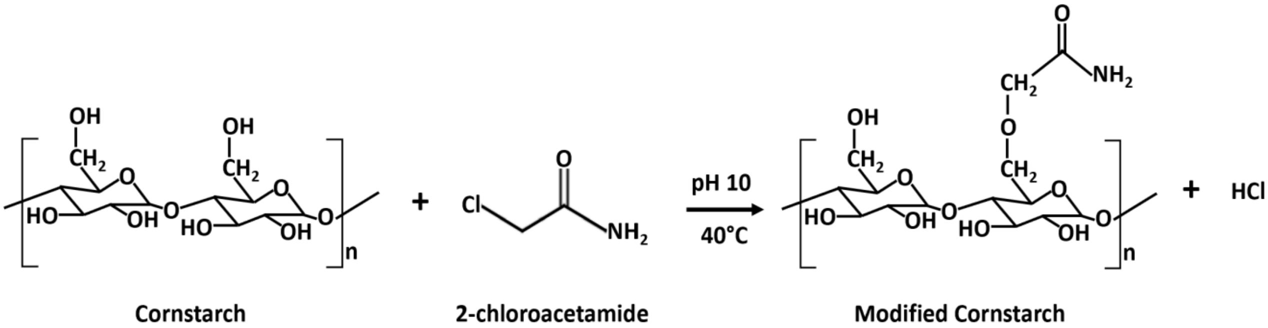


Figure 4*:* Etherification reaction of cornstarch with 2-chloroacetamide.

The modified starch will be dissolved and reacted with formaldehyde in an aqueous medium to produce *N*-hydroxymethyl starch-amide-based permanent wet strength additive. It is expected that the reactive hydroxyl groups of *N*-hydroxymethyl starch-amide may contribute to improving covalent bonding among OCC pulp fibers like commercial permanent paper wet strength agent polyamide epichlorohydrin (PAE). Similarly, a part of the modified starch will be dissolved and reacted with glyoxal in an aqueous medium to produce a temporary wet strength additive, glyoxylate starch amide. It is expected that the reactive aldehyde group of glyoxylate starch-amide may contribute to improving hemiacetal bonding (ether bond) among OCC pulp fibers like commercial temporary paper wet strength agent glyoxylate polyacrylamide (GPAM). In addition, chitosan will be dissolved in acetic water and reacted with glyoxal to produce glyoxylate chitosan-based temporary wet strength additive with antimicrobial activity. The strength properties (wet and dry) of *N*-hydroxymethyl starch-amide-treated paper sheets, glyoxylate starch-amide-treated paper sheets, and glyoxylate chitosan-treated paper sheets will be determined and compared to commercial GPAM and PAE-treated paper strength properties. To characterize the modified starch, acid-base titration, degree of etherification, and degree of substitution, infrared spectroscopy (ATR-IR), SEM, XRD, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) will be used.

Furthermore, *N*-hydroxymethyl starch-amide and glyoxylate starch-amide will be blended with different types of hydrophobic agents (AKD, Zein, and PDMS) separately to produce a bio-based high-barrier coating additive. The barrier properties of biobased coating-coated paper sheets will be determined and compared to synthetic plastic-coated paper sheet properties.

2. LITERATURE REVIEW

2.1 Paper sheet and OCC grade

Paper is generally known as a thin sheet material produced by mechanically and chemically processing lignocellulosic fibers that are derived from wood, grasses, or other vegetable sources in water through a fine mesh, leaving the fibers evenly distributed on the surface, and then followed by pressing and drying. The term lignocellulose refers to plant biomass that consists of cellulose, hemicelluloses, and lignin. The carbohydrate polymers cellulose and hemicellulose are tightly bound together to the lignin (***Brautaset, T.; & Elllingsen, T. E., 2011).*** Paper can be manufactured using two methods: chemical pulping or mechanical pulping. The papermaking process consists of two parts; the first part is the treatment of materials and includes processes such as converting wood chips to pulp, washing and bleaching, refining, beating, and sizing; the second part is forming the paper sheet in a Fourdrinier machine ***(Salim, H., 2016)*** (see Figure 5)**.**

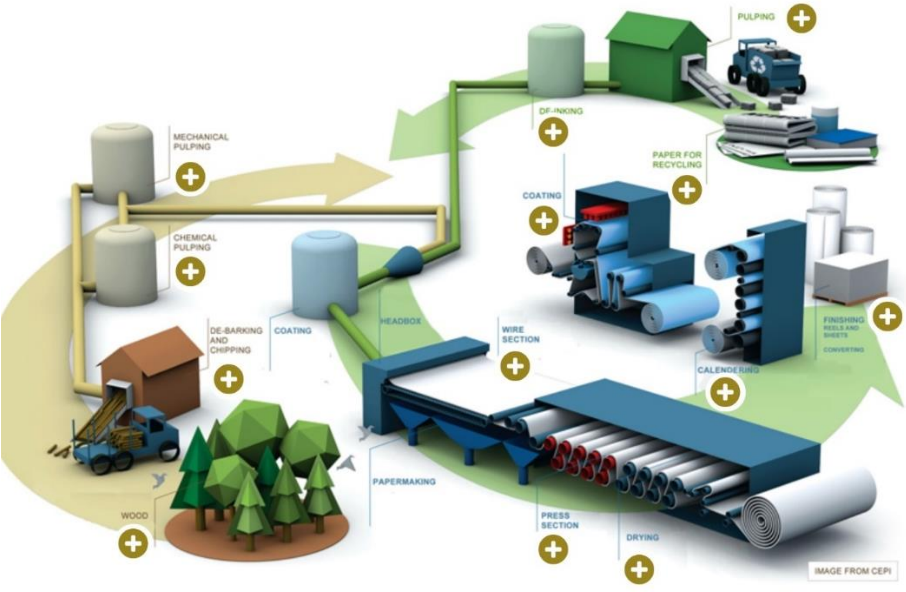


Figure 5: Overview of the papermaking process, from wood to paper. Source: Confederation of Paper Industries

The number one use of paper is as a packaging material ***(Suzano & AFRY, 2023).*** The corrugated boxes handle the pressure from stacking very well, which makes them ideal for shipping. Post-use corrugated packaging material is commonly known as OCC containers. Its multiple-layer structure very easily recognizes them (see Figure 6). A wavy middle layer keeps the cardboard light but also provides it the strength to carry products. If kept clean, the recycling of OCC is a straightforward process. On average, a corrugated box contains roughly 50% recycled fibers ***(Hellobaler China, 2017).*** A corrugated box is widely used for shipping and food packaging because of its strength, lightness, durability, recyclability, and cost-effectiveness ***(Singh, S. P.; & Burgess, 2001).***

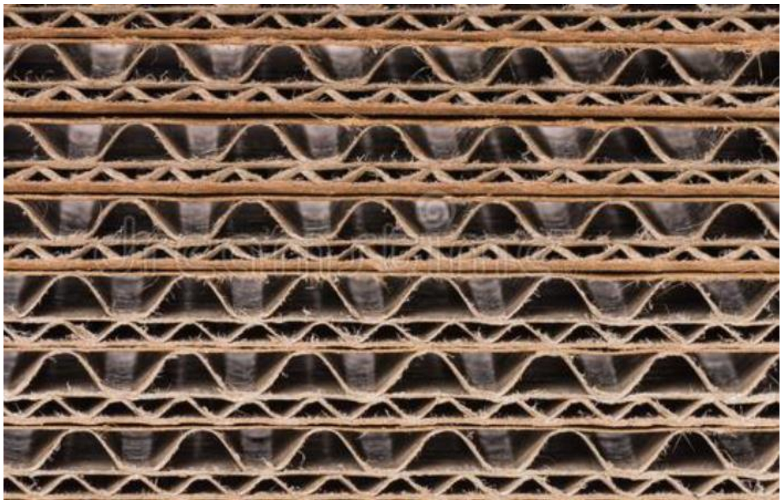


Figure 6: Side view image of OCC.

Source: https://www.dreamstime.com/photos-images/corrugated-cardboard-side.html

2.2 Cornstarch

Cornstarch is a carbohydrate that is composed of glucose repeat units formed through dehydration reactions in the cell wall. Cornstarch is generally comprised of 30% amylose and 70% amylopectin, where amylose is a linear-chain polymer with α-(1,4)-glycosidic linkage, and amylopectin is a branched-chain polymer with α-(1,4) and α-(1,6)-glycosidic linkage in the backbone chain ***(Jenkins, P. J.; & Donald, A. M. J., 1995).*** The main functional group present in the glucose repeating unit of cornstarch are hydroxyls (-OH) (See Figure 7) which may be easily derivatized through chemical modification ***(Haq, F.; et al, 2019).***

Starch, in general, is often used in the paper industry as a surface sizing agent to achieve desired smoothness, gloss, and quality of printing ***(Sharma, M.; et al, 2020).***

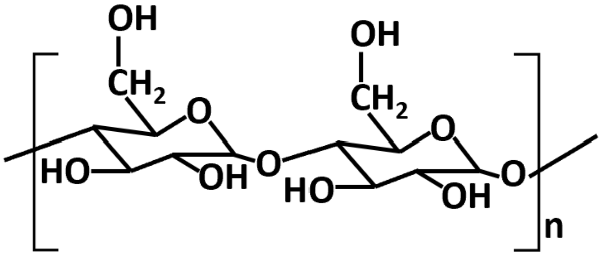


Figure 7: Chemical structure of cornstarch.

2.2.1 The chemical properties of cornstarch

As shown in Figure 7, the glucose monomer constitutes of three hydroxyl groups. The polyhydroxyl functional groups are found on C-2, C-3, and C-6 which are free from the α-(1,4)-glycosidic linkage and pyranose ring formation. The hydroxyl group at the C-2 and C-3 locations are secondary alcoholic groups while the C-6 hydroxyl group is a primary alcohol. In general, alcoholic groups are classified as weak acids, and the acidity of alcohol decreases from primary, to secondary, to tertiary alcohol ***(John I. B. & Larry K. B., 1970).*** Due to its pyranose structure, the ether bond (C-O-C) in the ring is stable and not very reactive unless in acidic or basic conditions at elevated temperatures. This is similar for the glycosidic linkages. In addition, the polymer is densely packed with intra- and intermolecular hydrogen bonds. This results in the C-6 hydroxyl group to be the most susceptible to chemical interaction, followed by hydroxyl groups on C-2 and C-3 ***(Tomasik, P. &Schilling, C.H., 2004)***.

2.3 The modification of cornstarch

The modification of cornstarch has been done since the 1940s. The introduction of new functionality in the starch is called chemical modification of cornstarch. The new functionality refers to the newly added functional groups such as acetyl, amine, amide, carboxyl, or any other functional groups which gives additional functional properties to the starch ***(Wang, L.; et al, 2016)***. Even though there are many various methods to modify starch, some of the most important methods include cross-linking, esterification, and etherification ***(Chen, Q.; et al, 2015)***. Starch and modified starch are commonly used in various industries such as food, paper, textile, mining, and cosmetics. Other notable modifications of starch include grafting and dual modification of starch. Products of such modifications are typically used in water treatment, usually for the removal of heavy metals and dyes from water.

2.3.1 Cross-linking of cornstarch

Cross-linking is the phenomenon of connecting two polymer chains by the formation of chemical bonds (covalent bond) ***(Arora, B.; et al, 2017)***. Epichlorohydrin (EPI), $POCl_3$, citric acid, and glyoxal are the most familiar cases of cross-linking agent. Epichlorohydrin is a highly reactive electrophilic compound which allows it to react with alcohol, salts, and fatty acids. This results in the wide use of epichlorohydrin to produce vinyl polymers, food flavoring agents, polyurethane plasticizers, and PAE (polyamide-epichlorohydrin) However, it is worth noting that in the present, epichlorohydrin is widely labelled as an irritant and carcinogen ***(Hajipour, F.; Ahadi, E. M.; Firoozpour, L., 2024)***.

Jyothi et al. crosslinked cassava starch by epichlorohydrin and catalysts and increased the water binding capacity of the starch which results in an increase in the gelatinization point of starch ***(Jyothi, A. N., et al, 2006)***.

Guo et al. prepared cross-linked porous starch by crosslinking with epichlorohydrin and followed by hydrolysis with α-amylase enzyme. This cross-linked porous starch was used for the removal of methylene blue from water and was found to be safe and biodegradable ***(Guo, L., et al, 2013)***.

Singh, V. & Nath, L. K. cross-linked sago starch with $POCl_3$ which resulted in a highly substituted cross-linked starch phosphate having higher thermal stability and swelling behavior ***(Singh, V. & Nath, L. K., 2012)***.

Reddy et al. cross-linked starch films with citric acid to improve their tensile strength and thermal stability and to decrease their dissolution in water and formic acid ***(N. Reddy and Y. Yang, 2010)***.

According to patent US5032683A, directly adding aqueous glyoxal to starch dispersion/various starch blends at temperatures of at least 70ºC forms cross-linked starch which has coatable viscosity. The resulting starch film provides a film with good strength and elongation properties (Source: US5032683A, Omnova Services Inc.).

2.3.2 Esterification of cornstarch

Esterification of starch can be carried out with acids and their derivatives due to the presence of large number of hydroxyl groups in starch. To obtain product with high degree of substitution, the reaction should be carried out in organic solvent ***(Chen, Q.; et al, 2015)***.

Zarksi, A. et al. esterified potato starch with 1-butyl-3-methylimidaolium chloride and lipase as a catalyst. The maximum DS was found to max out at 0.22 (60ºC, 4hours). The product was used for the treatment of biodegradable packaging ***(Zarksi, A.; et al, 2016).***

Zuo, Y. F. et al esterified cornstarch with malic anhydride. The product is further treated with PLA to form a high tensile strength and bending strength composite ***(Zuo, Y. F.; et al, 2015)***.

Grano, H. et al esterified starch betainate (a cationic starch derivative) with betainyl chloride and the product was found to greatly increase the strength of paper ***(Grano, H.; et al, 2000)***.

2.3.3 Etherification of cornstarch

The etherification of cornstarch is divided into four parts and is on the basis of product obtained: non-ionic, anionic, cationic, and amphoteric etherification.

Shi, Y., Ju, B. & Zhang, S. synthesized a tertiary amine starch ether by reacting 2,4-bis(dimethylamino)-6-chloro-[1,3,5]triazine with cornstarch. This non-ionic starch ether was used as a flocculating agent for the removal of dye ***(Shi, Y., Ju, B. & Zhang, S, 2012)***.

Carboxymethyl starch is the most important anionic starch and is found to be a useful flocculant in wastewater treatment. Yanli et al prepared carboxymethyl starch by reaction of starch with monochloroacetic acid in the presence of sodium hydroxide ***(Yanli W.; et al, 2009)***.

Cationic starch is an example of a product of cationic etherification of starch. Cationic starch is produced by reacting starch with reagents containing amino, ammonium, or sulphonium/phosphonium groups ***(Wurzburg, O. B., 1986)***. Cationic starches are commonly used in the papermaking and water-treatment industry due to their effective flocculating property.

Amphoteric starches are generally prepared by reacting starch with sulfate, phosphate, and carboxyl groups to provide anionic functionality, while the cationic groups are typically quaternary ammonium or tertiary amino groups ***(Chen, Q.; et al, 2015)***. Amphoteric starch is an excellent flocculating agent because it can remove both cationic and anionic impurities simultaneously.

2.3.4 Using chloroacetamide to modify cornstarch

In this study, the modification of cornstarch is achieved through reaction with chloroacetamide. Chloroacetamide is a reactive nucleophile due to its chlorine atom. The proposed reaction mechanism for the modification of cornstarch with chloroacetamide is via an S_N2 reaction pathway as shown in Figure 8 below. As discussed in section 2.2.1, the C-6 hydroxyl group is the most receptive to chemical interaction. Since the hydroxyl group on C-6 is a primary alcohol hydroxyl group, it is unlikely to form a carbocation on its own. This implies that the substitution reaction will most likely to undergo S_N2 reaction pathway ***(Abdel-Latif; et al, 2019)***. The chlorine group found in the chloroacetamide molecule is highly electronegative. This means that the chlorine shifts the electron cloud towards itself and causes the Carbon atom attached to it to have a partial positive charge. This induced partial positive charge allows the Oxygen atom from the C-6 hydroxyl group to interact with the partial positive charged Carbon. The interaction shown in (1) results in the sharing of electron between Oxygen and Carbon, resulting the Oxygen to carry a positive charge as shown in (2). Due to Oxygen having a much higher electron negativity than Hydrogen, and Hydrogen having a high tendency to lose electron, the positively charged Oxygen atom will draw an electron from the H atom attached to it to regain an electron and balance the positive charge and regain its stability. The resulting positively charged Hydrogen will easily accept an electron from the negatively charged chlorine as shown in (2) and will stabilize their charge and form H-Cl as a byproduct as shown in (3).

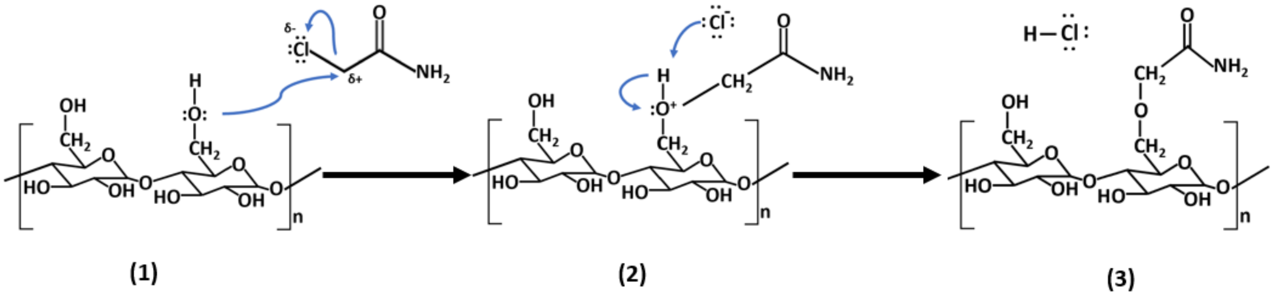


Figure 8. Proposed reaction pathway for the modification of cornstarch with chloroacetamide.

2.4 Chitosan

Chitosan is the world's second most abundant biopolymer ***(Muhd, A. A.; &Farhana, A., 2019)*** after cellulose. Chitosan is the main derivative of chitin (see Figure 9), and it has been industrially used due to its wide applications. In today's papermaking industry, chitin/chitosan has gained significant interest due to its chemical structure and properties ***(Zhaoping, S.; et al, 2018).*** Wet-end applications of chitin/chitosan include retention or drainage agents, also as potential wet and dry strength agents. Its good film-forming properties allow it to be used as a surface coating as well. Because its chemical structure contains reactive amino groups and hydroxyl groups, chitosan has the potential to form hydrogen bonds with the fibers if they are sufficiently close enough, which also adds to the development of paper strength.

A study from 2002, performed by Lertsutthiwong, P. et al found that chitosan can be used as dry strength additive in neutral, acidic, or alkaline conditions depending on the system requirements ***(Lertsutthiwong, P. et al, 2002)***. More recent studies showed that there is a synergistic effect when chitosan is used with other products such as CMC and this become a more common practice to achieve desired cellulosic fiber network strength properties ***(Fatehi P.; et al, 2010)***.

Khantayanuwong et al found that treating handsheets with 0.5 o.d. wt.% chitosan improves most mechanical properties of handsheets such as bursting index, folding endurance, tensile index, and modulus of elasticity, but found minimal impact on tearing strength ***(Khantayanuwong S., Khemarom C., Salaemae S., 2017)***. In a separate study, Hamzeh Y. et al used chitosan with polyvinyl alcohol (PVA) to improve both wet and dry tensile of OCC furnish ***(Hamzey, Y.; et al, 2013)***. Other studies include forming xylan/chitosan complex ***(Mocchiutti P; et al, 2016)***, CMC/chitosan complex ***(Wu T., & Farnood R, 2014)***, maleic anyhydride acylated chitosan ***(Chen***

Z.; et al, 2013), and soy flour/chitosan dual system complex ***(Arboleda J.C; et al, 2014)*** have been prepared to enhance paper strength. All these complexes were found to be potential strength agents in the paper industry. The combination of chitosan and bentonite is more commonly observed in wet-end additive systems. It was suggested that the bentonite functions as a bridge between chitosan molecules which allows it to behave like a higher molecular weight polymer ***(Ashori, A.; et al, 2013).*** The increase in wet and dry strength of chitosan-treated paper is due to the interaction of the hydroxyl groups of chitosan forming hydrogen bonds with the weakly polar areas of the fiber surfaces ***(Adel A.M; et al, 2014)***. The film-forming potential of chitosan also promotes Van der Waals forces between fibers and further facilitates hydrogen bonds to occur ***(Adel A.M; et al, 2014).***

In addition to the above, chitosan derivatives also provide anti-microbial and antibacterial properties to the paper. The polycationic nature of the chitosan macromolecule disrupts the equilibrium dynamics of microbes resulting in the inhibition of microbial growth ***(Anahita, R. S.; Mina, S.; Azadeh, B., 2019).*** Proven anti-microbial activity and its ability to increase the mechanical resistance of pulp products make chitosan derivatives an excellent choice as a wet-end additive. Such derivatives are commonly used in food wrappers, sanitary paper, and hospital papers. Biopolymers such as chitosan, chitin, and cellulose are highly important polysaccharides because of their readily available massive quantities, low cost of manufacturing, and wide distribution ***(Rohan, S. D.; et al, 2018)***.

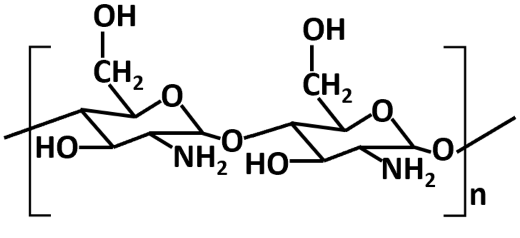


Figure 9: Chemical structure of chitosan.

2.5 GPAM

GPAM, which is short for glyoxalated polyacrylamide, is used in a variety of paper grades to provide with dry and temporary wet strength. As its name suggests, it is formed by reacting polyacrylamide (PAM) with glyoxal, shown in Figure 10.

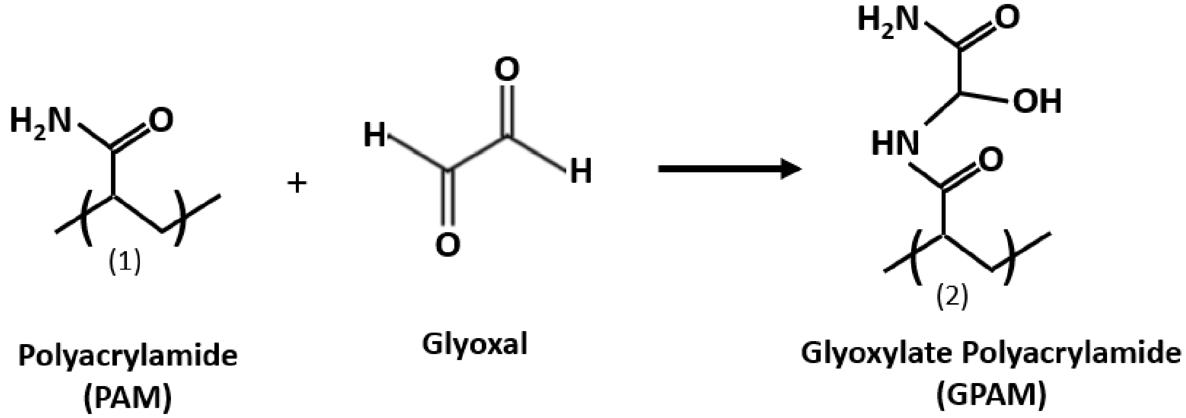


Figure 10: Chemical reaction of PAM with glyoxal.

Source: https://patents.google.com/patent/US7119148B2/en

According to the patent by inventors Cornel. H. et al., the reaction is as shown above where glyoxal (CHOCHO) reacts with pendant amide groups on the polyacrylamide backbone (1) according to the following reaction to produce a polyacrylamide having a pendant glyoxalated group (2). A second reaction involves the so-formed aldehyde moiety on the polymer backbone with another amide group, such as belonging to another macromolecule and leads to building molecular weight and cross-linking ***(Cornel, H.; et al, 2004).*** Although polyacrylamide is considered low toxicity, its precursor acrylamide is classified as a neurotoxin and carcinogen ***(Herth, G.; et al, 2015).*** Thus, it is natural that many would think of the possibility that polyacrylamide is contaminated with acrylamide and are concerned when the polymer is intended to be used in daily products and near food. Studies also find that polyacrylamide is only partially biodegraded by the action of amidases and produces ammonia and polyacrylates. Polyacrylates are generally considered difficult to biodegrade because only a select few soil microbes can degrade them ***(Nyyssölä, A.; & Ahlgren, J., 2019).***

2.6 PAE

Polyamide epichlorohydrin is a water-soluble cationic thermosetting resin. It is formed through a polymerization reaction between epichlorohydrin and polyalkylamide in an aqueous solution. The reaction of a polyamide (with secondary amine) with epichlorohydrin is shown in Figure 11 below.

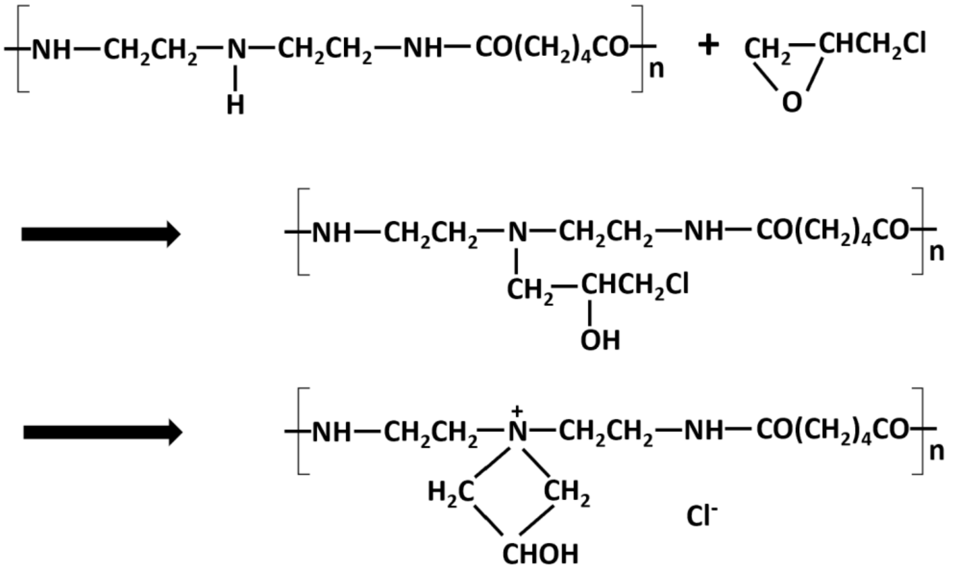


Figure 11: Polymerization reaction of polyamide with epichlorohydrin.

Source: https://patents.google.com/patent/EP0515750A2/en

PAE is intended to be used as a permanent wet strength additive, and it requires a high curing temperature (105°C) to be effective ***(Chan, L. L., 1991).*** According to the CDC, prolonged exposure to epichlorohydrin typically harms organs such as the eyes, skin, liver, kidney, respiratory system, and reproductive system.

2.7 Paper strength and common paper strength agents

The strength of paper is generally divided into two domains; dry strength and wet strength properties. Paper is formed when fibers come together due to the interactions between the fibers. Many factors, such as the strength of the individual fibers, the bonded area, the strength of inter-fiber bonds, and the distribution of the fibers and bonds, inherently result in the dry strength of the paper when the paper is dried ***(Marton, J., 1996)***. The dry strength of the paper is essential because it gives it the ability to withstand mechanical stress, especially for applications such as packaging, wrapping, or sealing. The primary contributor to this kind of resistance can be attributed to the number of hydrogen-bonds or ionic and covalent bonds that formed during the sheet formation process. There are several ways to increase the dry strength of the sheet, and one of the most convenient ways is the addition of dry-strength additives. It is also common for wet-strength additives to contribute to the dry strength of the sheet. Commercial paper strength agents such as cationic polyacrylamide (CPAM), anionic polyacrylamide (APAM), and glyoxylate polyacrylamide (GPAM) are commonly used in a variety of paper, cardboard, tissue, and paper towel grades to increase the dry strength of substrate but these commercial paper strength agents are petroleum based and non-biodegradable. Table 1 below shows some common paper strength agents ***(Vladimir, G. et al, 2012)***.

Table 1: Common paper strength agents.

Common Paper Strength Agents	Form of Delivery	Mode of Addition	Dry Strength	Wet Strength
Natural Polymers				
Native Starch	Dry	Surface	Yes	No
Cationic Starch	Dry	Wet end or surface	Yes	No
Carboxymethylcellulose (CMC)	Dry	Wet end	Yes	No
Synthetic Resins				
Glyoxylate Polyacrylamide (GPAM)	Liquid	Wet end	Yes	Yes (temporary)
Cationic Polyacrylamide (CPAM)	Liquid	Wet end	Yes	No
Anionic Polyacrylamide (APAM)	Liquid	Wet end or surface	Yes	No
Amphoteric PAM	Liquid	Wet end	Yes	No
Polyamide Epichlorohydrin (PAE)	Liquid	Wet end	Yes	Yes (permanent)

The wet strength of the paper is a measure of how well the web of fibers holding the paper together can resist a force of rupture when the paper is wet. A wet tensile value of 15% or higher results in a paper being considered a high-wet strength paper ***(Neimo & Leo, 1999).*** A significant example of the importance of both dry and wet strength is household tissue paper grade. The tissue paper needs sufficient dry strength to withstand the stress when being pulled apart from another sheet or its container and sufficient wet strength so that it can be used to absorb liquids and clean surfaces and then eventually break down after prolonged exposure to water/liquids.

2.8 Plastic (microplastics) as food packaging material

Petroleum-based plastics are widely used as packaging materials and are commonly made up of thermoplastic resins. Plastics are intensively used as packaging material all over the world because it can be easily molded and be used in a wide variety of products ***(Harshita, G., 2020).*** Table 2 below lists several common plastic polymers that are used for making food containers, and each of these plastic polymers has different hazardous physical and chemical properties. In addition to food containers, disposable paper cups are usually composed of a high-grade paper board that is lined with a polyethylene coating on the inner surface, and is extensively used in daily life.

Table 2: Commonly used polymers for plastic food containers ***(PlasticsEurope, 2020)***

Polymer Type		**Packaging Application**
PP	Polypropylene	Food packaging, sweet and snack wrappers, hinged caps
HDPE	High-density polyethylene	Milk bottles
LDPE	Low-density polyethylene	Food packaging film, food containers, and trays
PS	Polystyrene	Dair and fishery food packaging
PET	Polyethylene terephthalate	Water bottles, soft drink cartons, and juice containers

Due to the rising concern of microplastic consumption, many researchers have come up with different ideas to provide an alternative to petroleum-based plastics. Several bioplastics were studied with their fabrications or modifications using nanocomposites to improve their functionality ***(Jariyasakoolroj, P.; et al, 2020).*** Other efforts include modifying and utilizing processed food by-products, including fruits, vegetables, and grains, to form nanocomposites to make bioplastic. However, natural bioplastics are still lacking in moisture sensitivity, water vapor permeability, and water solubility ***(Grujić, R.; et al, 2017).*** This has become a challenge for researchers to modify bioplastics to overcome these limitations. Some researchers are also exploring using protein-based films and coatings as an alternative to plastics ***(Chen, H.; et al, 2019).***

2.9 Environmental impacts

Another important aspect to compare between GPAM vs Glyoxylate Starch Amide (GSA), and PAE vs N-hydroxymethyl acrylamide is their impact to the environment. Even though most of the materials listed above are either generally recognized as safe, or FDA approved for certain uses at certain amounts, it is worth mentioning that epichlorohydrin and formaldehyde are both volatile and considered hazardous. Epichlorohydrin is toxic and may cause cancer and mutations. Although it is highly toxic to humans, epichlorohydrin is not expected to bioaccumulate in and persist in the environment. This is because in water, epichlorohydrin breaks-down by both biological and non-biological means. Formaldehyde vapor is toxic and may cause severe respiratory tract and skin irritation ***(CDC)***. Formaldehyde is a naturally occurring substance that can be found in nature and the human body. Minimum amounts of formaldehyde are even present in grains and cheese to kill pathogens. Even though it is a naturally occurring substance, it can still be harmful. Because it is volatile, its vapor readily breaks down into formic acid and carbon monoxide, which can contribute to acid rain and smog. Formaldehyde is rarely found in drinking water because it readily biodegrades in air, water, and soil by both aerobic and anaerobic conditions. Polyacrylamide is not significantly toxic to humans and the environment but the acrylamide monomer used for its synthesis is known to be absorbed through food contamination or dermal exposure and result in damages to organs, the nervous and reproductive systems, cause cancer, and found to cause oral cavity in animal studies ***(Int. J. Toxicity, 2004)***. Due to its high water solubility, it is expected that acrylamide is found in water and leaching from soil to groundwater. Acrylamide was found to be biodegradable in surface water and sediments but may not biodegrade in ground water and is persistent in aquatic environments. The short-term impacts include death of animals such as birds or fish, and death or slow growth rate of plants. The long term or chronic effects on aquatic life after several exposure include shorter lifespan, reproductive problems, and changes in appearance and behavior. There is no long-term data reported on acrylamide on plant, birds, or land animals.

2.10 Market size and economic analysis

According to a study reported by Zion Market Research, the global polyacrylamide (PAM) market size was valued at USD 5.39 billion in 2022, or 2.3 million metric tons. Ignoring any other factors, this suggests an average selling price of USD 2344/ton. In their report, it is projected that this market size will continue to grow with a compound annual growth rate of 8.34% to USD 10.23 billion, by the end of 2030. The largest drivers of this sector are the water treatment industry (about 38%), followed by the oil and gas industry (about 30%), papermaking (about 20%), and the rest by combined other applications. These number suggests that the global polyacrylamide market is valued at approximately USD 1.1 billion. In another report, by GrandViewResearch, the US polyacrylamide market size for 2023 was estimated to be about USD 0.75 billion and is projected to have a compound annual growth rate of 3.6% until 2030, which is more conservative. In papermaking, anionic, cationic, and non-ionic polyacrylamide can be used as flocculating agents for drainage and retention aids, and to develop dry strength in the finished paper product. The global epichlorohydrin market was valued at $2.73 billion in 2021, and is expected to reach $4.52 billion by 2029, growing at a compound annual growth rate (CAGR) of 6.50% from 2022 to 2029 ***(imarcgroup, & straitsresearch)***. The market volume was about 2.16 million metric tons in 2022, and is forecast to grow to about 2.91 million metric tons worldwide by 2030 ***(imarcgroup, & straitsresearch)***. The estimated average selling price of epichlorohydrin is USD 1264/ton.

Additionally, VerifiedMarketReports reported that the market size of polyamide epichlorohydrin resin (PAE) was valued at USD 2.39 billion in 2023 and is projected to grow to USD 3.9 billion by 2030, with a compound annual growth rate of 6.65%. PAE resin is well-known for their diverse adhesive and cross-linking characteristics. In papermaking, PAE is an excellent wet strength resin that improves dimensional stability during handling, and provides water resistance to paper which allows paper products to be used as packaging ***(VerifiedMarketReports)***.

More information on market pricing was reported by imarc, the price of polyacrylamide can vary widely depending on location. Although not specific to glyoxalated polyacrylamide, the report states that the price of polyacrylamide in December 2023 were: USA – USD 2680/MT, China – USD 1135/MT, Germany – USD 3670/MT. Although the approximate price of PAE was not stated in the report, the price of epichlorohydrin, which is one of the materials needed to synthesize PAE, was estimated to be about USD 1849/MT in the USA, and can range from USD 1166-2639/MT depending on the geographical location.

The market size of cornstarch was valued at USD 20.42 billion in 2022 and is expected to grow to USD 40.14 billion by the end of 2031 with a compound annual growth rate of 7.80% ***(straitsresearch)***. The main drivers are the Food&Beverage (F&B) industry, pharmaceuticals, and paper industry. In terms of tonnage, the cornstarch market size was approximately 86.4 million metric tons in 2023. This is further divided into three roughly equal portions; native starch, modified starch, sweeteners ***(straitsresearch)***. This suggests that native cornstarch was responsible for about 29 million metric tons of the cornstarch market size. Although it is a huge shortcut, dividing the USD market value (USD 20.42 billion) of cornstarch by the tons produced (86.4

million tons), would suggest that the average selling price of cornstarch, regardless of grade and application, was approximately USD 236/ton. According to Research Insights' report, the global Cationic Starch market size was valued at USD 1.61 billion in 2023. With growing demand in downstream market, the Cationic Starch is forecast to a readjusted size of USD 2.23billion by 2030 with a CAGR of 4.8%. There are no explicit data on the valuation of the chloroacetamide market size and global usage volume. Several market research institutions (Insightful Market Research, Verified Market Reports, Market Research Intellect, SouthEast News Channel) reports a growing chloroacetamide market. The main drivers are organic synthesis, preservatives, and pharmaceuticals. It is also reported that chloroacetamide market is growing due to new technologies and discoveries adding significant value, but also face some challenges due to consumer preference and government regulations. The global glyoxal market was valued at $1.46 billion in 2022, and is expected to grow to $2.25 billion by 2032, with a compound annual growth rate (CAGR) of 4.4% ***(factmr)***. An estimated 3.6 million metric tons of glyoxal was produced in 2023. These numbers suggest an average selling price of USD 406/ton. Oil & gas industry is the largest driver for glyoxal end-use applications, the paper industry only holds about 15% of the market share, approximately USD 300 million, in 2023 ***(factmr, markets&research)***. The formaldehyde market is also projected to grow from USD 7.5 billion in 2022, to USD 12.88 billion by the end of 2032 with an annual compound growth rate of 6.20% ***(factmr, markets&research)***. The global demand for formaldehyde was 23 million metric tonnes in 2022. These numbers suggest an average selling price of USD 326/ton. Although the market share is divided into numerous applications (i.e furniture, construction, research, pharmaceutics, manufacturing), the paper industry is not viewed to hold a significant share.

Since all the materials involved are projected to have a CAGR of approximately 4-8%, it is likely that there will be sufficient material supply. A rough financial analysis is performed in the next section to provide an impression of the feasibility of the developed technology in this work. Using all the estimated numbers discussed above, Table 3 shows that there is a potential savings of USD 1127/ton from the material costs when comparing GPAM to glyoxylate starch amide. Table 4 shows that there is a potential savings of USD 1188/ton from the material costs when comparing PAE to N-hydroxymethyl starch amide. Although these calculations show potential savings, there are other factors to consider as well since the polysaccharide-based additives increases the number of materials handled and processed from two materials, to three materials. More in-depth financial evaluation is required to draw a final economic feasibility conclusion.

Table 3: Material cost comparison between GPAM and glyoxylate starch-amide.

	GPAM		Glyoxylate Starch Amide		
Material	Polyacrylamide	Glyoxal	Cornstarch	2-chloroacetamide	Glyoxal
USD per MT	2344	406	460	1000	406
Ratio	1	1	1	1	0.4
Material Cost per MT, USD	2750		1622.4		
Assumptions: Polyacrylamide and glyoxal ratio of 1:1 Chloroacetamide price used was based of a vendor in China					

Table 4: Material cost comparison between PAE and N-hydroxymethyl starch-amide.

	PAE		N-hydroxymethyl Starch Amide		
Material	Polyamido resin	Epichlorohydrin	Cationic Starch	2-chloroacetamide	Formaldehyde
USD per MT	1650	1264	650	1000	326
Ratio	1	1	1	0.75	1
Material Cost per MT, USD	2914		1726		

Assumptions:
Polyamido resin and epichlorohydrin ratio of 1:1
Cationic Starch price used was based of a vendor in China
Chloroacetamide price used was based of a vendor in China

3. PROBLEM STATEMENT, HYPOTHESIS, RESEARCH OBJECTIVES

3.1 Problem statement

Considering the volume of polyacrylamide produced, these materials have been heavily scrutinized concerning environmental and health impacts ***(Environment Canada; Health Canada, 2009) (Dotson, G.S., April 2011).*** Nervous system effects such as muscle weakness, numbness in hands and feet, sweating, unsteadiness, and clumsiness were reported in some acrylamide workers. This information was reported by Agency For Toxic Substances and Diseases Registry (ATSDR).

In addition to the concerns associated with polyacrylamide, the usage of epichlorohydrin as a reagent further escalates the concern because several international health agencies classify it as a carcinogen ***(Environment Canada; Health Canada, 2008).***

Along with additives, plastic food packing sometimes also contains stabilizers, which may lead to serious carcinogenic impacts on humans or mild health effects such as abdominal cramps and vomiting ***(Cherif, L. M.; et al, 2017).*** Several toxic metals like lead (Pb), cadmium (Cd), antimony (Sb), tin (Sn) is also present as additives in plastic food packaging and storage containers ***(Ekta, B. J.; et al, 2021).*** Inhalation, ingestion, and skin contact are the dominant sources of microplastics to human exposure, and ingestion is one of the most important sources of potential exposure ***(Ekta, B. J.; et al, 2021).***

3.2 Hypothesis

It is proposed that reactive hydroxyl group or aldehyde functionalized polysaccharides may contribute to improving covalent or hemiacetal bonding among pulp fiber by developing an extensive chemically bonding network.

Attempt to test the hypothesis as follows:

- By developing polysaccharide-based wet and dry strength additives that are capable of ether linkages with pulp fibers
- Measure the resultant properties:
  1. Wet and dry strength
  2. Burst strength
  3. Inter-fiber bonding strength

3.3 Research Objectives

The objective of this research was to develop a bio-based paper wet strength agent to replace petroleum-based paper wet strength agents like polyamide epichlorohydrin (PAE) and glyoxylate polyacrylamide (GPAM), especially for the application of hygienic paper products.

The objectives are:

3.3.1 Synthesis of glyoxylate starch amide for temporary wet strength of pulp products

The corn starch will be modified with 2-chloroacetamide ($ClCH_2$-$CONH_2$) in the presence of sodium hydroxide in an aqueous medium and then reacted with glyoxal to produce glyoxylate starch-amide-based temporary wet strength additive. It is expected that the reactive aldehyde of glyoxylate starch-amide may contribute to improving hemiacetal bonding (ether bond) among OCC pulp fibers like GPAM.

3.3.2 Synthesis of N-hydroxymethyl starch amide for permanent wet strength of pulp products

The corn starch will be modified with 2-chloroacetamide ($ClCH_2$-$CONH_2$) in the presence of sodium hydroxide in an aqueous medium and then reacted with formaldehyde to produce N-hydroxymethyl starch-amide-based permanent wet strength additive. It is expected that the reactive hydroxyl groups of N-hydroxymethyl starch-amide may contribute to improving covalent bonding among OCC pulp fibers like PAE.

3.3.3 Preparation of starch-based coating additive from blending of hydrophobic agent and glyoxylate starch amide or N-hydroxymethyl starch amide

Hydrophobic agents such as AKD, zein and PDMS will be blended with glyoxylate starch amide or N-hydroxymethyl starch amide to make water-insoluble starch-based coating additive.

A preliminary experiment was conducted to examine the effect of the coating barrier on the surface and strength properties of the OCC pulp hand sheet. Upon completely drying the hydrophobic agent blended glyoxylate starch-amide additive, a film was formed, shown in Figure 12. This finding provided this study a basis to further investigate the potential of using glyoxylate starch amide as a foundation to develop a bio-based barrier coating material, and if the casted film could be further developed into a bioplastic.

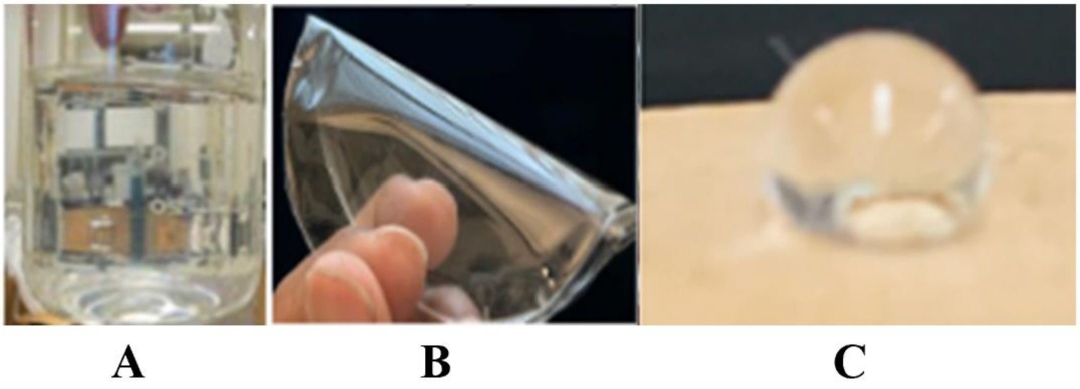


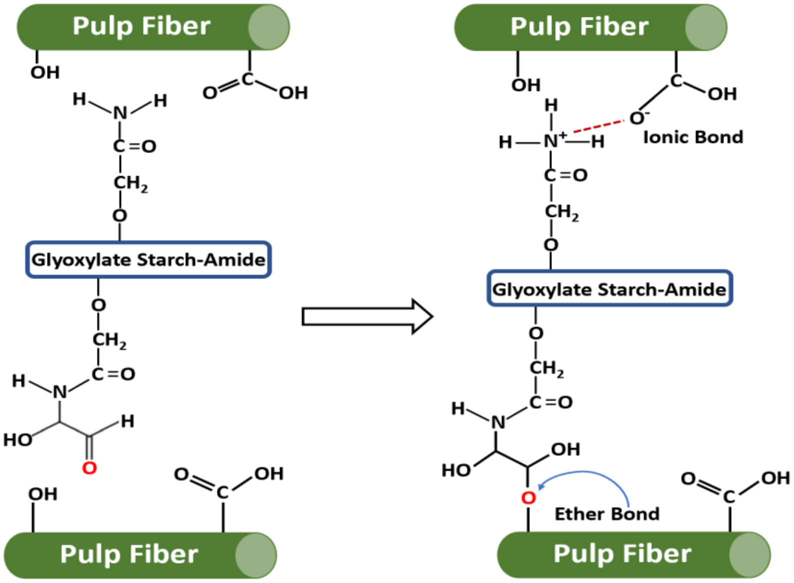
Figure 12: Pictures of the different forms glyoxylate starch amide taken at WMU-CEAS: (A) liquid glyoxylate starch amide with hydrophobic agent, (B) casted glyoxylate starch amide-based coating, (C) glyoxylate amide starch-based coating-coated paper.

3.3.4. Characterize the wet and dry strength properties and antimicrobial properties of the synthesized glyoxylate chitosan additive-treated paper products

Chitosan is dissolved in water in the presence of hydrochloric acid and then reacted with glyoxal to produce glyoxylate chitosan solution. It is expected that the reactive aldehyde group of glyoxylate chitosan may contribute to improving hemiacetal bonding (ether bond) among OCC pulp fibers. The positively charged soluble chitosan derivative is expected to interact with the net negatively charged bacterial surfaces and causes a disruption in their stability like quaternary ammonia solution.

4. SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF GLYOXYLATE STARCH-AMIDE FOR ENHANCING WET AND DRY PAPER STRENGTH

Graphical Abstract



4.1 Abstract

The objective of this research was to develop a bio-based paper strength agent to replace petroleum-based paper wet strength agents such as polyamide epichlorohydrin (PAE) and glyoxylate polyacrylamide (GPAM), especially for the application of hygienic paper products. Cornstarch was modified with 2-chloroacetamide in the presence of sodium hydroxide in aqueous media through etherification. The modification reaction conditions, such as modifying agent concentration, solid-to-liquor ratio, reaction time, and temperature, were optimized based on the acetamide functional group incorporated into cornstarch. Further, modified cornstarch was reacted with glyoxal to produce glyoxylate starch-amide. 2 % glyoxylate starch-amide (based on dry pulp weight) was thoroughly mixed with recycled OCC pulp slurry before preparing the paper for testing the physical properties. The wet tensile index, dry tensile index, and dry burst index of the glyoxylate starch-amide-treated OCC paper increased by 429%, 39%, and 44%, respectively, compared to the control sample. In addition, comparative studies were done between glyoxylate starch-amide and commercial paper strength agents GPAM and PAE. The wet tensile index of 1% glyoxylate starch-amide-treated tissue paper was about 60-70% higher than commercial GPAM and PAE. The increase in wet strength of paper products agreed with increased covalent bonding between glyoxylate starch-amide and pulp fiber. According to our pilot plant trial results, glyoxalated chitosan increased the wet tensile index, dry tensile index, and dry burst index of the OCC paper by 582%, 90%, and 95%, respectively, compared to the control sample.

Keywords: Cornstarch, modifying agent, glyoxylate starch-amide, pulp, physical properties.

4.2 Experimental Section

4.2.1 Materials

Cornstarch was supplied from Sigma Aldrich, St. Louis, MO, (CAS no. 9005-25-8). 2-chloroacetamide (CAS no. 79-07-2), 2-propanol (CAS no 67-63-0), glyoxal solution (CAS no. 107-22-2), hydrochloric acid (CAS no.7647-01-0), and sodium hydroxide (CAS no. 1310-73-2) were purchased as a reagent grade from Sigma Aldrich, St. Louis, MO. Glyoxylate polyacrylamide (GPAM) was supplied from Kemira, Atlanta, GA, and Polyamide epichlorohydrin (PAE) was supplied form Solenis, Wilmington, DE. Tissue paper was supplied from Georgia Pacific.

4.2.2 Chemical modification of cornstarch

5.0 g cornstarch was dispersed with 150 mL water in a conical flask. About 10 mL NaOH (15%) solution was combined with dispersed cornstarch into a conical flask. The pH of the mixture was measured by using a pH meter and was found to be 10. The mixture was stirred using a magnetic bar for 10 minutes, and 5.0g of 2-chloroacetamide was slowly added to allow a reaction with cornstarch. The reaction mixture was stirred with a magnetic stirrer at 40°C for 5 hours, and the temperature was raised to 90°C for 10 minutes, followed by ambient cooling to room temperature. The product was filtered, washed with deionized water until neutral pH, and then air-dried overnight for further study ***(Li, S.; et al, 2011).*** The yield was calculated as the actual yield divided by the total raw materials multiplied by 100. The product yield was found to be 68%. The reaction scheme is shown in Figure 13.

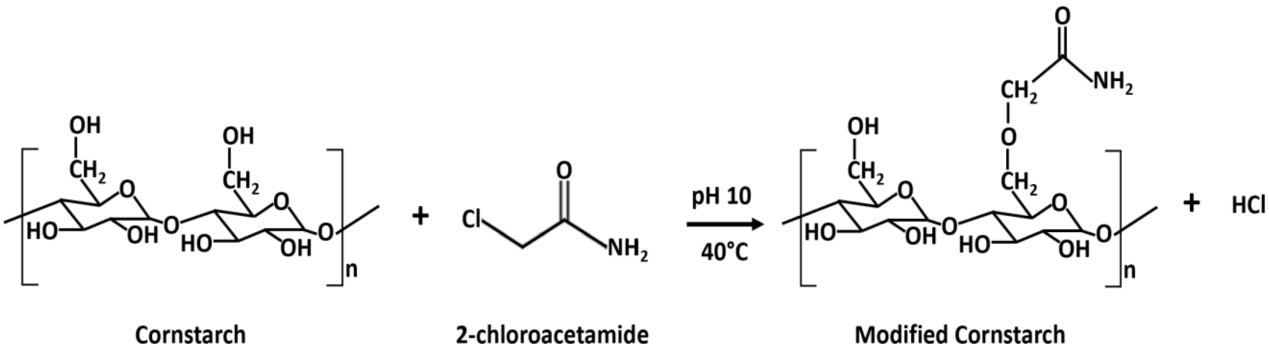


Figure 13: Etherification reaction of cornstarch with 2-chloroacetamide.

4.2.3 Preparation of glyoxylate starch amide

The modified cornstarch (5g) was dissolved into 100 mL of hot water in a 500 mL round bottom flask. About 2g of glyoxal was added to the cornstarch solution, while the reaction mixture was stirred at 50°C for 90 minutes to produce glyoxylate starch-amide for further characterization ***(Yuan, Z. Y.; & Hu, H., 2012).*** The product yield was found to be 100%. The proposed reaction scheme is shown in Figure 14.

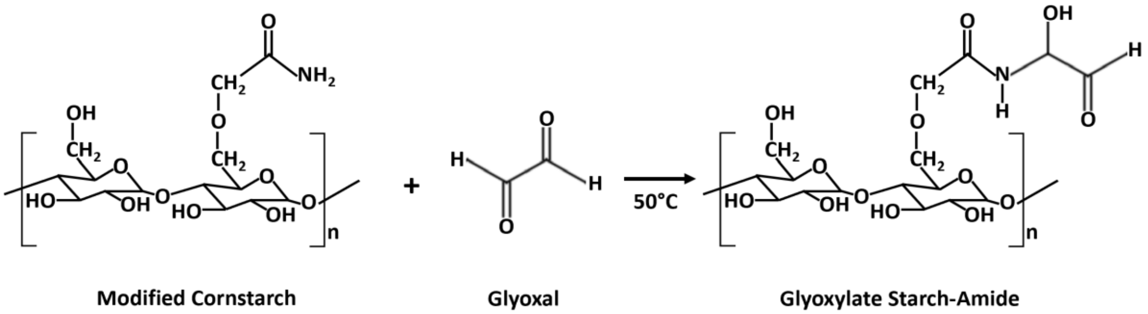


Figure 14: Condensation reaction between modified cornstarch with glyoxal.

4.3 Characterization

4.3.1 Determination of amine content

A known amount of modified cornstarch sample was dissolved in 50 mL water to which was added a known amount of 0.1M HCl solution to react with the amine functional group of modified starch. The remaining excess amount (unreacted) of HCl is determined by titration with 0.1M NaOH solution ***(Sweidan, K.; et al, 2011).*** Phenolphthalein was used as the indicator. The amine group content (%) was calculated as follows ***(Sweidan, K.; et al, 2011).***

$$NH_2\ (\%) = \frac{(C1V1 - C2V2) \times 16 \times 100}{W(100 - \%H2O)} \qquad (1)$$

Where,

C_1 = Concentration of HCl (M)

V_1 = Volume of HCl (mL)

C_2 = Concentration of NaOH (M)

V_2 = Volume of NaOH

W = Weight of the sample (g)

4.3.2 Determination of degree of etherification

The degree of etherification was done by following the standard test method *ASTM* D1439-03. Calculations were done by using the obtained titration values and the formula below.

$$A = \frac{(BC - DE)}{F} \qquad (2)$$

G (Degree of Etherification, %) $= \frac{0.162A}{1-0.058A}$ X 100 (3)

Where,

A = milliequivalents of acid consumed per gram of sample

B = NaOH solution added (mL)

C = normality of the NaOH solution

D = HCl required for the titration of the excess NaOH (mL)

E = normality of the HCl

F = modified cornstarch used (g)

162 = gram molecular mass of the anhydroglucose unit of cornstarch

58 = net increase in molecular mass of anhydroglucose unit for each acetamide ($-CH_2CONH_2$) group substituted

4.3.3 ATR analysis

IR spectra peaks of the modified cornstarch was recorded by using a Perkin Elmer Spectrum 100 FTIR Spectrometer. Spectra were obtained after 64 scans over 600 – 4000 cm^{-1} ***(Sawant, N.; Salam, A.; Lucia, L.,2020).***

4.3.4 XRD analysis

The X-ray diffraction of modified cornstarch was analyzed with Rigaku Smart lab X-Ray Diffractometer. The crystallinity index (CI) of the cornstarch and modified cornstarch was determined using the following parameters: X-ray diffraction patterns with CU KR radiation (λ

1.5406 Å) at 40 kV and 30 mA were recorded in the range of (2ϴ) 10—50° ***(Zhang, H.; et al, 2005).*** The crystallinity index (CI) was determined according to equation 4:

$$CI = 100[(I_{002} - I_{am}) / I_{002})] \tag{4}$$

Where,

I_{002} is the intensity of the principal cornstarch peak at 2ϴ = 18.0° and I_{am} is the intensity attributed to amorphous cornstarch given at 2ϴ = 22.7°.

4.3.5 SEM analysis

Scanning Electronic Microscopy was used to examine the surface topography and composition of the untreated OCC paper and glyoxylate starch-amide treated OCC paper. Liquid nitrogen was used to prepare the sample. To improve the contrast and make the samples more conductive, the sample was sputter-coated with platinum under a vacuum before imaging ***(Salam, A.; et al, 2011).***

4.3.6 Thermal gravimetric analysis

Thermogravimetric behavior of modified cornstarch was studied using a TGA Q500 from 30-600 °C at a temperature ramp of 5 °C/min followed by isothermal heating at 600 °C for 2 minutes ***(Tian, Y.; et al, 2011).***

4.3.7 Differential scanning calorimeter

A differential scanning calorimeter DSCQ100 was used to analyze the modified cornstarch. The sample was subjected to a 2 °C /min temperature ramp from 30–200 °C followed by isothermal heating at 200 °C for 2 min ***(Christian, D.; et al, 2008).***

4.4 Paper hand sheet preparation method

The paper hand sheets were prepared according to TAPPI Standard Method T 205 and conditioned according to TAPPI T402. Approximately 2% glyoxylate starch-amide additive was added into the OCC pulp slurry and allowed to mix for 20 minutes before making a paper hand sheet. A hand sheet molder was used to make a hand sheet in the presence or absence of a glyoxylate starch-amide additive. The paper sheets were left to dry in a conditioned room (23°C, 50% RH) for three days before testing their physical properties.

4.5 Paper properties testing method

4.5.1 Dynamic drainage rate

The drainage rate of the pulp was tested in reference to TAPPI T261. A dynamic drainage jar (DDJ) was used to test the pulp samples.

4.5.2 Gloss testing

The gloss of the OCC paper hand sheet was tested by following TAPPI T 480 test. A Glossmeter was used to test the sample.

4.5.3 Roughness testing

The roughness (Sheffield method) of the OCC paper hand sheet was tested by following TAPPI T 538 test. Roughness was tested using a L&W roughness tester.

4.5.4 Tensile strength

The tensile strength of the OCC paper hand sheet was tested by following TAPPI T220 test. Tensile strength was tested using INSTRON 4301 tensile tester.

4.5.5 Burst resistance

The burst resistance of the OCC paper hand sheet was tested by following TAPPI T 403. Burst strength was tested by using a Mullen Tester.

4.5.6 Tear resistance

The tear strength of the OCC paper hand sheet was tested by following TAPPI T414. An Elmendorf tear tester was used to test the tear resistance.

4.5.7 Internal bond strength (Scott type)

The internal bond strength of the OCC paper hand sheet was tested by following TAPPI T 569.

4.6 Results and discussion

4.6.1 Characterization of modified cornstarch

The acetamide group was incorporated into cornstarch through etherification with 2-chloroacetamide in the presence of sodium hydroxide. The optimum reaction conditions results are shown in Table 5. During modification, while all other variables remained constant, comparatively better amine content of modified cornstarch was obtained at 100% 2-chloroacetamide concentration, solid-to-liquor ratio 1:30, reaction time 5 hours, and temperature of 40 °C. The average values are shown below in Table 5.

Table 5: Modification reaction optimization

Modifying Agent Concentration		Time		Temperature		Solid to Liquor Ratio (S:R)	
Chloroacetamide add on %	Percentage of amine content into cornstarch	Reaction Time (hr)	Percentage of amine content into cornstarch	Reaction Temp. (°C)	Percentage of amine content into cornstarch	S: R	Percentage of amine content into cornstarch
10	1.16	1	4.50	20	13.79	1:10	4.36
25	4.36	2	10.02	30	15.53	1:20	10.16
50	8.42	3	12.49	40	19.89	1:30	19.49
75	12.34	4	13.95	50	19.37	1:40	18.87
100	19.02	5	19.22	60	19.61	1:50	17.67

4.6.2 Amine content

The amine content of cornstarch increased from 0.0% (control) to 19.49%. The surface changes of modified cornstarch were further investigated through analysis of the degree of etherification. In cornstarch, the basic sugar monomer contains roughly three hydroxyl groups. The percent etherification of modified cornstarch was determined by titration and found to be 52%. The ATR spectra of the cornstarch and modified cornstarch are shown in Figure 15, in which the cornstarch shows a band at 3309 cm^{-1} attributed to the O–H, 2931cm^{-1} corresponds to C–H stretching vibrations, while there is no peak over the region of 1500−1650 cm^{-1}, indicating no amide groups on the cornstarch backbone. However, the modified cornstarch shows a sharp peak at 1594 cm^{-1} that corresponds to the C=O stretching of an amide ***(Alonso, D.; et al, 2009).***

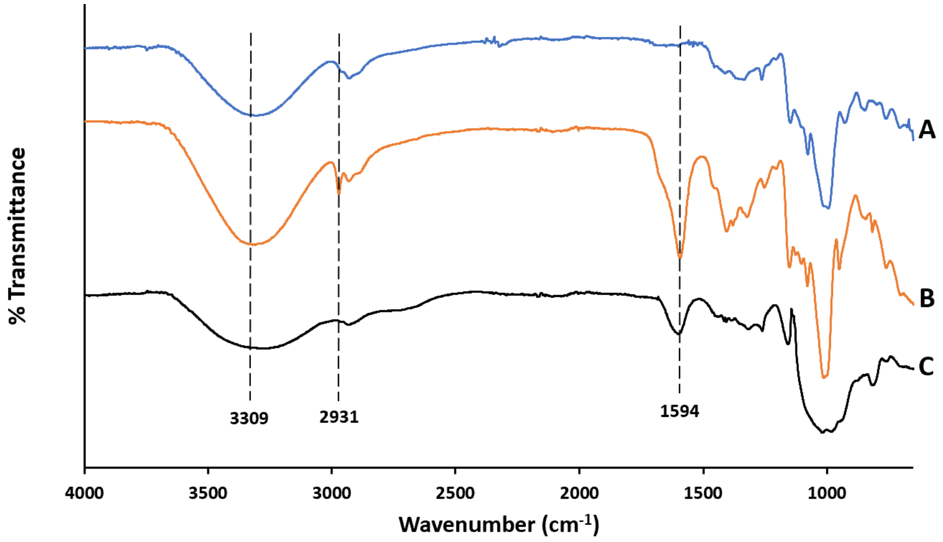


Figure 15: ATR spectra of A (cornstarch), B (modified cornstarch), and C (glyoxylate starch-amide).

4.6.3 XRD analysis

The X-ray diffraction patterns of cornstarch and modified cornstarch were collected with a Rigaku Smartlab X-Ray Diffractometer. The results are shown in Figure 16. The crystallinity index of cornstarch was found to be 49% but did not include any crystalline regions for modified cornstarch and glyoxylate starch-amide (Fig.16) ***(Shi, R.; et al, 2007).*** This indicates that the chemical modification completely altered its crystallinity and produced non-crystalline (amorphous) cornstarch.

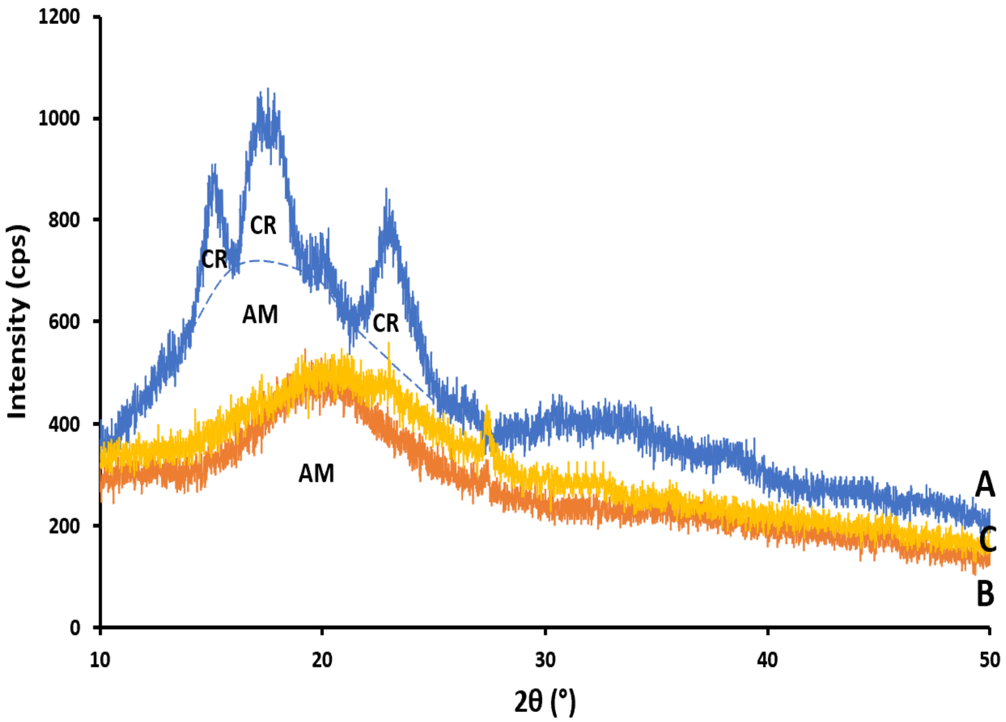


Figure 16: XRD analysis of cornstarch (A), modified cornstarch (B), and glyoxylate starch-amide(C). (Note: CR = Crystalline region, and AM = Amorphous region.)

4.6.4 Thermal behavior

The thermogravimetric behavior of modified cornstarch was evaluated at a 5 °C/min heating ramp (Table 6), over which a weight loss was observed at ~ 100 °C due to the evaporation of water ***(Salam, A.; Lucia, L. A.; Jameel, H., 2013).*** However, weight loss > 140°C was due to thermal decomposition ***(Liu, X.; et al, 2008).*** In comparison, 2-chloroacetamide had a single sharp decomposition peak at 170°C. The cornstarch showed a single weight loss peak at 312.5 °C, while modified cornstarch and glyoxylate starch-amide showed a decrease for the maximum weight loss temperature, but their residual masses were significantly higher after heating to 600 °C. The reduction in maximum degradation temperature may be explained by the modifying agent's lower decomposition temperature. A layer of chloroacetamide is etherified on the surface of the cornstarch, which has a lower temperature of degradation ***(Menzel, C.; et al, 2020).*** More precisely, the DSC thermal behavior of the modified cornstarch was evaluated with a 2 °C/min heating ramp up to 200 °C (Table 6). Chloroacetamide has a very sharp melting point at 142.5 °C, whereas for cornstarch, an endothermic peak was found at 165.1 °C. However, melting points for modified cornstarch and glyoxylate starch-amide decreased, as illustrated in Table 6, which may be because of the low melting modifying agent which is in modified cornstarch through etherification reaction ***(Li, S.; Mujyambere, J. M. V.; Liu, M., 2011).***

Table 6: Thermal behavior properties of cornstarch, modified cornstarch, and glyoxylate starch-amide.

Sample	**TGA maximum (DTG) degradation temp (°C)**	**Residual char at 600°C (%)**	**DSC melting point (°C)**
2-Chloroacetamide	170	29.3	142.5
Cornstarch	312.5	10.8	165.1
Modified Cornstarch	195.1	24.8	159.2
Glyoxylate Starch-amide	182.7	29.1	152.5

4.7 Application of glyoxylate starch-amide into pulp products

4.7.1 Effect of glyoxylate starch-amide on drainage rate

The untreated OCC pulp masterbatch has a 0.3% consistency, and then 1% additive dosage of glyoxylate starch-amide (GSA) and GPAM was added separately into 0.3% consistency OCC pulp. The test was carried out at room temperature in a Dynamic *Britt Jar*, and the stirrer speed was set to 1000 RPM. The average drainage rate of the untreated OCC pulp, GPAM-treated OCC pulp, and GSA-treated OCC pulp fiber was found to be 3.19 mLs-1, 3.50 mLs-1, and 3.70 mLs-1, respectively. Figure 17 shows that the glyoxylate starch-amide additive-treated pulp slurry has an increased drainage rate by about 5% and 16% compared to the GPAM-treated OCC pulp and untreated OCC pulp slurry (control), respectively.

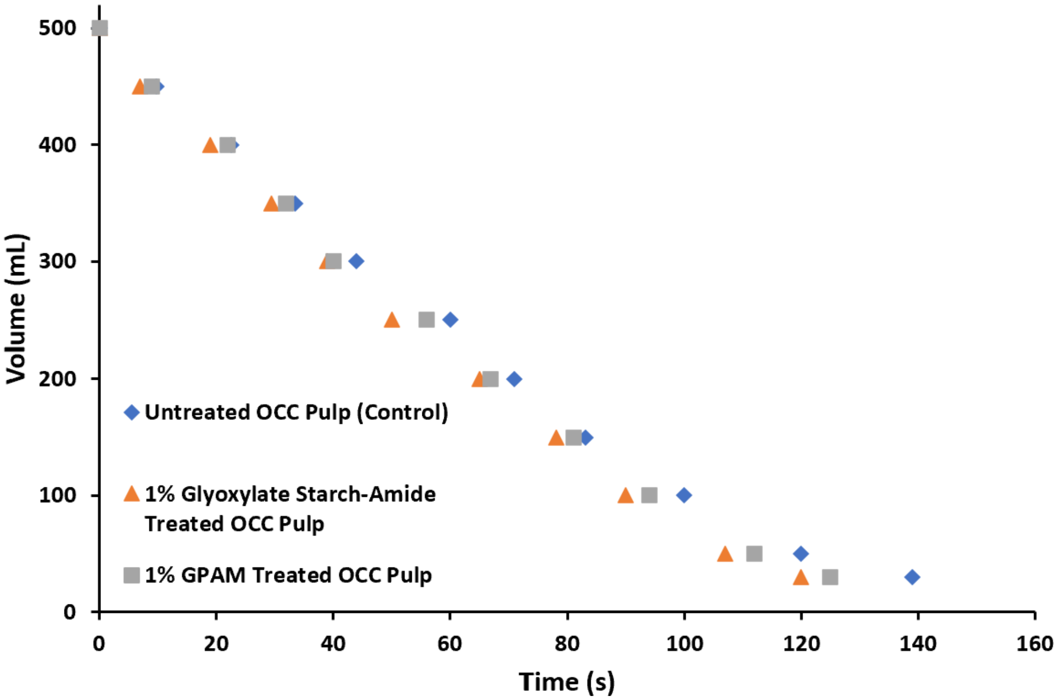


Figure 17: Drainage rate of untreated OCC pulp, glyoxylate starch-amide (GSA) treated OCC pulp, and GPAM treated OCC pulp. (Note: 1% additive dosage was added into pulp slurry)

4.7.2 Effect of glyoxylate starch-amide additive on the wet strength of OCC paper hand sheet

Wet strength is one of the most critical properties of generic paper substrates such as recycled paper, wrapping paper, liner boards, napkins, tissues, and towels. These substrates need sufficient resistance to be successfully applied in packaging, wrapping, food box, cleaning wipe, tissue and towel, and napkin. In general, the good wet strength of paper products requires covalent bonds between pulp fibers and wet-strength additives. In manufacturing pulp fiber-related products, polyamide epichlorohydrin (PAE) and glyoxylate polyacrylamide (GPAM) is commonly used as wet strength additives to increase the wet strength of wrapping paper, liner boards, napkins, and tissue towels. Glyoxylate starch-amide is a bio-based wet strength additive that significantly increases the wet strength of pulp fibers products and is biodegradable. Figure 18 shows the wet strength index (tensile) with variable percent glyoxylate starch-amide additive treated-OCC pulp hand sheet. The wet tensile index increases with the increased amount of glyoxylate starch-amide additive of up to 2% and then plateaus. This may happen due to an increase in covalent bonds (hemiacetal formation) between pulp fibers and glyoxylate starch-amide with increased glyoxylate starch-amide additive concentration, after which we saturate the bonding between glyoxylate starch-amide with cellulose ***(Yuan, Z.Y; Hu, H., 2012).***

It was observed from Figure 18 that the wet tensile index of glyoxylate starch-amide additive treated OCC recycled pulp hand sheet increased ~ 429% higher than the control sample.

When compared to a commercial grade product, GPAM, for dosage 0.1% to 0.5%, it was found that glyoxylate starch-amide performed similarly to GPAM, albeit slightly less. The highest gain in wet tensile index is observed at 0.5% dosage, 133% increase when OCC pulp was treated with GPAM, and 112% when OCC pulp was treated with glyoxylate starch amide. Shown in Figure 19.

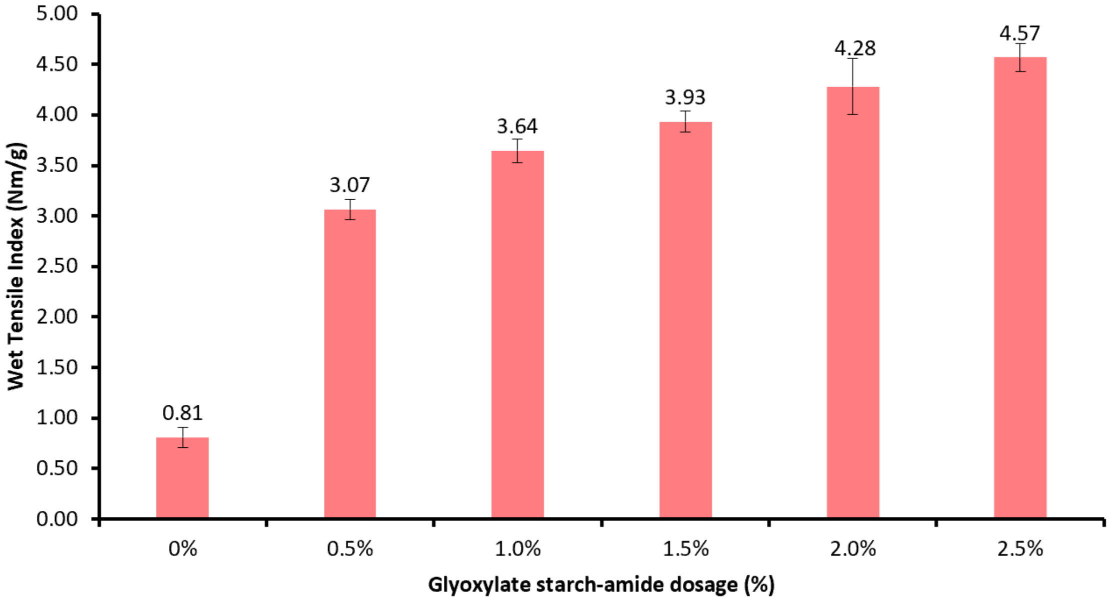


Figure 18: Effect of glyoxylate starch-amide on the wet tensile index of OCC paper hand sheet.

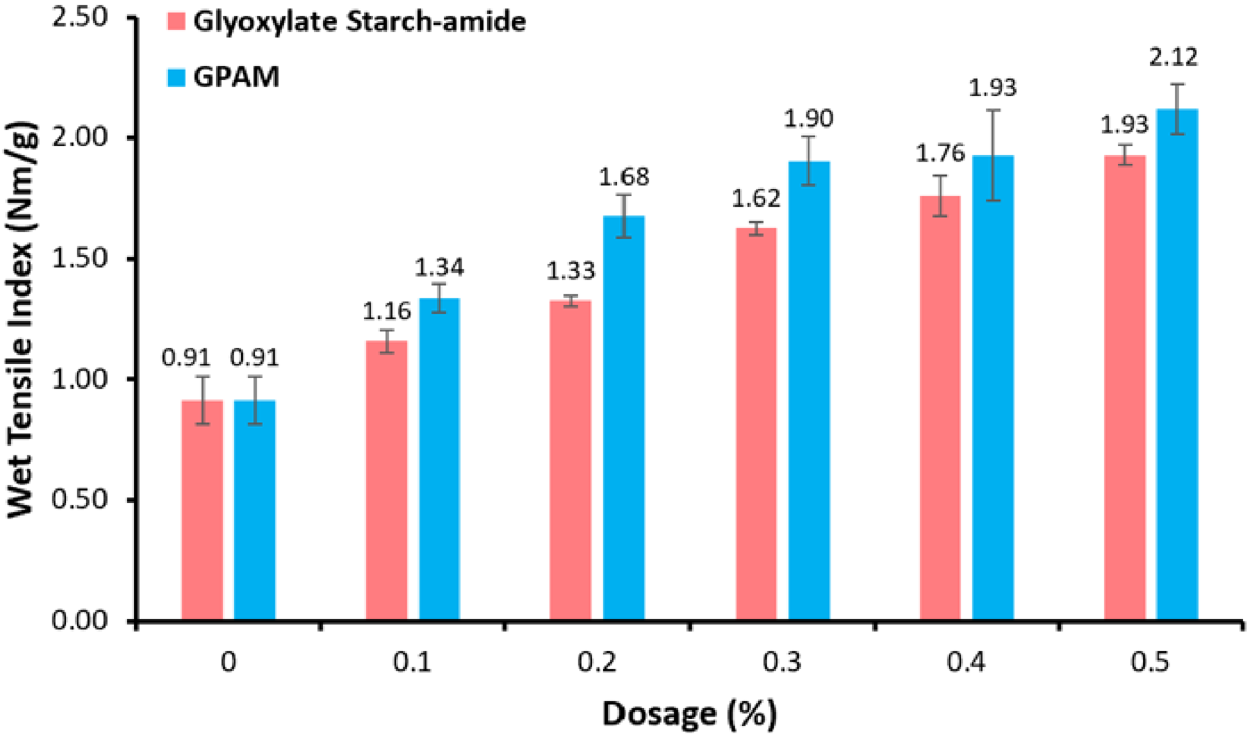


Figure 19: Comparing the effect of glyoxylate starch-amide vs GPAM on the wet tensile index of OCC paper hand sheet.

4.7.3 Effect of glyoxylate starch-amide additive on the dry strength of OCC paper hand sheet

Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need sufficient mechanical resistance for applications requiring packaging, wrapping, or sealing ***(Fotie, G.; Limbo, S.; Piergiovanni, L., 2020).*** In general, this kind of resistance can be attributed at the molecular level to the adequate development of hydrogen bonds or ionic and covalent bonds. Commercial paper strength agents such as cationic polyacrylamide (CPAM), anionic polyacrylamide (APAM), and glyoxylate polyacrylamide (GPAM) are commonly used in paper, cardboard, tissue, and paper towel grades to increase the dry strength but these commercial paper strength agents are petroleum-based polymer and non-biodegradable. Our paper hand sheet was prepared with OCC pulp (CSF = 550) with or without glyoxylate starch-amide additive. Figures 20, 21 & 22 show the dry tensile, burst, and tear index of the OCC recycled paper hand sheet. It is observed from Figures 20, 21 & 22 that the tensile, burst, and tear index increases with increased glyoxylate starch-amide addition up to 2% and then does not increase. This may be explained that the recycled OCC paper strength depends on the number of bonds and area of bonding sites of recycled pulp fibers because, after a certain amount of addition of glyoxylate starch-amide, the strength of the recycled paper did not increase due to saturation of bonding area of fibers ***(Yuan, Z.Y; & Hu, H.,2012).*** It can also be observed from figures 20, 21 & 22 that 2% glyoxylate starch-amide treated OCC paper hand sheet increased the tensile, burst, and tear index found to be 39, 44, and 48% compared to the control sample.

When compared to a commercial grade product, GPAM, for dosage 0.1% to 0.5%, it was found that glyoxylate starch-amide performed better than GPAM. The highest gain in dry tensile index is observed at 0.5% dosage, 36.1% increase when OCC pulp was treated with GPAM, and 49.2% when OCC pulp was treated with glyoxylate starch amide. Shown in Figure 23.

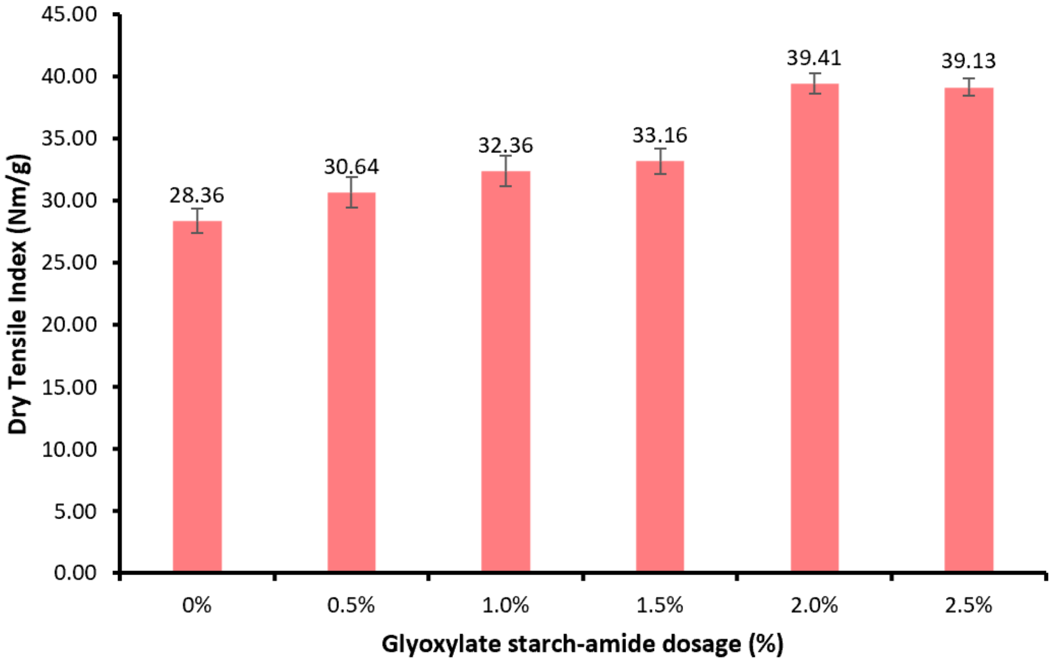


Figure 20: Effect of glyoxylate starch-amide on the dry tensile index of OCC recycled paper hand sheet.

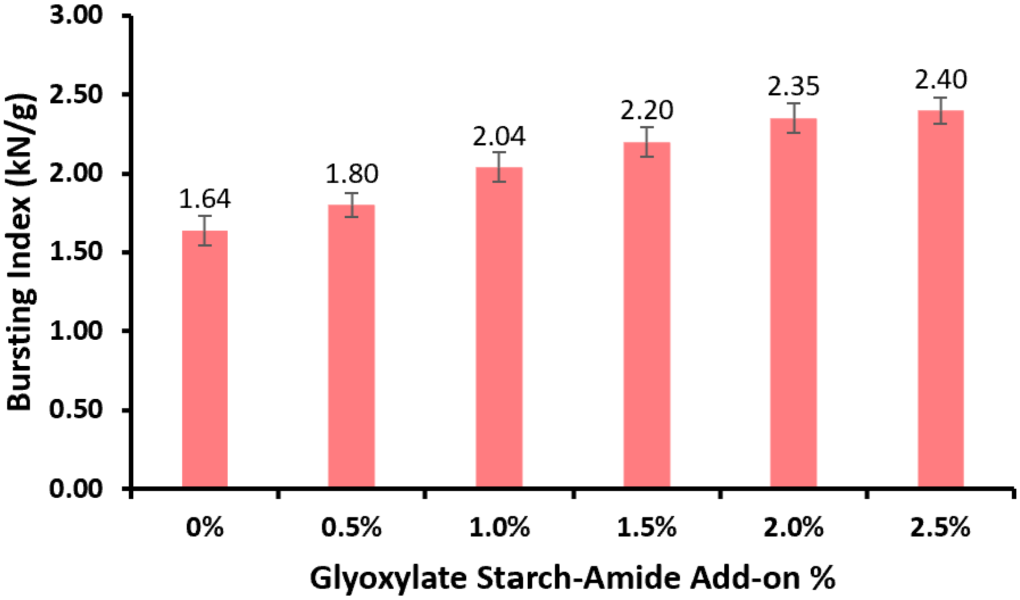


Figure 21: Effect of glyoxylate starch-amide on the burst index of OCC recycled paper hand sheet.

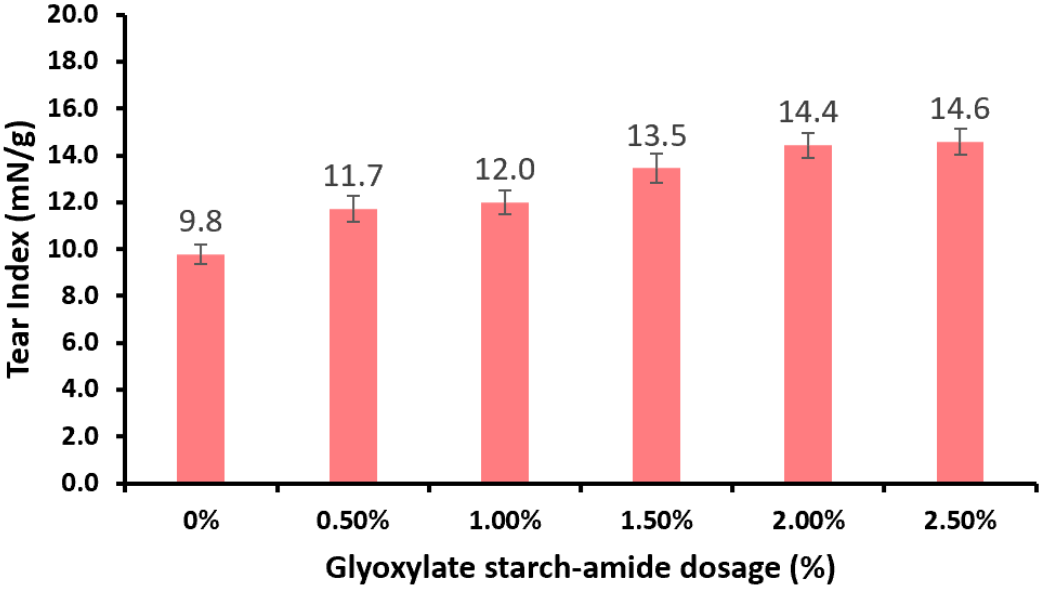


Figure 22: Effect of glyoxylate starch-amide on the tear index of OCC recycled paper hand sheet.

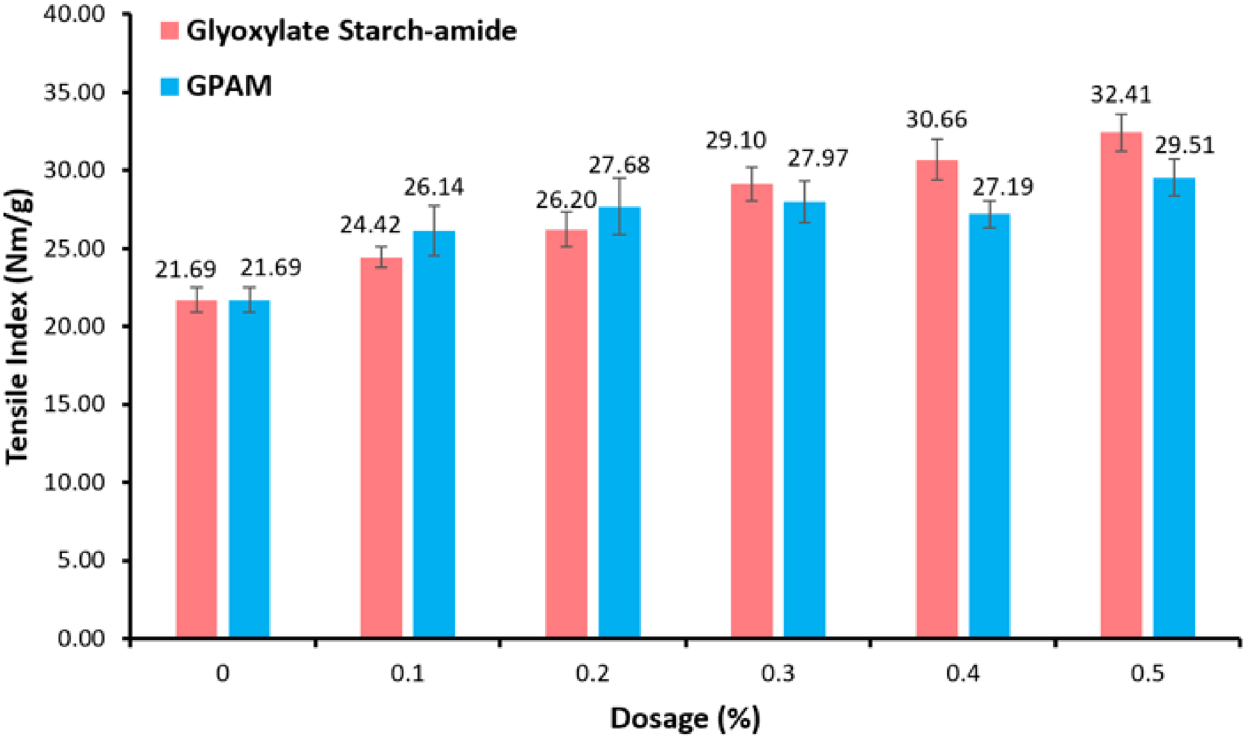


Figure 23: Comparing the effect of glyoxylate starch-amide vs GPAM on the dry tensile index of OCC paper hand sheet.

4.7.4 Effect of pH on the wet and dry strength of glyoxylate starch-amide treated OCC paper hand sheet

The effective pH of glyoxylate starch-amide additive in pulp slurry based on the wet and dry strength of additive-treated OCC paper was then determined. Figure 24 shows that the wet and dry strength of glyoxylate starch-amide additive-treated OCC paper at pH 4 to 8 was almost the same and then decreased slightly; the highest strength was found at pH 5. The pH range in the commercial papermaking process is 4 to 9. Figure 24 results indicate that the glyoxylate starch-amide additive is suitable at a pH range of 4 to 8, pH 9 is still favorable in the papermaking process.

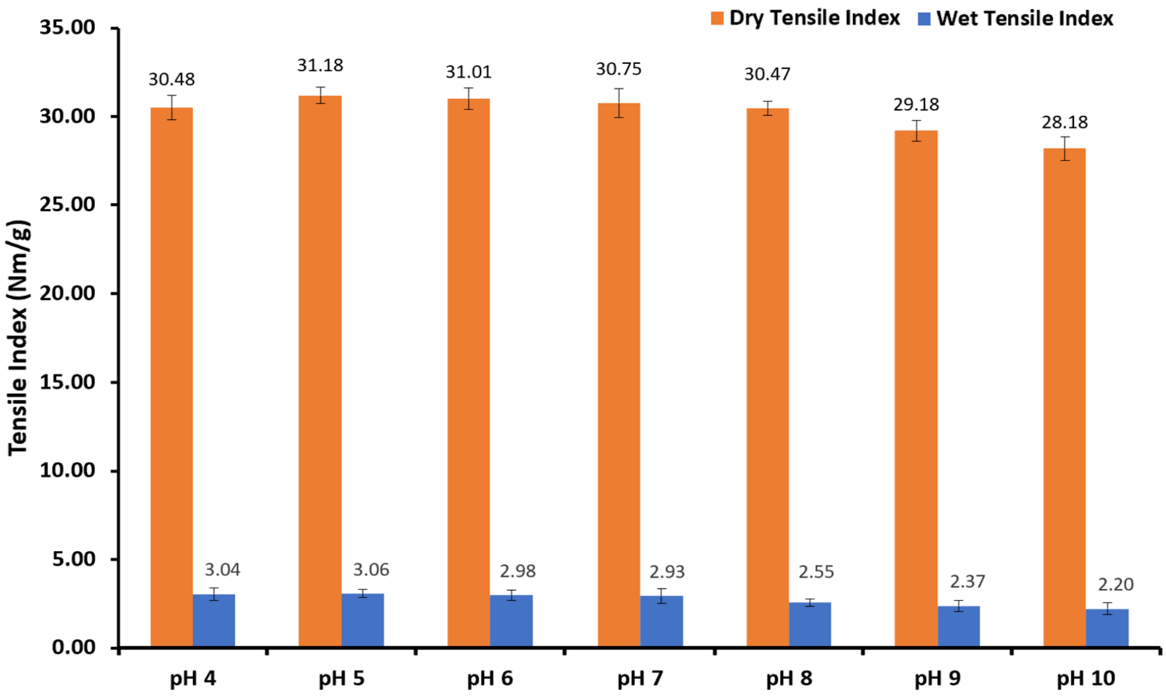


Figure 24: Effect of pH on the wet and dry strength of glyoxylate starch-amide treated OCC paper hand sheet.

4.7.5 Effect of glyoxylate starch-amide additive on tissue paper

Common wet-strength resins such as GPAM and PAE are typically used in tissue paper manufacturing ***(Miglierini, G., 2017).*** Wet strength is a favorable characteristic of tissue paper because it allows it to possess sufficient wet strength. A comparative study was done to see the effectiveness of glyoxylate starch-amide additive compared to commercial wet strength additives (GPAM and PAE). 1% dosage was added to tissue paper and then dried in an air oven at 105°C for 10 minutes to test wet strength. The wet tensile index of glyoxylate starch-amide, GPAM and PAE-treated tissue paper were found to be 3.01, 1.84, and 1.73, respectively. Figure 25 shows that the wet tensile index of glyoxylate starch-amide-treated tissue paper increased ~ 370% compared to the control (no additive) and was ~ 60-70% higher than commercial GPAM and PAE.

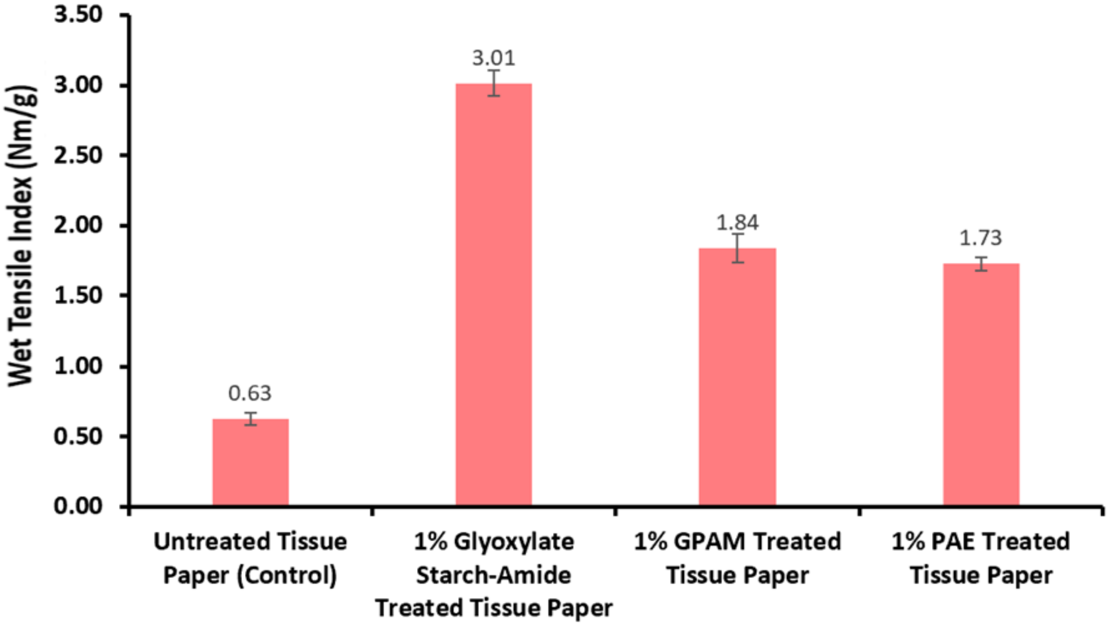


Figure 25: Effect of glyoxylate starch-amide on the wet tensile index of tissue paper.

4.7.6 Bond formation between glyoxylate starch-amide additive with OCC pulp

The functional groups of glyoxylate starch-amide are aldehyde (-CHO), amines (-NH2), and hydroxyls (-OH) which may form covalent (ether bond), ionic and hydrogen bonds with the hydroxyl (-OH), and carboxyl (-COOH) groups on pulp fibers during papermaking. The covalent bond (hemiacetal) formed between the aldehyde and hydroxyl group contributes to the wet strength of paper/tissue products ***(Yuan, Z.Y; & Hu, H., 2012).*** The hydrogen bonds, covalent bonds, and ionic bonds all contribute to the dry strength of paper/tissue products ***(Lu, C.; et al, 2020).*** An internal bonding strength of glyoxylate starch-amide additive-treated paper sheet was tested, and the results are shown in Figure 26. The internal bonding strength of glyoxylate starch-amide-treated paper sheet increases with glyoxylate starch-amide addition up to 2% and then only slightly increases (Fig. 25). Pulp fibers form more bonds when increasing the glyoxylate starch-amide in a bath. This may be explained by the chemical bonding sites between pulp fiber, and glyoxylate starch-amide have been saturated after the addition of 2% additive ***(Yuan, Z.Y; & Hu, H., 2012).***

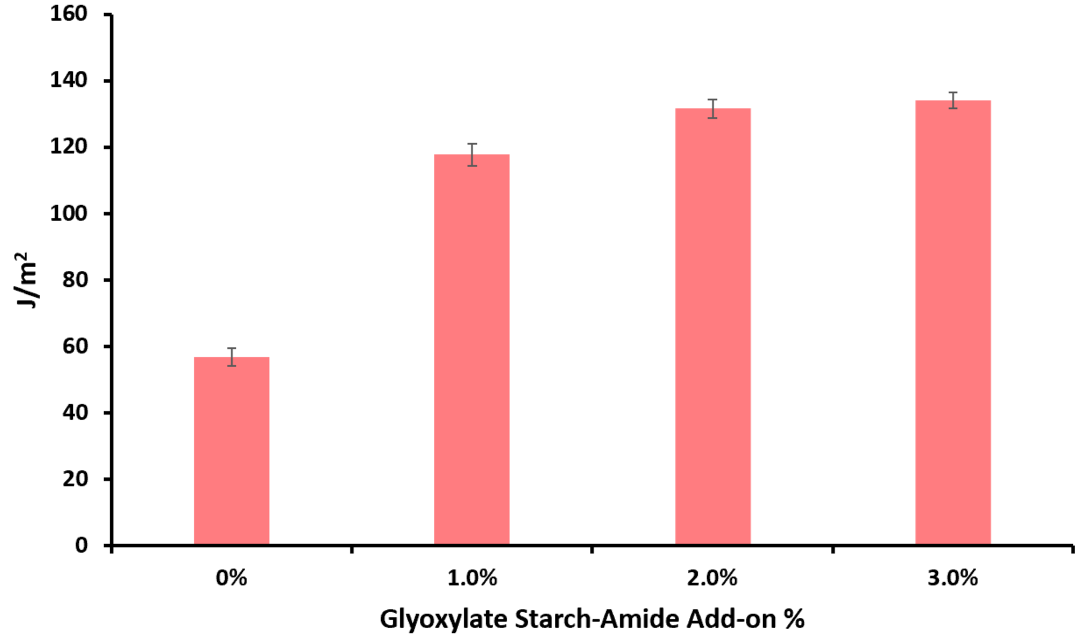


Figure 26: Effect of glyoxylate starch-amide on the internal bond strength of OCC paper sheet.

4.7.7 SEM image analysis of glyoxylate starch-amide additive treated OCC paper sheet

Scanning electron microscopy of OCC paper and glyoxylate starch-amide additive-treated OCC paper sheet is shown in Figure 27. The OCC paper sheet (control) shows a rougher surface with gaps appearing between pulp fibers, but the glyoxylate starch-amide additive treated OCC paper sheet SEM images reveal a more continuous and smoother surface because the glyoxylate starch-amide additive fills gaps. It may be that these additional interaction results in more overall bonding between the OCC pulp fibers in which the additive network increases the physical strength of the glyoxylate starch-amide-treated OCC paper sheet. The roughness and porosity of the glyoxylate starch-amide additive-treated OCC paper sheet was determined. The roughness and porosity (air permeability) were decreased by about 10% and 70%, respectively compared to the control sample.

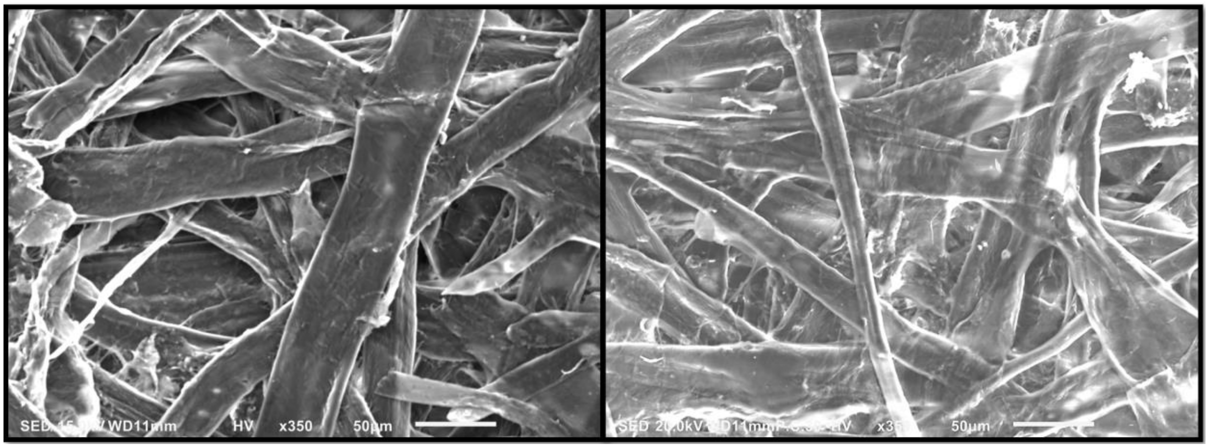


Figure 27: SEM images of untreated OCC paper sheet (left) and glyoxylate starch-amide additive-treated OCC paper sheet (right).

4.7.8 Coating of glyoxylate starch-amide additive onto OCC paper

A summary of the physical properties of coated and uncoated OCC paper sheets is presented in Table 7. Hand sheets were coated (one side) with 2.5% glyoxylate starch-amide and starch solution separately, using a bar applicator with 6 mils thickness. The hand sheets were then dried at 105 °C for 1 hour. The uncoated paper sheet was used as a control.

Table 7: Results of glyoxylate starch-amide coating on OCC paper sheets.

	Tensile				
	Dry Tensile Index (Nm/g)	**Wet Tensile Index (Nm/g)**	**Brightness Index**	**Gloss**	**Roughness (Sheffield Units)**
Uncoated OCC paper sheet (Control)	22.53	3.72	17.6	11.4	359.4
Cornstarch coated OCC paper sheet	32.51	7.29	17.8	11.7	318.03
Modified cornstarch coated OCC paper sheet	33.10	7. 56	17.6	11.8	319.7
Glyoxylate starch-amide coated OCC paper sheet	36.75	24.99	18.1	11.7	319.9

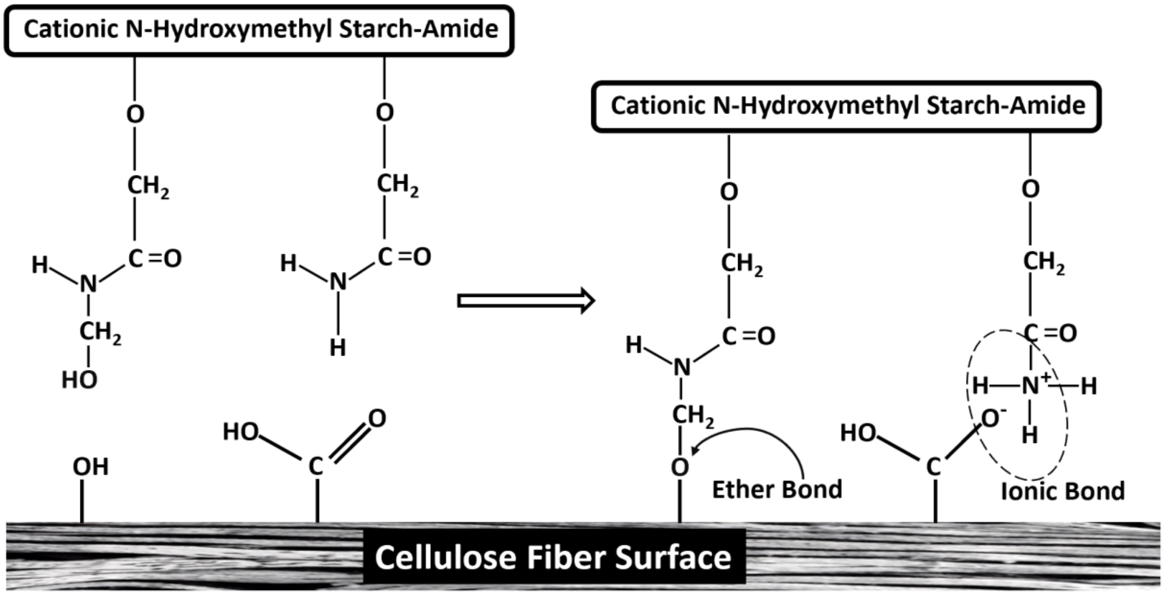
It is observed from Table 7 that the wet tensile index of glyoxylate starch-amide additive-coated OCC paper was 24.99, which is 572% higher than the uncoated OCC paper sheet (control), and ~ 243% higher than the modified cornstarch-coated OCC paper and cooked cornstarch solution-coated OCC paper. Similarly, the dry tensile index was 36.75, 63.12% higher than the uncoated OCC paper sheet (control) and ~ 12% higher than modified cornstarch-coated OCC paper and cooked cornstarch solution-coated OCC paper. This increased the wet tensile index of glyoxylate starch-amide additive-coated OCC paper perhaps glyoxylate starch-amide created additional covalency as well as ionic and hydrogen bonds between the pulp fibers during the drying of coated papers. In addition, Table 7 also shows that both coatings additives such as glyoxylate starch-amide and cooked cornstarch solution-coated paper slightly increase gloss and brightness compared to uncoated OCC paper sheet (control) but decreased roughness by approximately 11%.

4.8 Conclusions

A synthesized bio-based paper strength additive was prepared from cornstarch. Cornstarch was modified with 2-chloroacetamide in the presence of sodium hydroxide in aqueous medium via an etherification reaction to incorporate the acetamide group into cornstarch for further reaction with glyoxal. The optimum modification reaction conditions were obtained at 100% chloroacetamide concentration, solid-to-liquor ratio 1:30, modification reaction time 5 h, and temperature 40 °C. The degree of etherification of modified cornstarch was determined to be 52%. Further, modified cornstarch was reacted with glyoxal to produce GSA. Nearly 2% of GSA was blended with the OCC pulp slurry prior to making a paper hand sheet sample for testing physical properties. The wet tensile index increased 429% compared to the control. Similarly, dry tensile index, dry bursting index, and dry tear index increased by 39, 44, and 48%, respectively, compared to the control. Comparative studies were done between the GSA additive and commercial wet strength additives, such as GPAM and PAE. The wet strength index of 1% glyoxylate starch amide-treated tissue paper was found to be 3.01, which is ∼60−70% higher than the commercial paper wet strength additives GPAM and PAE and ∼5 times higher than the control sample. In addition, when the OCC paper sheet was coated with a 2.5% GSA solution, the wet and dry tensile index increased ∼572 and 63%, respectively, while there was also a decrease in roughness compared to the control sample. The increased wet and dry strength is in agreement with increased bonding between the GSA and pulp fibers.

5. A BIO-BASED SYNTHESIZED N-HYDROXYMETHYL STARCH-AMIDE FOR ENHANCING WET AND DRY STRENGTH PROPERTIES OF PAPER PRODUCTS

Graphical Abstract



Bond formation between cationic N-hydroxymethyl starch-amide and pulp fiber

5.1 Abstract

The aim of this research was to develop a bio-based paper strength agent for the replacement of petroleum-based paper strength agents. Cationic starch was modified with 2-chloroacetamide in an aqueous medium. The modification reaction conditions were optimized based on the acetamide functional group incorporated into cationic starch. Further, the modified cationic starch was dissolved in water and then reacted with formaldehyde to produce N-hydroxymethyl starch-amide. 1 % N-hydroxymethyl starch-amide was mixed with OCC pulp slurry before preparing the paper sheet for testing the physical properties. The wet tensile index, dry tensile index, and dry burst index of the N-hydroxymethyl starch-amide-treated paper increased by 243%, 36%, and 38%, respectively, compared to the control sample. In addition, comparative studies were done between N-hydroxymethyl starch-amide and commercial paper wet strength agents GPAM and PAE. The wet tensile index of 1% N-hydroxymethyl starch-amide-treated tissue paper was like GPAM and PAE and 2.5 times higher than the control sample.

Keywords: Cationic-starch, synthesis, N-hydroxymethyl starch-amide, paper properties.

5.2 Experimental Section

5.2.1 Materials

Cationic cornstarch was supplied from Tate & Lyle, Decatur, IL. 2-chloroacetamide (CAS no. 79-07-2), 2-propanol (CAS no. 67-63-0), formaldehyde solution [37% in water, 10-15% methanol as stabilizer] (CAS no. 50-00-0), hydrochloric acid (CAS no.7647-01-0), and sodium hydroxide (CAS no. 1310-73-2) were purchased as a reagent grade from Sigma Aldrich, St. Louis, MO. Glyoxylate polyacrylamide (GPAM) was supplied from Kemira, Atlanta, GA. Polyamide epichlorohydrin (PAE) was supplied from Solenis, Wilmington, DE.

5.2.2 Chemical modification of cationic starch

5.0 g cationic starch was dissolved with 150 ml water in a conical flask. About 10mL NaOH (15%) solution was combined with dissolved cationic starch in a conical flask. The mixture was stirred using a magnetic bar for 10 minutes, and slowly added 5.0 g of 2-chloroacetamide to allow the reaction with cationic starch. The reaction mixture was stirred with a magnetic stirrer at 40°C for 5 hours and raised to 80°C for 10 minutes, followed by ambient cooling to room temperature. The product was filtered, washed with deionized water until neutralized pH, and then air-dried overnight for further study ***(Li, S.; Mujyambere, J. M. V.; Liu, M., 2011)***. The yield of the product was about 70%. The reaction scheme is shown in Figure 28.

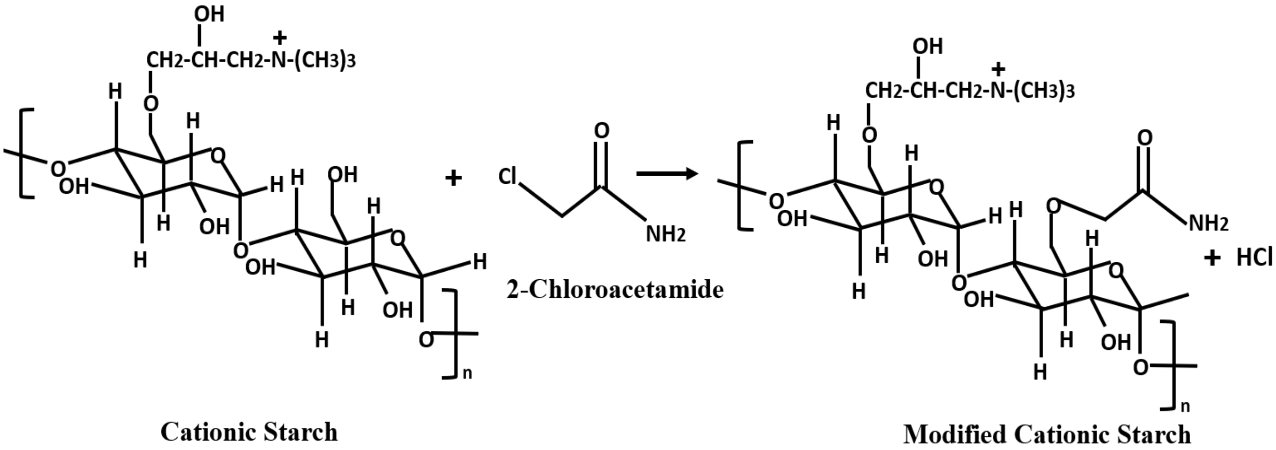


Figure 28: Etherification reaction of cationic starch with 2-chloroacetamide.

5.2.3 Preparation of N-hydroxymethyl starch-amide

The modified starch (5 g) was dissolved into 100 ml of hot water in a 500 ml round bottom flask. About 5.0 g of aqueous formaldehyde solution (37% in water) was added to the modified cationic starch solution, while the reaction mixture was stirred at 50°C for 90 minutes to produce N-hydroxymethyl starch-amide for further characterization ***(Paulsson; Grawe; Törnqvist, 2002)***. The N-hydroxymethyl starch-amide product was heated at 90°C for 10 minutes to remove unreacted formaldehyde if it is present in the solution prior to use in the paper product. The yield of the product was about 100%. The proposed reaction scheme is shown in Figure 29.

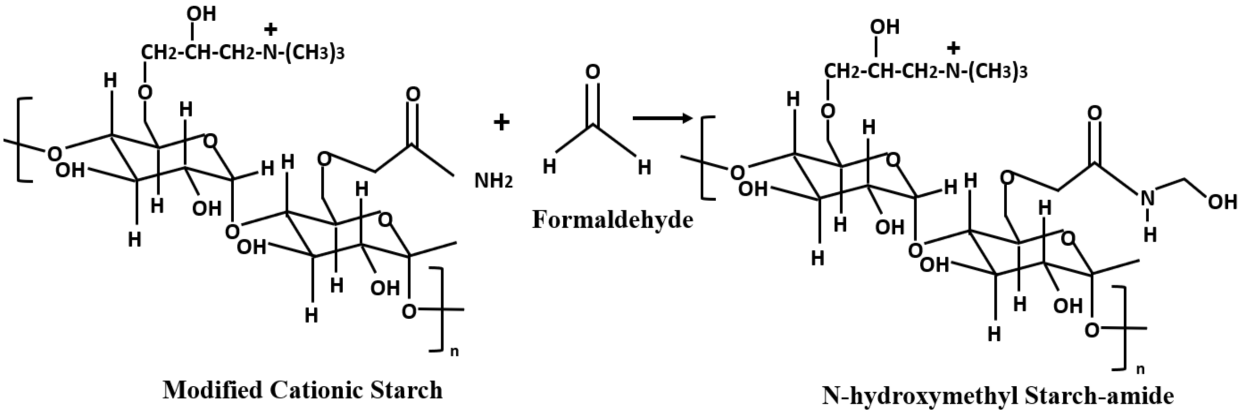


Figure 29: Condensation reaction between modified cationic starch with formaldehyde.

5.3 Characterization

5.3.1 Determination of amine content

A known amount of modified cationic starch sample was dissolved in 50 mL water, which was added to a known amount of 0.1M HCl solution to react with the amine functional group of modified cationic starch. The remaining excess amount (unreacted) of HCl is determined by titration with 0.1M NaOH solution. Phenolphthalein was used as the indicator. The water content of each sample was also determined by Karl-Fischer titration ***(Sweidan; et al, 2011)***. The amine group content was calculated as follows:

$$\text{Amine content (\%)} = \frac{(C_1V_1 - C_2V_2) \times 16 \times 100}{W(100 - \%H_2O)} \qquad (5)$$

Where,

C_1 = Molar concentrations of HCl

C_2= Molar concentrations of NaOH

V_1 = Volume of HCl

V_2 = Volume of NaOH

W = Weight of the sample

5.3.2 Determination of degree of etherification

The degree of etherification was calculated according to the standard method ASTM D 1439-03. A known amount of dried modified cationic starch was added to 100 mL of water, followed by 25.0 mL of 0.5 N NaOH solution. The mixture is stirred and heated to boiling temperature, and boiled for 20 minutes. The excess NaOH solution is titrated with 0.5N HCl solution. Phenolphthalein was used as the indicator. Calculation of the degree of etherification (G) is as follows:

$$A = \frac{BC - DE}{F} \tag{6}$$

$$\text{Degree of Etherification (G)} = \frac{0.162A}{1 - 0.058A} \tag{7}$$

Where,

A = milliequivalents of acid consumed per gram of sample

B = NaOH solution added (mL)

C = normality of the NaOH solution

D = HCl required for the titration of the excess NaOH (mL)

E = normality of the HCl

F = modified cationic starch used (g)

162 = gram molecular mass of the anhydroglucose unit of starch

58 = net increase in molecular mass of anhydroglucose unit for each acetamide ($-CH_2CONH_2$) group substituted

5.3.3 Determination of the degree of substitution

The degree of substitution is calculated as follows ***(Liu, Z.; et al, 2022)***.

Degree of Substitution (DS) = $\frac{162 \times C \times V}{m - M \times C \times V}$ (8)

Where,

M = Molar mass of alkyl group

C = Concentration of silver nitrate standard solution(ml/l)

m = Weight of the ether

V = Volume of consuming silver nitrate standard solution (ml)

162 = Gram molecular mass of the anhydro glucose unit of starch

5.3.4 ATR analysis

IR spectral peaks of the modified cationic starch were recorded by using a Perkin Elmer Spectrum 100 FTIR Spectrometer. Spectra were obtained after 64 scans over 600 – 4000 cm^{-1} **(*Christian; et al, 2008)***.

5.3.5 XRD analysis

The X-ray diffraction of modified cationic starch and N-hydroxymethyl starch-amide were analyzed with Rigaku Smart lab X-Ray Diffractometer. The crystallinity index (CI) of the cationic starch and modified cationic starch was determined using the following parameters: X-ray diffraction patterns with Cu KR radiation (λ 1.5406 Å) at 40 kV and 30 mA were recorded in the range of (2Θ) 10-40° ***(Salam, A.; Lucia, L; Jameel, H., 2014)***.

The crystallinity index (CI) was determined according to equation 9:

$$CI = 100[(I_{002} - I_{am}) / I_{002})] \qquad (9)$$

Where,

I_{002} is the intensity of the principal cornstarch peak at 2Θ = 18.0° and I_{am} is the intensity attributed to amorphous cornstarch given at 2Θ = 21.4°.

5.3.6 SEM analysis

Scanning Electronic Microscopy was used to examine the surface topography and composition of the untreated OCC paper and N-hydroxymethyl starch-amide treated OCC paper. Liquid nitrogen was used to prepare the sample. To improve the contrast and make the samples more conductive, the sample was sputter-coated with platinum under a vacuum before imaging ***(Salam, A.; et al, 2010).***

5.3.7 Thermal gravimetric analysis

Thermogravimetric behavior of modified cationic starch and N-hydroxymethyl starch-amide were studied using a TGA Q500 from 30-600 °C at a temperature ramp of 5 °C/min followed by isothermal heating at 600 °C for 2 minutes ***(Alonso, D.; et al, 2009).*** TGA was carried out in a Nitrogen atmosphere.

5.3.8 Differential scanning calorimeter

A differential scanning calorimeter DSCQ100 was used to analyze the modified cationic starch and N-hydroxymethyl starch-amide. The sample was subjected to a 2 °C /min temperature ramp from 30–200 °C followed by isothermal heating at 200 °C for 2 min ***(Shi.; et al, 2007).***

5.4 Paper hand sheet preparation method

The paper hand sheets were prepared according to TAPPI Standard Method T 205. Approximately 1% N-hydroxymethyl starch-amide additive (by mass of oven dry OCC pulp) was added into an OCC pulp slurry and allowed to mix for 30 minutes before making a hand sheet. A hand sheet molder was used to make hand sheet in the presence or absence of a N-hydroxymethyl starch-amide additive. The sheets were left to dry in a conditioned room for three days before testing their physical properties.

5.5 Paper properties testing method

5.5.1 Dynamic drainage rate

The drainage rate of the pulp was tested in reference to TAPPI T261. A dynamic drainage jar (DDJ) was used to test the pulp samples.

5.5.2 Gloss testing

The gloss of the OCC paper hand sheet was tested by following TAPPI T 480 test. A Technidyne Glossmeter was used to test the sample.

5.5.3 Roughness testing

The roughness (Sheffield method) of the OCC paper hand sheet was tested by following TAPPI T 538 test. Roughness was tested using a L&W roughness tester.

5.5.4 Tensile strength

The tensile strength of the OCC paper hand sheet was tested by following TAPPI T220 test. Tensile strength was tested using INSTRON 4301 tensile tester.

5.5.5 Burst resistance

The burst resistance of the OCC paper hand sheet was tested by following TAPPI T 403. Burst strength was tested by using a Mullen Tester.

5.5.6 Internal bond strength (Scott type)

The internal bond strength of the OCC paper hand sheet was tested by following TAPPI T 569.

5.6 Results and discussion

5.6.1 Characterization of modified cationic starch

An acetamide group was incorporated into cationic starch to perform an etherification reaction with 2-chloroacetamide in the presence of sodium hydroxide. During modification, while all other variables remained constant, comparatively better amine content of modified cationic starch were obtained at 75% of chloroacetamide concentration, 4.0 hours of reaction time, 40 °C of reaction temperature and solid to liquor ratio 1:30.

5.6.2 Amine content

The amine content of cationic starch increased from 0.0% (control) to 19.4%. The surface changes of modified cationic starch were further investigated through analyses of the degrees of etherification and substitution (DS). In starch, the basic sugar monomer contains roughly three hydroxyl groups. The percent etherification and degree of substitution of modified cationic starch were 21% and 1.4, respectively. The ATR spectra of the cationic starch and modified cationic starch are shown in Figure 30, in which the cationic starch shows a band at 3291.33 cm−1 attributed to the O–H, 2917.65 cm-1 corresponds to C–H stretching vibrations, while there is no peak over the region of 1500−1650 cm−1, indicating no amide groups on the cationic starch. However, the modified cationic starch and N-hydroxymethyl starch amide shows a sharp peak at 1625.14 cm−1 that corresponds to the C=O stretching of the amide ***(Salam, A.; Lucia, L. A.; Jameel, H., 2013)***.

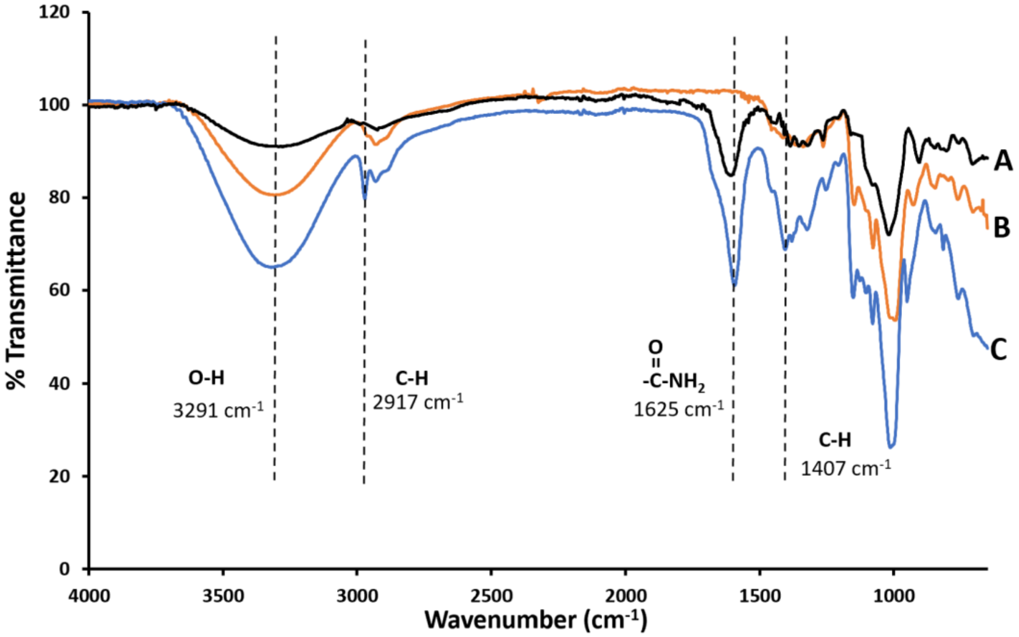


Figure 30: ATR spectra of A (N-hydroxymethyl starch-amide), B (cationic starch), and C (modified cationic starch).

5.6.3 XRD analysis

The X-ray diffraction patterns of cationic starch, modified cationic starch, and N-hydroxymethyl starch-amide were collected with a Rigaku Smartlab X-Ray Diffractometer. The *XRD pattern* is shown in Figure 31. The Crystallinity Index of cationic starch was found to be 35% but did not include any crystallinity of modified cationic starch and N-hydroxymethyl starch-amide ***(Dome, K.; et al, 2020)***. This indicates that the chemical modification completely altered its crystallinity and produced non-crystalline (amorphous) starch.

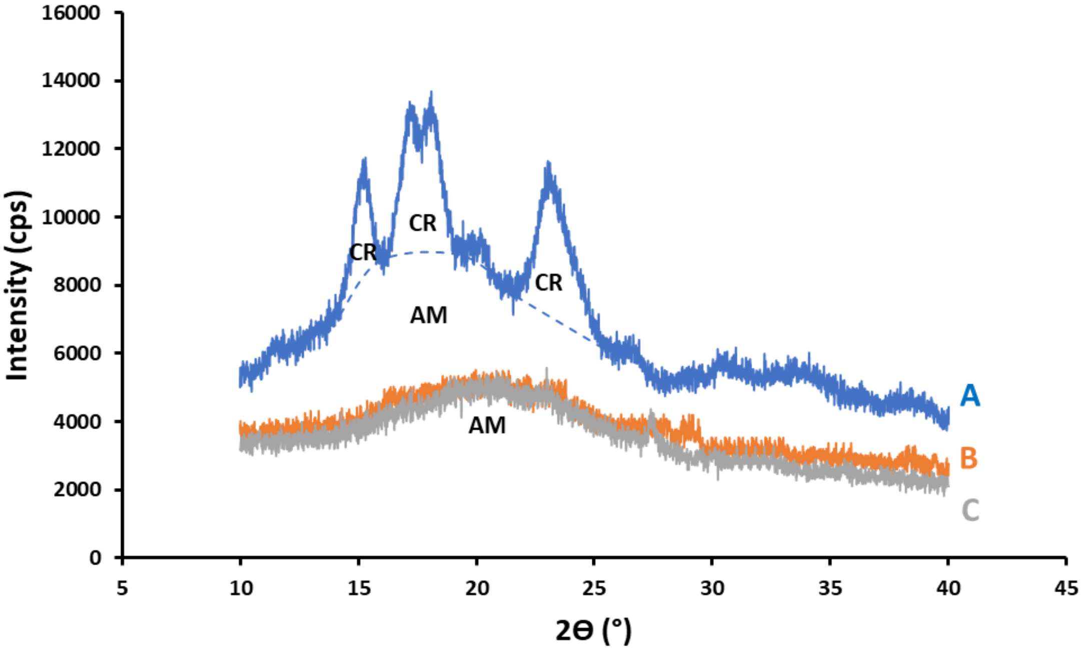


Figure 31: XRD analysis of A (cationic starch), B (modified cationic starch), and C (N-hydroxymethyl starch-amide).

5.6.4 Thermal behavior

The thermogravimetric behavior of modified cationic starch was evaluated at a 5 °C/min heating ramp over which a weight loss was observed ~ 100 °C due to evaporation of water ***(Liu, X.; et al, 2008)***. However, weight loss above 150 °C was due to thermal decomposition ***(Bernabe, P.; Peniche, C.; Arguelles-Monal, W., 2005)***. In contrast, 2-chloroacetamide had a single sharp decomposition peak at 168°C. The cationic starch showed a single weight loss peak at 360.2°C, while modified cationic starch showed a decrease for the maximum weight loss temperature, but the residual mass was significantly higher after heating to 600 °C. Similarly, a lower single weight loss peak was found in N-hydroxymethyl starch-amide at 266.5°C but significantly increased residual char. This may be explained by the fact that the modifying agent has a lower decomposition temperature ***(Salam, A.; Venditti, R. A.; Pawlak, J. J.; El-Tahlawy, K., 2010)***.

A layer of chloroacetamide is etherified on the surface of the cationic starch and then further reacted with formaldehyde, which has a lower temperature of degradation ***(Salam, A.; Venditti, R. A.; Pawlak, J. J.; El-Tahlawy, K., 2011)***. More precisely, the DSC thermal behavior of the modified cationic starch was evaluated with a 2 °C/min heating ramp up to 200 °C. Chloroacetamide has a very sharp melting point at 139.7 °C, whereas for the cationic starch an endothermic peak was found at 165.1 °C. However, melting points for modified cationic starch and N-hydroxymethyl starch-amide decreased, which may be because of low melting modifying agent (chloro-acetamide and formaldehyde), which is in modified cationic starch through etherification and condensation reaction (***Li, S.; Mujyambere, J. M. V.; Liu, M., 2011)*** & ***(Paulsson; Grawe; Törnqvist, 2002)***. The Thermal behavior results are shown in Table 8 below.

Table 8: Thermal behavior properties of synthesized modified cationic starch.

Sample	**TGA maximum (DTG) degradation temp (°C)**	**Residual char at 600 °C (%)**	**DSC melting point (°C)**
Chloro-acetamide	168	29.3	139.7
Cationic starch	360.2	7.2	165.1
Modified cationic starch	275.1	20.6	153.0
N-hydroxymethyl starch-amide	266.5	38.3	120.8

5.7 Application of N-hydroxymethyl starch-amide into pulp products

5.7.1 Effect of N-hydroxymethyl starch-amide on drainage rate

The untreated OCC pulp masterbatch has a 0.3% consistency, and then 1% additive dosage of N-hydroxymethyl starch-amide and commercial GPAM were added separately into 0.3% consistency OCC pulp. The test was carried out at room temperature and pressure at 1000 RPM. The average drainage rate of OCC pulp slurry (control), GPAM treated, and N-hydroxymethyl starch-amide treated OCC pulp slurry was 3.42ml/s, 3.4ml/s, and 3.81 ml/s, respectively. This means the N-hydroxymethyl starch-amide additive-treated pulp slurry increased the drainage rate by about 11% compared to GPAM-treated pulp slurry and OCC pulp slurry (control).

5.7.2 Effect of N-hydroxymethyl starch-amide additive on the wet strength of OCC paper hand sheet

Wet strength is one of the most important properties of generic paper substrates, such as recycled paper, wrapping paper, liner boards, napkins, tissues, and towels. These substrates need sufficient resistance to be successfully applied in packaging, wrapping, food box, cleaning wipe, tissue and towel, and napkin. In general, the good wet strength of paper products requires covalent bonds between pulp fibers and wet-strength additives. In the manufacture of pulp fiber-related products, polyamide epichlorohydrin (PAE) and glyoxylate polyacrylamide (GPAM) are commonly used as wet strength additives to increase the wet strength of wrapping paper, liner board, napkin, tissue, and towel. The widespread use of these non-biodegradable petroleum-based wet-strength additives in the paper-making industry has been raising environmental and health concerns ***(Mohammad, N. et al, 2011) (Howard, R. C.; & Jowsay, C. J., 1989)***. N-hydroxymethyl Starch-amide is a bio-based wet strength additive that significantly increases the wet strength of pulp fibers products and is biodegradable. Figure 32 shows the wet strength index (tensile) of an

OCC pulp hand sheet that is treated with varying percentages of N-hydroxymethyl starch amide additive. The wet tensile index increases with the increase of N-hydroxymethyl starch-amide additive up to 1% and then more or less the same. This may happen due to an increased covalent bond between the alcoholic hydroxyl group of pulp fibers and the reactive hydroxyl group of N-hydroxymethyl starch-amide with increased N-hydroxymethyl starch-amide additive concentration, after which we saturate bonding between N-hydroxymethyl starch-amide with cellulose (***Obokata, T.; & Isogai, A., 2007)***. It was observed from Figure 32 that the wet tensile index of N-hydroxymethyl starch-amide additive treated OCC recycled pulp hand sheet increased ~ 243% higher than the control sample.

When compared to a commercial grade product, PAE, for dosage 0.1% to 0.5%, it was found that N-hydroxymethyl starch-amide performed similarly to PAE, albeit slightly less. The highest gain in wet tensile index is observed at 0.5% dosage, 183% increase when OCC pulp was treated with PAE, and 155% when OCC pulp was treated with N-hydroxymethyl starch-amide. Shown in Figure 33.

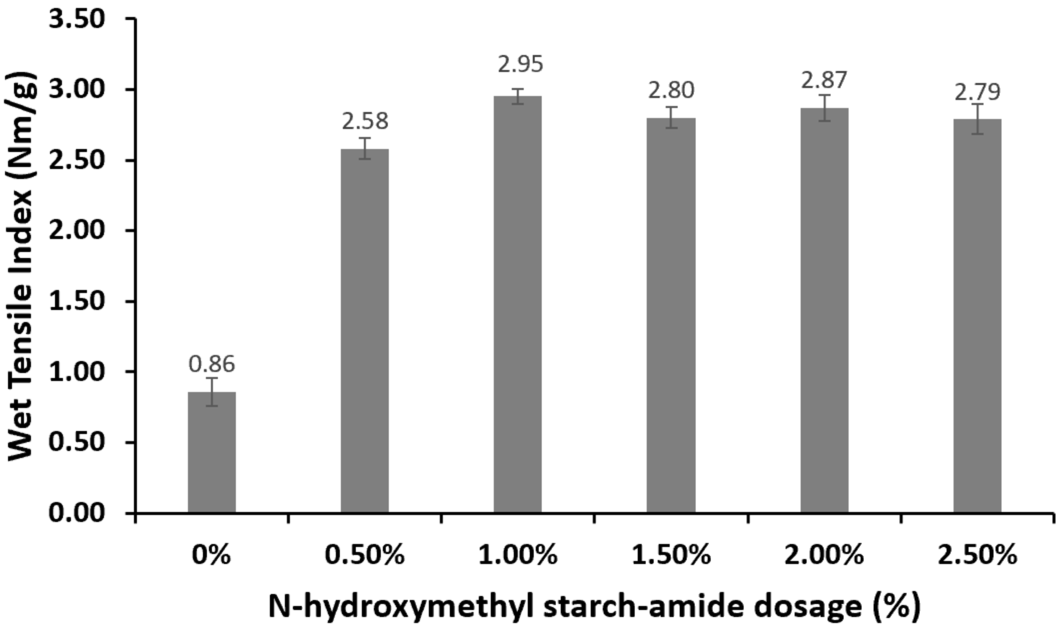


Figure 32: Effect of N-hydroxymethyl starch-amide on the wet tensile index of OCC paper.

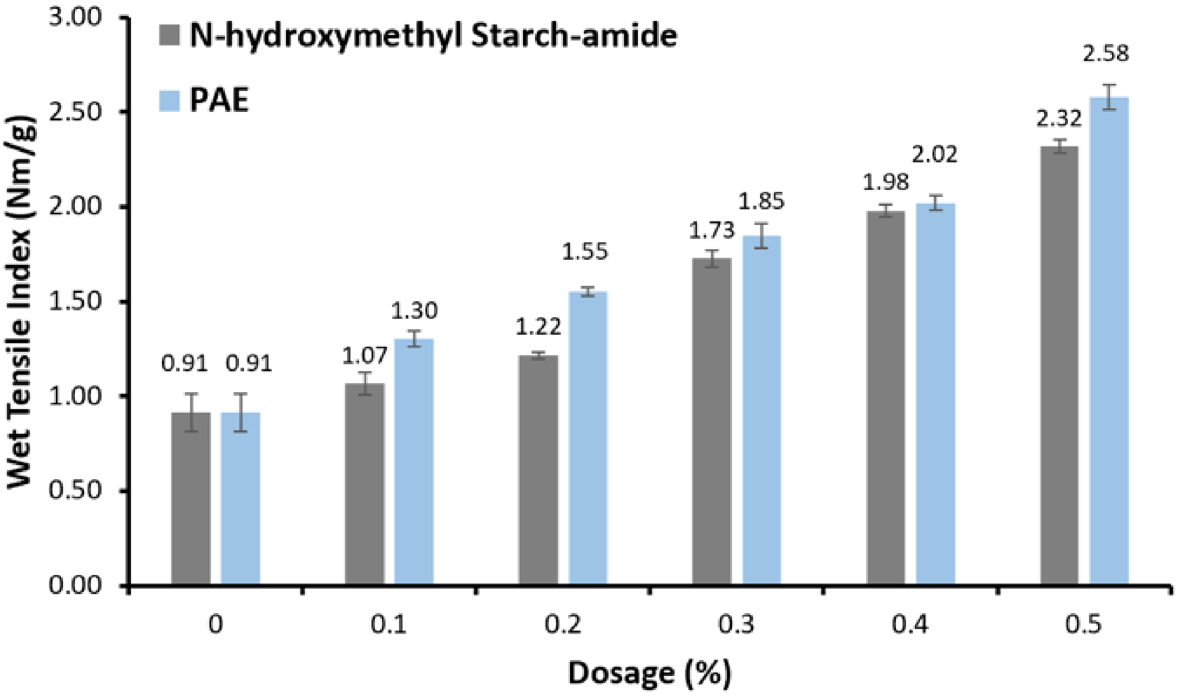


Figure 33: Comparing the effect of N-hydroxymethyl starch-amide vs PAE on the wet tensile index of OCC paper hand sheet.

5.7.3 Effect of N-hydroxymethyl starch-amide additive on the dry strength of OCC paper hand sheet

Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need to be sufficiently resistant for applications that require packaging, wrapping, or sealing ***(Fotie, G.; Limbo, S.; Piergiovanni, L., 2020)***. Generally, this kind of resistance can be attributed at the molecular level to the adequate development of hydrogen bonds or ionic and covalent bonds. Commercial paper strength agents such as cationic polyacrylamide (CPAM), anionic polyacrylamide (APAM), and glyoxylate polyacrylamide (GPAM) are commonly used in paper, cardboard, tissue, and paper towel grades to increase the dry strength but these commercial paper strength agents are petroleum-based polymers and non-biodegradable ***(Mohammad, N. et al, 2011) (Howard, R. C.; & Jowsay, C. J., 1989)***. Our pulp hand sheet was prepared with OCC pulp (CSF = 490) with or without the N-hydroxymethyl starch-amide additive. Figure 34 & 35 shows the dry tensile and burst index of OCC recycled pulp hand sheet. It is observed from Figures 34 & 35 that the dry tensile and burst index increases with increased N-hydroxymethyl starch-amide addition up to 1% and then did not increase. This may be explained by the fact that OCC recycled paper strength depends on the quantity of bonds and area of bonding sites of recycled pulp fibers, and after a certain amount of addition of N-hydroxymethyl starch-amide, the recycle paper did not increase in strength. It can also be observed from figures 34 & 35 that 1% N-hydroxymethyl starch-amide treated OCC pulp hand sheet increased the dry tensile, and the burst index was found to be 36 and 38 % compared to the control sample. In addition, to compare N-hydroxymethyl starch-amide with cationic starch, we made an OCC pulp hand sheet with 1% cationic starch. The dry strength of the cationic starch-treated OCC hand sheet increased by about 10% compared to the control sample, which was significantly lower than 1% N-hydroxymethyl starch-amide-treated OCC pulp hand sheet.

When compared to a commercial grade product, PAE, for dosage 0.1% to 0.5%, it was found that N-hydroxymethyl starch-amide performed very similarly to PAE, albeit slightly less. The highest gain in dry tensile index is observed at 0.5% dosage, 21.7% increase when OCC pulp was treated with PAE, and 20.7% when OCC pulp was treated with N-hydroxymethyl starch-amide. Shown in Figure 36.

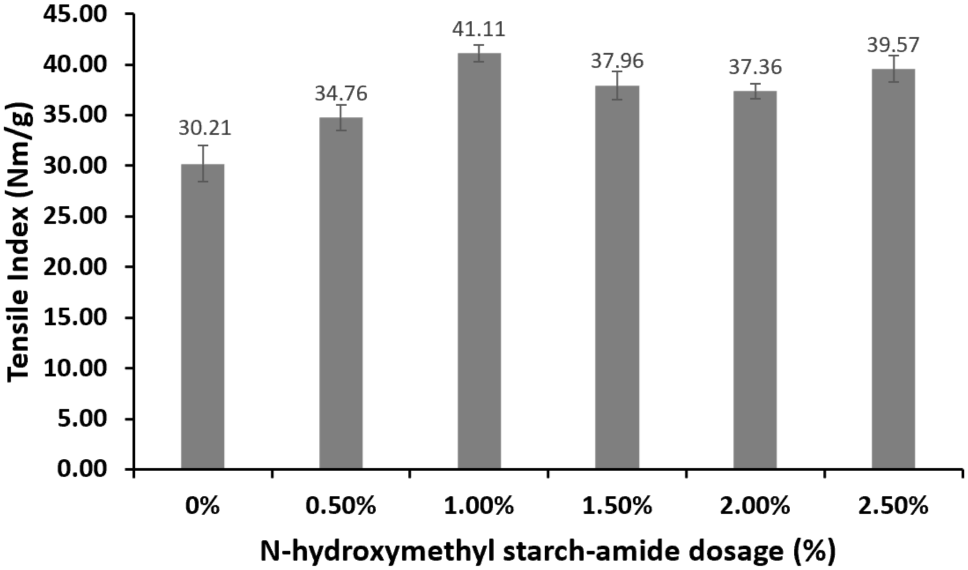


Figure 34: Effect of N-hydroxymethyl starch-amide on the dry tensile index of OCC recycled paper.

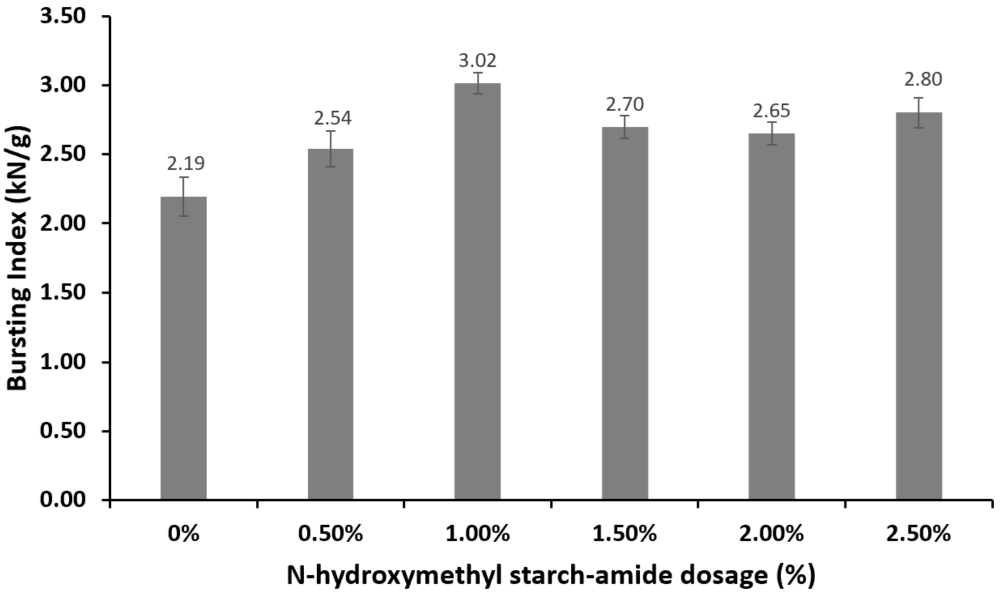


Figure 35:Effect of N-hydroxymethyl starch-amide on the dry burst index of OCC recycled paper.

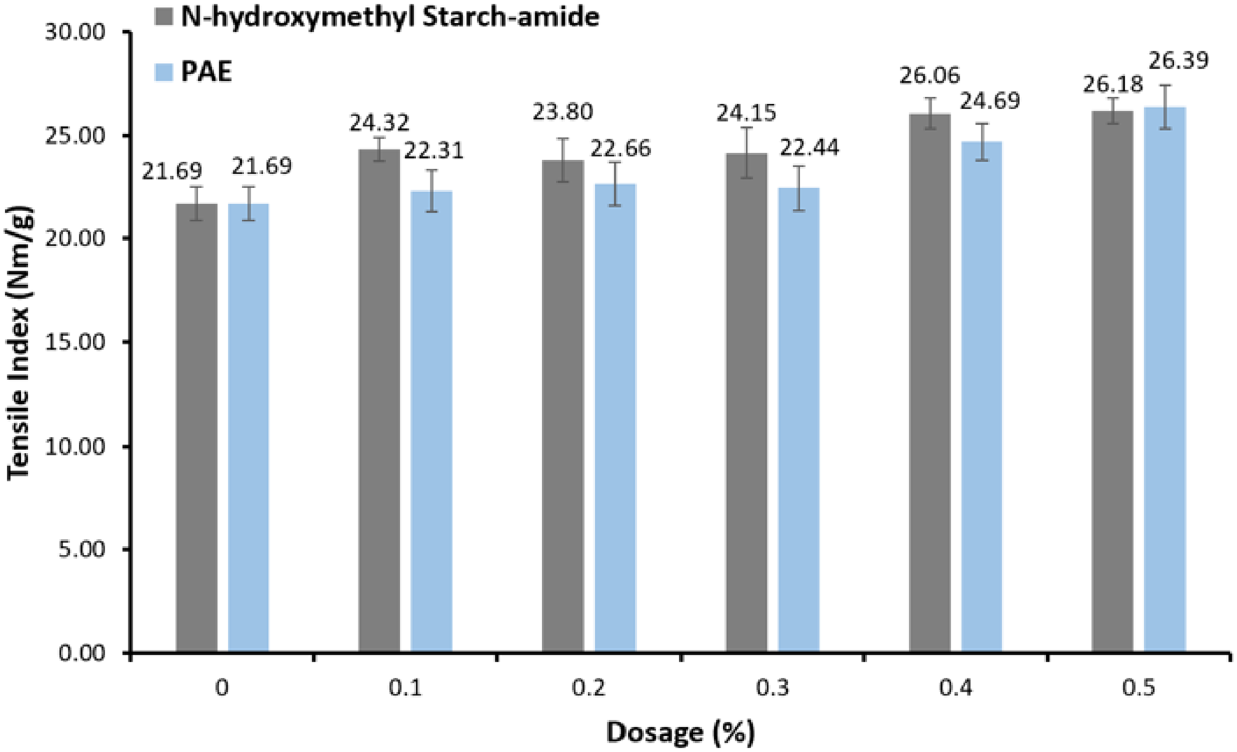


Figure 36: Comparing the effect of N-hydroxymethyl starch-amide vs PAE on the dry tensile index of OCC paper hand sheet.

5.7.4 Effect of pH on the wet strength of N-hydroxymethyl starch-amide-treated OCC paper sheet

The effective pH of N-hydroxymethyl starch-amide additive onto the OCC pulp slurry was determined based on the wet strength by various pH (note; the pH was adjusted from 3 to 10 by adding acetic acid or sodium hydroxide solution into the paper molding machine prior to making a hand sheet) additive-treated OCC paper sheet. The additive-treated OCC paper sheet was dried at room temperature (condition room) and 165°C (air oven) separately. Figure 37 shows that the N-hydroxymethyl starch-amide additive performed better at acidic pH (3 to 6), and the highest wet strength was found at pH 5. It is also observed that the wet strength of 165°C dried paper was significantly higher (100%) than room temperature dried paper sheet (Fig. 37). This may be explained by the fact that N-hydroxymethyl starch-amide is a high-temperature sensitive additive to form the higher amount of covalent bonds between pulp fiber and additive.

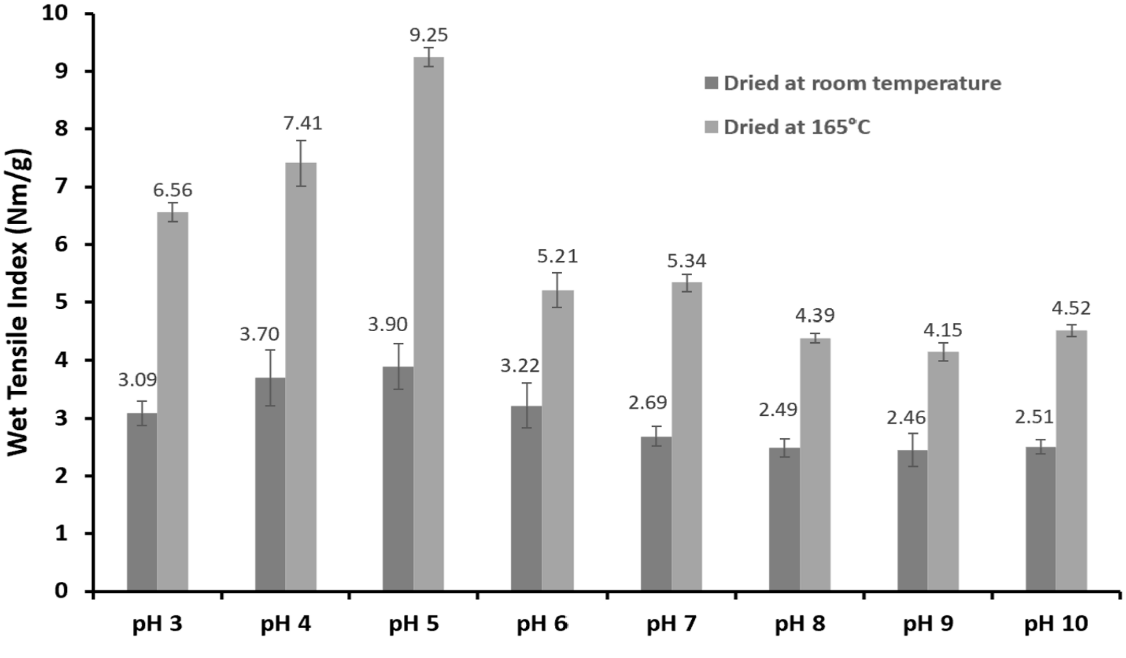


Figure 37: Effect of pH on the wet strength of N-hydroxymethyl starch-amide treated OCC paper dried at room temperature and 165°C separately.

5.7.5 Effect of N-hydroxymethyl starch-amide additive on tissue paper

Wet strength is a favorable characteristic of tissue paper because it allows it to possess sufficient wet strength. Most common wet-strength resins, such as G-PAM and PAE, are typically used in tissue paper manufacturing ***(Miglierini, 2017)***. A comparative study was done to see the effectiveness of the N-hydroxymethyl starch-amide additive compared to commercial wet strength additives (GPAM and PAE). Approximately 1% dosage was added to a tissue paper (30gsm) and then dried in an air oven at 165°C for 5 minutes to test wet strength. The wet tensile indices of GPAM, PAE, and N-hydroxymethyl starch-amide-treated tissue paper was found to be 1.76, 1.78, and 1.68, respectively. Figure 38 shows that the wet tensile index of N-hydroxymethyl starch-amide-treated tissue paper increased ~ 143% compared to the control (no additive) and was almost the same as commercial additives such as GPAM and PAE.

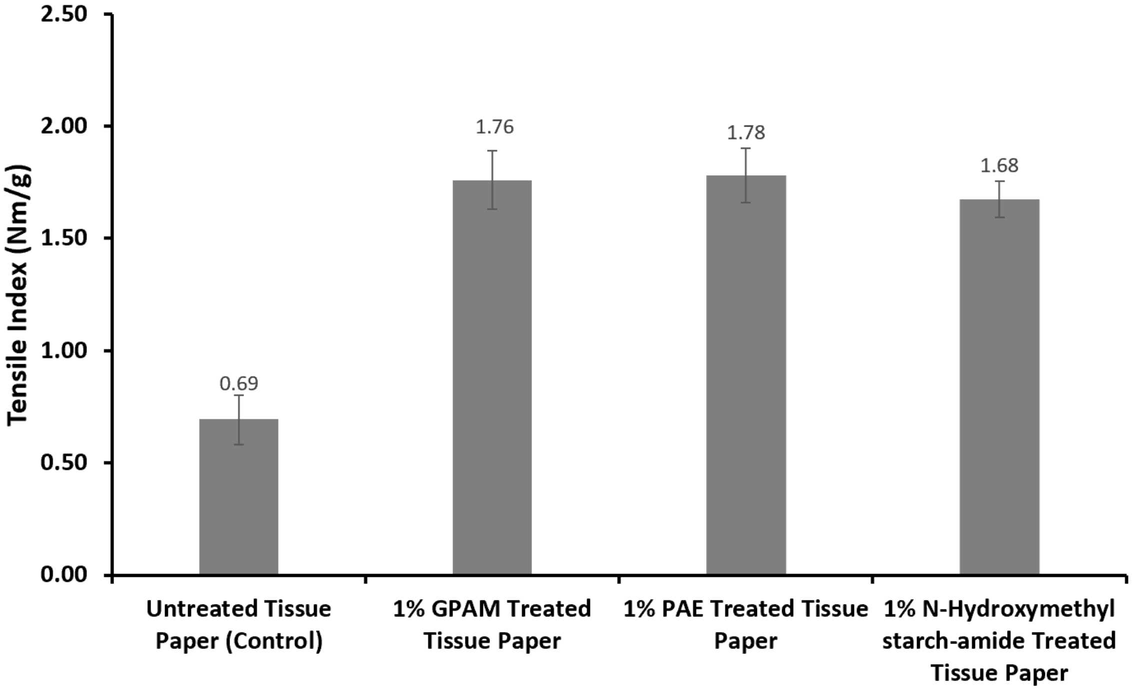


Figure 38: Effect of N-hydroxymethyl starch-amide on the wet tensile index of tissue paper.

5.7.6 Bond formation between N-hydroxymethyl starch-amide with OCC pulp

The functional groups of N-hydroxymethyl starch-amide are reactive hydroxyl group (-OH), amines (-NH2), and alcoholic hydroxyls (-OH), which may form covalent, ionic, and hydrogen bonds with the hydroxyl (-OH) and carboxyl (-COOH) groups on pulp fibers during papermaking. The covalent bond is formed between the reactive hydroxyl group and alcoholic hydroxyl group to contribute to the wet strength of paper/tissue products ***(Bates, N. A., 1969)*** (***Obokata, T.; & Isogai, A., 2007)***. The hydrogen bond, covalent bond, and ionic bond all contribute to the dry strength of paper/tissue products. The internal bonding strength of the N-hydroxymethyl starch-amide additive-treated paper sheet was tested, and the results are shown in Figure 39. The internal bonding strength of N-hydroxymethyl starch-amide-treated paper sheet increases by about 41.12% with N-hydroxymethyl starch-amide addition up to 1% and then is the same. This may be explained that the chemical bond formation being saturated between pulp fiber and N-hydroxymethyl starch-amide after the addition of 1% additive.

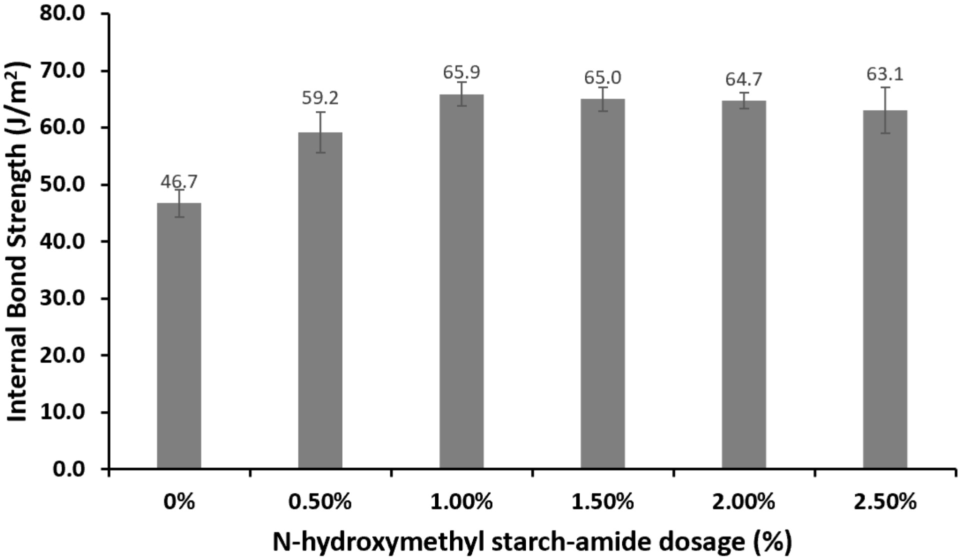


Figure 39: Effect of N-hydroxymethyl starch-amide starch on the internal bond strength of OCC paper sheet.

5.7.7 SEM image analysis of N-hydroxymethyl starch-amide treated OCC paper sheet

Scanning electron microscopy of OCC paper and N-hydroxymethyl starch-amide additive-treated OCC paper is shown in Figure 40. The OCC pulp sample control shows a rougher surface with gaps appearing between pulp fibers, but the N-hydroxymethyl starch-amide-treated OCC paper sheet SEM images reveal a more continuous and smoother surface because gaps are filled by the N-hydroxymethyl starch-amide additive. It may be that these additional interaction results in more overall bonding between the pulp fibers in which the additive network increases the physical strength of the N-hydroxymethyl starch-amide starch-treated OCC paper sheet.

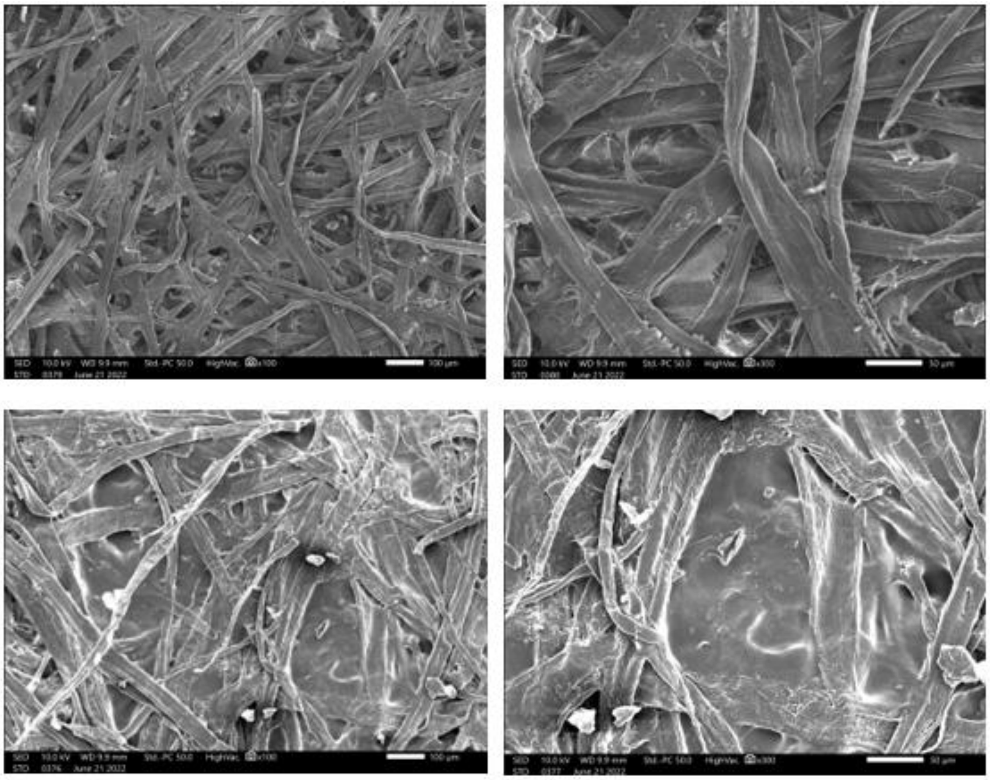


Figure 40: SEM images of untreated OCC paper sheet (top) and N-hydroxymethyl starch-amide additive-treated OCC paper sheet (bottom).

5.7.8 Coating of N-hydroxymethyl starch-amide onto OCC paper

A summary of the physical properties of coated (one side) and uncoated OCC paper sheets is presented in Table 9. Hand sheets were coated with 2.5% N-hydroxymethyl starch-amide and cationic starch solution separately, using a bar applicator with 6 mils thickness. The hand sheets were then dried at 165 °C for 5 minutes. The uncoated paper hand sheet was used as control.

Table 9: Results of N-hydroxymethyl starch-amide starch coating on OCC paper sheets.

	Tensile				
	Dry Tensile Index (Nm/g)	Wet Tensile Index (Nm/g)	Brightness Index	Gloss	Roughness (Sheffield Units)
Uncoated OCC paper (Control)	18.67	2. 72	17.0	11.8	364.1
Cationic starch coated OCC paper	27.50	3.28	17.3	15.7	241.0
N-hydroxymethyl starch-amide coated OCC paper	33.11	8.75	17.9	16.1	230.5

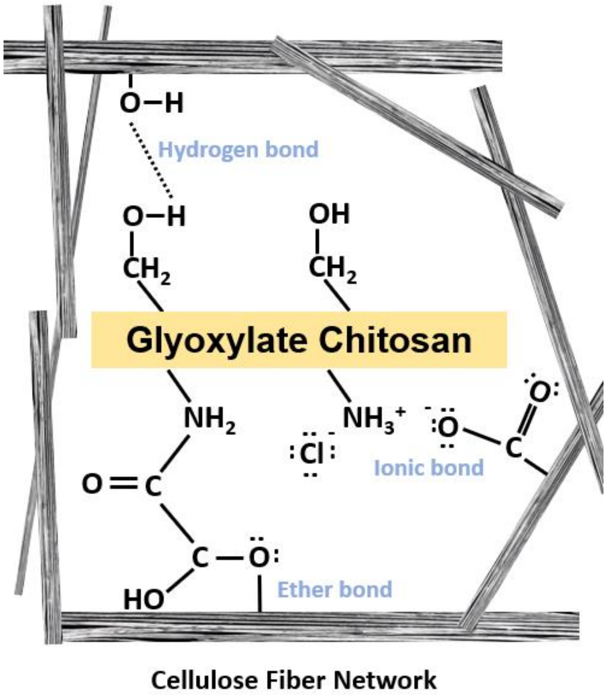
It is observed from Table 9 that the average wet tensile index of N-hydroxymethyl starch-amide additive-coated OCC paper was 8.75, which is 221% higher than the uncoated OCC paper sheet (control), and ~ 166% higher than cooked cationic starch solution-coated OCC paper. Similarly, the average dry tensile index was 33.11, which is 77% higher than the uncoated OCC paper sheet (control), and ~ 20% higher than cooked cationic starch solution-coated OCC paper. This increased wet tensile index of N-hydroxymethyl starch-amide additive-coated OCC paper, perhaps N-hydroxymethyl starch-amide formed additional covalency as well as ionic and hydrogen bonds between the pulp fibers during the drying of coated papers. In addition, Table 9 also shows that both coating additives N-hydroxymethyl starch-amide and cooked cationic starch solution-coated paper increased gloss and significantly decreased roughness compared to uncoated OCC paper sheet (control).

5.8 Conclusions

A synthesized bio-based paper strength additive was prepared from cationic starch. Cationic starch was modified with 2-chloroacetamide in the presence of sodium hydroxide in an aqueous medium via an etherification reaction to incorporate the amine functional group into cationic starch for further reaction with formaldehyde. The optimum modification reaction conditions were obtained at 75 % chloroacetamide concentration, solid to liquor ratio of 1:30, a reaction time of 4 h and a temperature of 40 ◦C. The degree of etherification and degree of substitution of modified cationic starch were determined to be 21 % and 1.4. Further, modified cationic starch was reacted with formaldehyde to produce N-hydroxymethyl starch-amide. About 1 % of N-hydroxymethyl starch-amide was blended with the OCC pulp slurry prior to making a paper hand sheet sample for testing physical properties. The wet tensile index increased 243 % compared to the control. Similarly, the dry tensile and bursting index increased by 36 and 38 % respectively, compared to control. Comparative studies were done between N-hydroxymethyl starch-amide additive and commercial wet strength additives such as GPAM and PAE. The wet strength index of 1 % N-hydroxymethyl starch-amide treated tissue paper was found to be 1.68 Nm/g which is 2.5 times higher than the control sample and almost the same as commercial paper wet strength additives GPAM and PAE. In addition, when the OCC paper sheet was coated with a 2.5 % Nhydroxymethyl starch-amide solution, the wet and dry tensile index increased ~221 and 77 %, respectively, while there was also a slightly increased gloss and significantly decreased roughness compared to the control sample. The increased wet and dry strength agrees with increased bonding between the reactive hydroxyl group of N-hydroxymethyl starch-amide and the alcoholic hydroxyl group of pulp fibers.

6. SYNTHESIS AND EVALUATION OF GLYOXYLATE CHITOSAN AS AN ANTI-MICROBIAL WET AND DRY STRENGTHENING AGENT FOR PULP PRODUCTS

Graphical Abstract



6.1 Abstract

The aim of this work is to develop a bio-based antimicrobial paper additive to increase both wet and dry paper strength for paper product. The chitosan will be dissolved in acidic water and then reacted with glyoxal to make glyoxylate chitosan solution. The glyoxylate chitosan solution will be mixed with OCC pulp slurry to make paper hand sheets. The glyoxylate chitosan additive reduced drainage time by 5%, and increased dry tensile strength by 36%, and wet tensile strength by 428%. The resulting paper sheet also inhibited bacterial growth by 90-95%. Furthermore, a pilot-scale trial was performed to compare chitosan solution, glyoxylate chitosan, cPAM. Most notably, the pilot-scale trial showed that cPAM, chitosan solution, and glyoxylate chitosan

increased the wet tensile index of 150 GSM OCC paper by 75%, 278%, and 582% respectively compared to control sample.

Keywords: Chitosan, glyoxylate chitosan, antimicrobial, pulp slurry, cPAM (cationic polyacrylamide).

6.2 Experimental Section

6.2.1 Materials

Chitosan (medium molecular weight) was supplied from Sigma-Aldrich, St. Louis, MO, (CAS no. 9012-76-4). Hydrochloric acid (CAS no.7647-01-0) was purchased as a reagent grade from Sigma-Aldrich, St. Louis, MO. Glyoxal solution was purchased from Sigma-Aldrich, St. Louis. MO, (CAS no. 107-22-2). Polyacrylamide epichlorohydrin (Kymene 821) was purchased from Solenis. Hydrochloric acid was purchased from Sigma-Aldrich, St. Louis. MO, (CAS no. 7647-01-0). Sodium hydroxide pellets were purchased from Sigma-Aldrich, St. Louis, MO, (CAS no. 1310-73-2). Poly-DADMAC was purchased from *Mütek Analytic.*

6.2.2 Preparation of chitosan solution

1.5 g of medium molecular weight chitosan flakes were dispersed in 92.5 mL of water by continuous stirring in a beaker. The mixture is stirred for 10 minutes to allow the chitosan flakes to be uniformly dispersed. 6.0 mL of the aqueous hydrochloric acid solution is slowly added to the mixture. Continue stirring the mixture for 30 minutes until the chitosan flakes are completely dissolved ***(Choudhury, N. et al*, *2012)***. Heating may speed up the rate of depolymerization of the chitosan. The reaction scheme is shown in Figure 41 below.

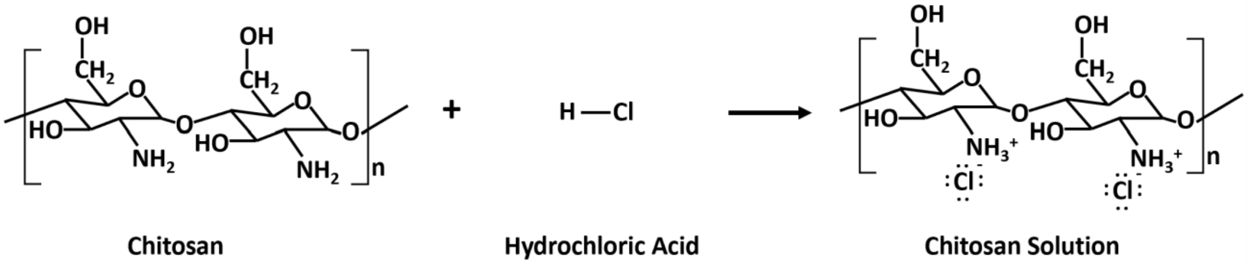


Figure 41: Reaction of chitosan with hydrochloric to form chitosan solution.

6.2.2 Preparation of chitosan additive

After the chitosan is completely dissolved, add 20 mL 40% glyoxal solution to the beaker and continue stirring for 30 minutes at 50°C. The reaction scheme is shown in Figure 42 below ***(Sapula, P., Bialik, K. & Malarz, K., 2023)***.

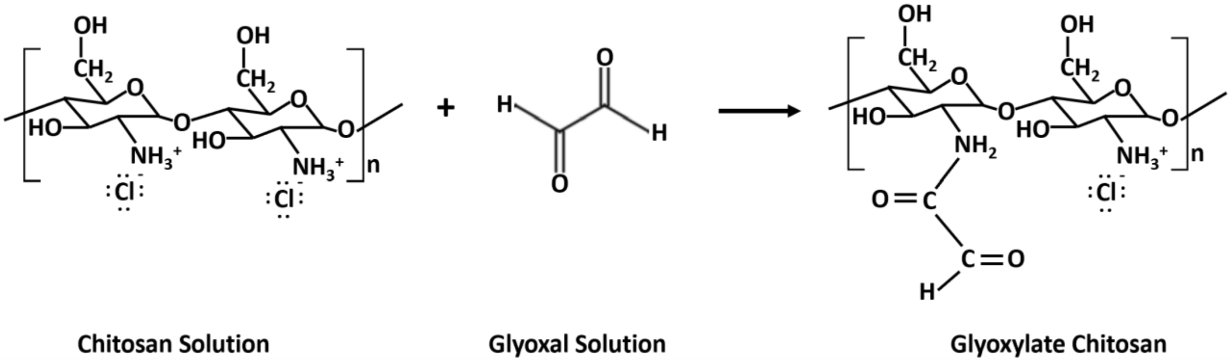


Figure 42: Glyoxalation of chitosan.

6.2.3 Paper hand sheet preparation method

The paper hand sheets were prepared according to TAPPI Standard Method T 205 and conditioned according to TAPPI T402. Approximately 0.3% chitosan solution and glyoxalated chitosan additive were added separately into the OCC pulp slurry and mixed for 20 minutes before making the paper hand sheet. A hand sheet molder was used to make a hand sheet in the presence or absence of a chitosan derivative additive. The paper sheets were left to dry in a conditioned room (23°C, 50% RH) for three days before testing their physical properties.

6.2.4 Antimicrobial activity studies in accordance to FTTS-FA-002

Antimicrobial activities of chitosan-based additives were tested in reference to FTTS-FA-002 test method. Antimicrobial activities were performed for two strains of bacteria (approximately 105 – 106 CFU/mL) with one Gram-positive bacteria (S. aureus) and one Gram-negative bacteria (E. coli). The bacterial culture was freshly prepared by growing a single loop of bacteria and incubated over 24 hours at 37°C ± 2°C. The bacterial culture was adjusted using a spectrophotometer to give the desired CFU/ml. 0.4 mL of this culture was diluted with 20ml of nutrient broth and incubated for two hours at 37°C ± 2°C. This culture was further diluted 20 times and used for all the tests.

Untreated OCC paper, chitosan solution-treated paper, and glyoxylate chitosan-treated paper sheets were individually swirled with 1 mL of the diluted bacteria inoculum and 100 mL of the neutralizing solution. Bacteria were shaken out using a vortex mixer. Serial Dilutions were performed. The test was conducted with nutrient agar as a medium in 95mm x 15mm Petri dishes. Serial Dilutions were made and the culture plates were incubated overnight at 37°C ± 2°C ***(FTTS-FA-002, 2022.***

6.3 Characterization

6.3.1 ATR analysis

ATR IR spectrum peaks of the modified cornstarch were recorded by using a PerkinElmer Spectrum 100 FTIR Spectrometer. Spectra were obtained after 64 scans over 600−4000 cm^{-1} ***(Sawant, N.; Salam, A.; Lucia, L, 2020)***.

6.3.2 Effect of chitosan additives on fiber charge

The fiber charge of the OCC fiber was calculated according to the formula, Eq. (10) ***(Mocchiutti et al, 2007).***

$$q = \frac{V \, x \, C}{Wt} \tag{10}$$

Where;

q = Fiber charge (μeq/L)

V = Consumed Poly-DADMAC volume (mL)

C = Titration concentration (meq/L)

Wt = Sample volume (mL)

6.3.3 Effect of chitosan additives on fiber charge

The drainage rate of the pulp was tested in reference to TAPPI T261. A dynamic drainage jar (DDJ) was used to test the pulp samples.

6.3.4 Tensile strength

The tensile strength of the OCC paper hand sheet was tested by following TAPPI T220 test. Tensile strength was tested using INSTRON 4301 Tensile Tester.

6.4 Results and discussion

6.4.1 ATR analysis

The ATR spectra of chitosan, chitosan solution, and glyoxylate chitosan are shown in Figure 43. The band at 3340 cm^{-1} can be attributed to O−H stretching, and 1620 cm^{-1} corresponds to N−H bending vibrations. However, the spectra of glyoxylate chitosan shows an additional peak at 1730 cm^{-1} that corresponds to the C=O stretching of an amide, indicating successful reaction between chitosan and glyoxal resulting in an amide.

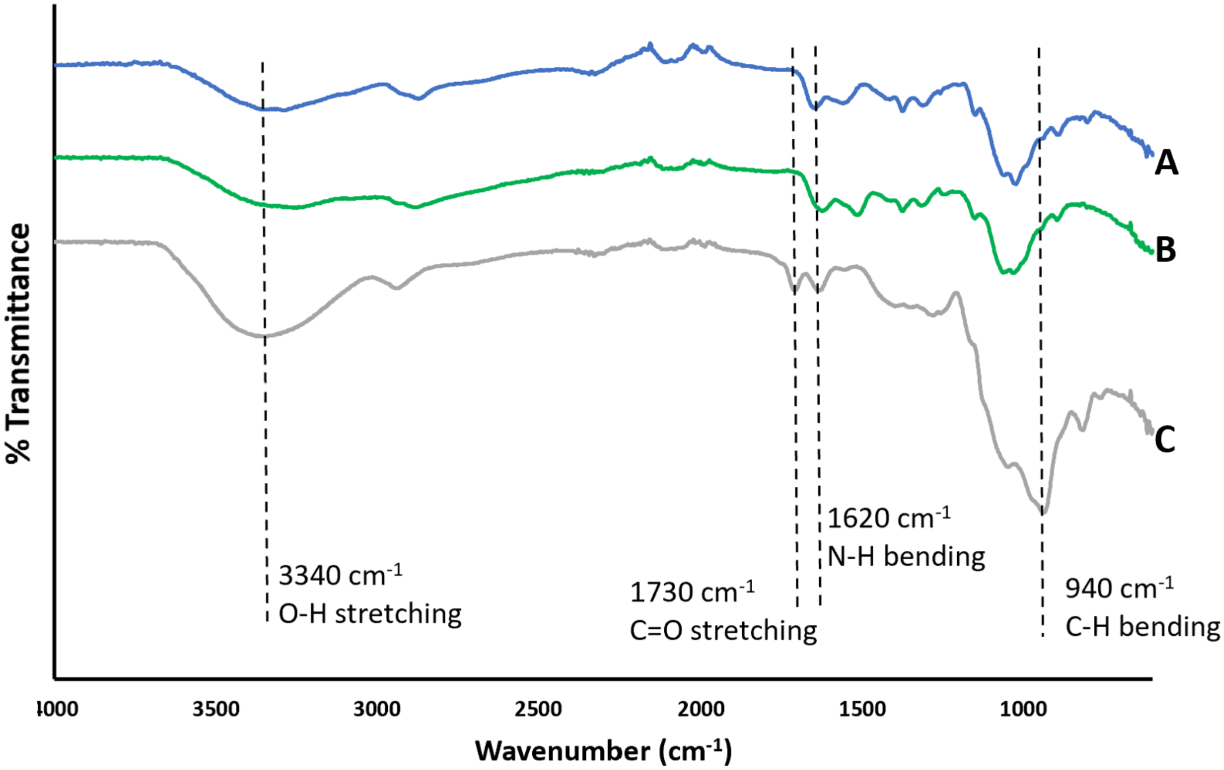


Figure 43: ATR spectra of chitosan (A), chitosan solution (B), and glyoxylate chitosan (C).

6.4.2 Fiber charge

Fiber charge is an important property of cellulose fibers that influences post-processing and the qualities of the end-use products. The fiber charge directly correlates to the presence of several anionic functional groups, such as carboxyl and ionizable hydroxyl group, which varies between different fiber sources and the chemical treatments it has undergone ***(Zhang, H.; et al, 2016).*** This study investigated the OCC fiber charge at different pH levels (4, 5, 6, 7, 8, 9) and the interaction between the fibers and the chitosan additives at the aforementioned pH levels. See figure 44.

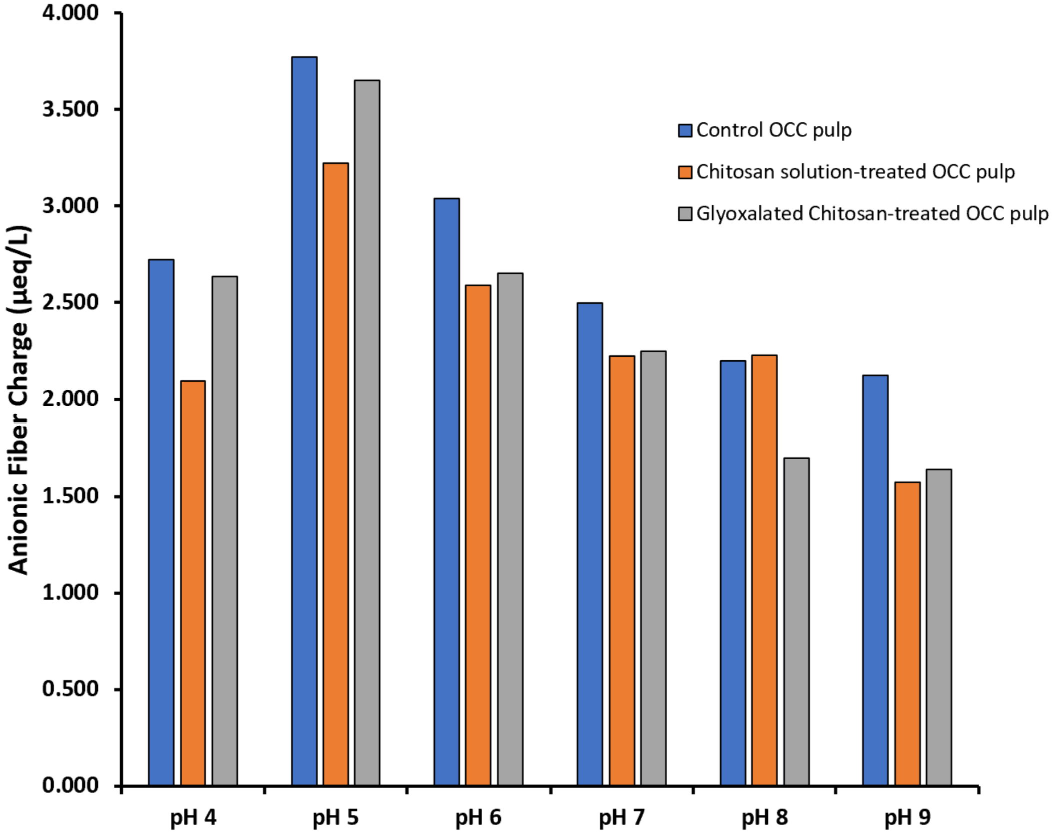


Figure 44: Effect of chitosan additives on fiber charge at different pHs.

6.4.3 Hand sheet time to formation

Generally, the chitosan additives slightly decrease the anionic charge on the control OCC pulp. This may be due to the additive forming bonds with the available carboxyl or ionizable hydroxyl groups, effectively reducing the anionic fiber charge. Further investigation revealed that the interaction in the system did not significantly affect the formation time of the hand sheet in the molding machine. The quickest and slowest time recorded for hand sheet formation was found to have a difference of approximately 5% and is shown in Table 10.

Table 10: Summary showed the time required to form hand sheet in the paper molding machine.

Time to Formation in the Paper Molding Machine (s)			
	Control OCC pulp	Chitosan solution-treated OCC pulp	Glyoxylate chitosan-treated OCC pulp
pH 4	8.30	8.15	8.25
pH 5	8.39	8.24	8.26
pH 6	8.15	8.33	8.14
pH 7	7.95	8.19	8.19
pH 8	8.05	8.29	8.25
pH 9	7.97	8.27	8.35

6.4.4 Effect of glyoxylate chitosan additive on the paper strength

The pulp hand sheet was prepared by utilizing OCC recycled pulp (CSF = 550) with or without adding the developed glyoxalated chitosan additive and commercial additives such as GPAM or PAE. The OCC recycled pulp without additives served as control. Table 11 shows the effect of different types of additives (0.5%) on the strength of the OCC paper. It is observed that GPAM, PAE, chitosan solution, and glyoxalated chitosan increased the dry tensile strength of the OCC paper sheet by about 15%, 14%, 31%, and 36%, respectively compared to control sample. Similarly, the wet tensile strength of the treated recycled OCC paper sheet increased by 30%, 33%, 65%, and 428%, respectively compared to control sample.

Table 11: The effect of different types of additives (0.5%) on the tensile index of the 60 GSM OCC paper sheet.

	Wet Tensile Index (Nm/g)	**Dry Tensile Index (Nm/g)**
Control	0.49	27.1
GPAM-treated OCC pulp	0.64	31.08
PAE-treated OCC pulp	0.65	30.92
Chitosan solution-treated OCC pulp	0.81	35.59
Glyoxylate chitosan-treated OCC pulp	2.59	36.97

6.4.5 Pilot-plant trial of chitosan solution and glyoxalated chitosan additive

To further understand the scalability effectiveness of the chitosan derivate additives, a pilot-scale trial was performed at Western Michigan University's paper pilot plant. The conditions for the trial were set to simulate a "typical" environment that is used in most industrial paper manufacturing plants. The machine trial conditions are: neutral pH (7-7.4), 150 GSM OCC, with 0.3% additive dosage. Four samples were run during the trial; control OCC, chitosan solution-treated OCC, glyoxalated chitosan-treated OCC, and cationic polyacrylamide (cPAM)-treated OCC (as a reference to an industrial additive). The results are shown in the table 12 below. It is observed that chitosan solution and glyoxalated chitosan-treated paper significantly increase all kind of paper strength compared to the control sample and it was much better than commercial paper strength agent cPAM. Table 12 shows that cPAM increased the dry tensile index, burst index, and STFI of the OCC paper by 12%, 22%, and 20%, respectively. Similarly, chitosan solution and glyoxalated chitosan increased the dry tensile index, burst index, and STFI of the OCC paper about 80-100%, ~95%, and ~75%. However, the effect of these additives on the wet tensile index of the OCC paper is significantly different. cPAM increased wet tensile index of the OCC paper by ~75%, chitosan solution by ~278%, and glyoxalated chitosan by ~582%. This is due to the glyoxylate chitosan has aldehyde (-CHO) functional groups, which forms covalent bond (hemiacetal) with the hydroxyl groups of the fibers ***(Yuan, Z.Y; Hu, H., 2012).***

Table 12**:** Effect of 0.3% dosage additive on the wet and dry tensile index of 150 GSM recycled OCC pulp hand sheets.

Pilot-scale trial results (150 GSM OCC)				
	Wet Tensile Index (Nm/g)	Dry Tensile Index (Nm/g)	Burst Index (kPam2/g)	STFI (lb/inch)
Control	0.33	12.23	1.34	15.80
Chitosan solution	1.25	20.10	2.56	24.67
Glyoxylate chitosan	2.25	24.50	2.66	27.73
cPAM	0.58	13.68	1.63	18.95

6.4.6 Antimicrobial properties of lab-scale glyoxalated chitosan additive-treated paper product and process water

The lab tests have shown impressive antimicrobial properties of the glyoxylate chitosan-treated paper sheet. Specifically, the glyoxylate chitosan treated paper sheet has been shown to consistently reduce growth of both gram-negative *E. coli* and gram-positive *S. aureus* by 90-95%. It was also found that no foul odor or color change were detected from the glyoxylate chitosan-treated pulp slurry after 21 days of observation period, and monitored the process water for 60 days. The observations are shown in figure 45.

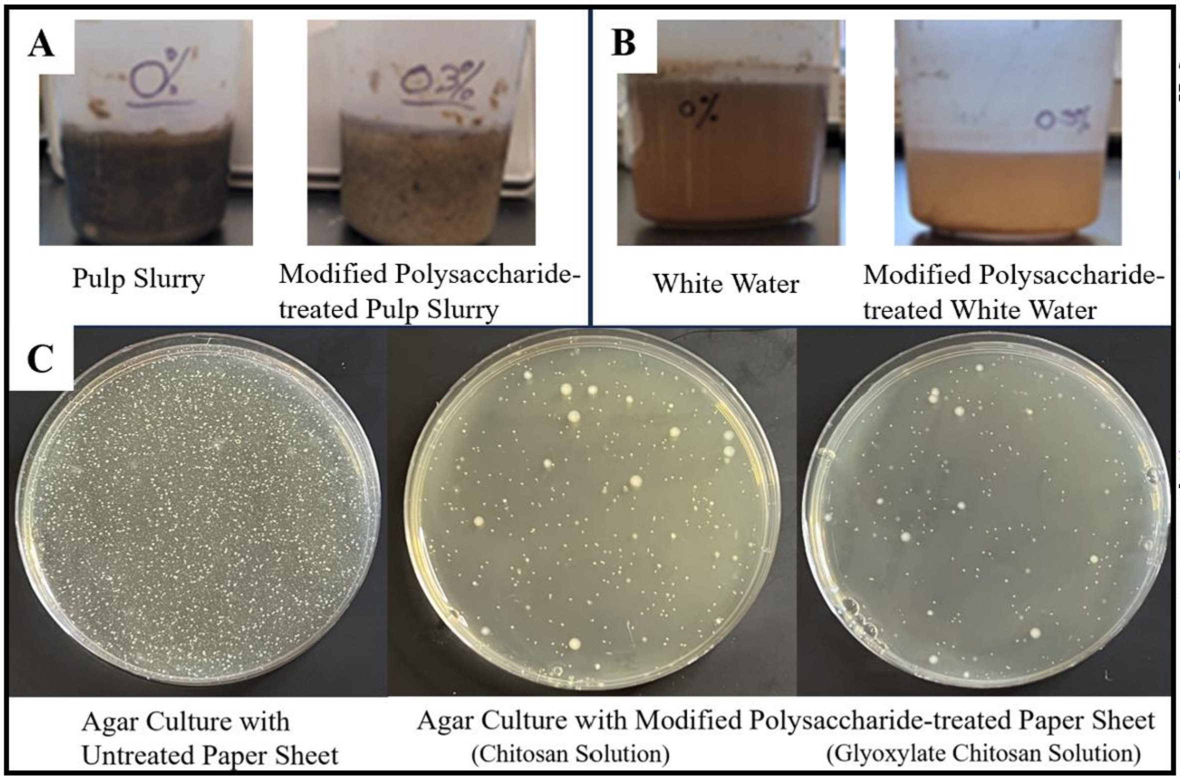


Figure 45: Decomposition and antimicrobial activity test results of (A) pulp slurries, (B) process water, and (C) agar culture.

6.4.7 Antimicrobial properties of pilot trial additive-treated paper product and process water

After conducting the pilot-scale trial, the pulp slurries treated with cPAM, chitosan solution, and glyoxylate chitosan were collected and monitored for a period of 11 weeks. The result showed that at the end of 11 weeks, only the glyoxylate chitosan-treated pulp slurry remained the same color compared to at week 0. The untreated pulp slurry, cPAM-treated pulp slurry, and chitosan solution-treated pulp slurry turned darker in color which can be associated with decomposition due to bacterial activities/mold shown in figure 46.

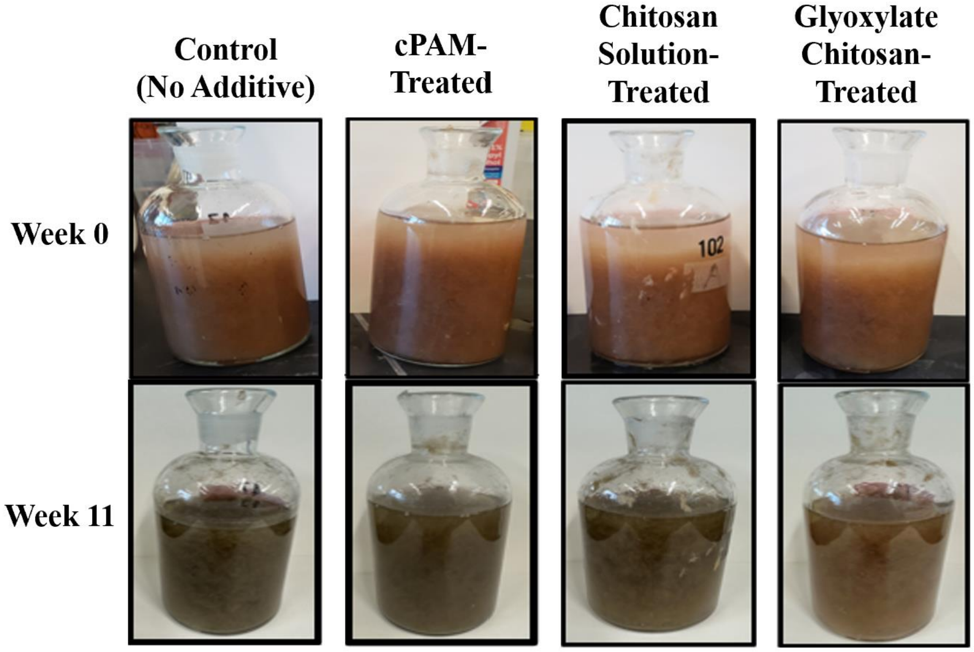


Figure 46: Transformation of untreated and additive-treated pulp slurry samples from week 0 to week 11.

6.4.8 Odor intensity

Odor intensity was recorded by three students in reference to ASTM E679 (although with limitations). During the 11-week monitoring period of the pilot-scale trial pulp slurries, the odor intensity/change in odor of the pulp slurries were recorded as well. The result showed that after 2 weeks, the odor of the untreated pulp slurry intensifies at the most rapid rate.

The cPAM-treated and chitosan solution-treated pulp slurries showed similar patterns, while the glyoxylate chitosan-treated pulp slurry showed no significant change in odor. At the end of the observation period, the untreated pulp slurry has the most intense odor, followed by chitosan solution-treated pulp slurry, then closely followed by cPAM treated pulp slurry, and glyoxylate chitosan-treated pulp slurry showed almost no change in odor, shown in figure 47. The change in odor/increase in odor intensity can be associated with decay. This result is in parallel with the result obtained from the transformation observation test.

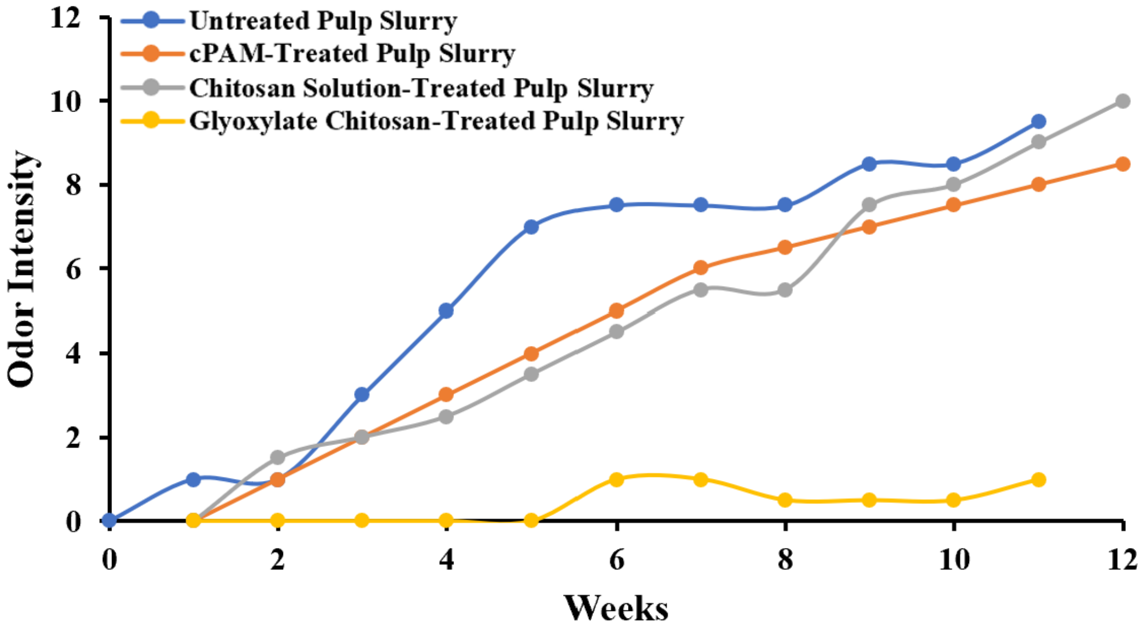
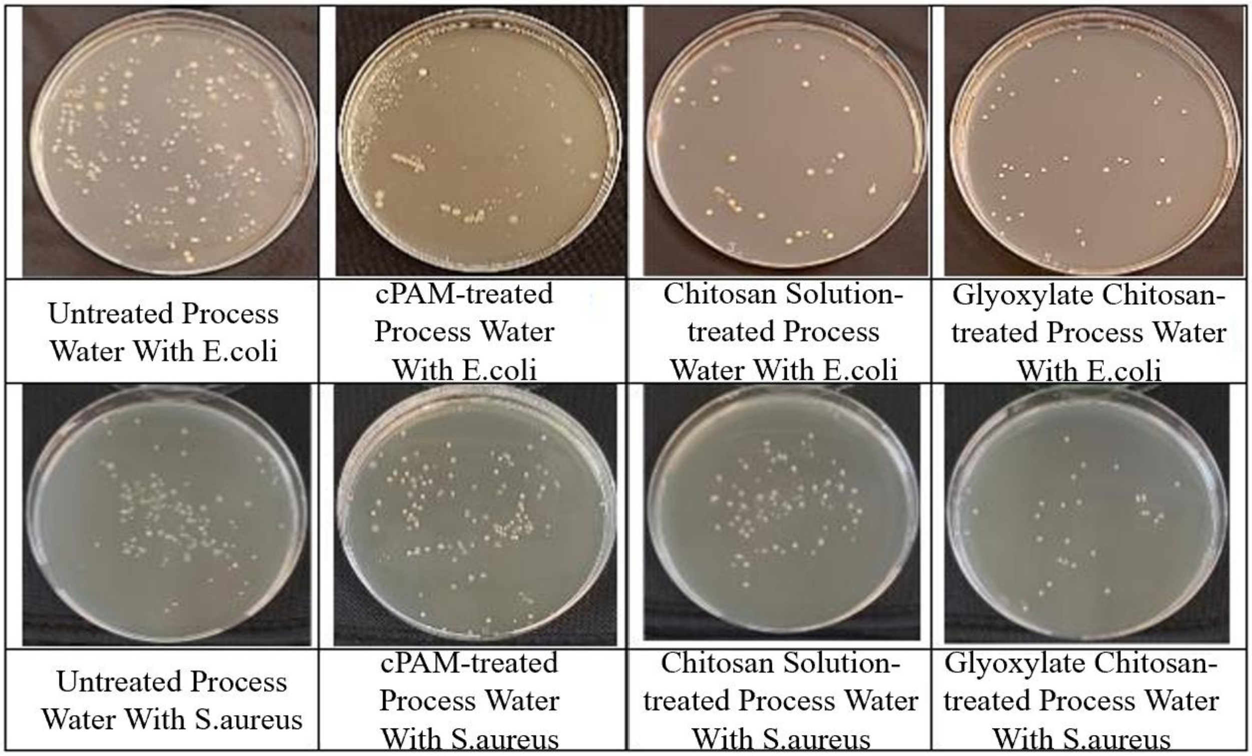


Figure 47: Odor intensity of untreated and additive-treated pulp slurry samples from week 0 to week 11-12.

6.4.9 Bacteria culture test

In addition to the transformation observation and odor intensity monitoring study, the anti-microbial activity of cPAM, chitosan solution, and glyoxylate chitosan were quantified using bacterial cultures on agar plates (FTTS-FA-002 standard test method). As mentioned before, the test was performed on E.coli (gram-negative) and S.aureus (gram-positive). The tests were performed three times to analyze the antimicrobial activity of each additive in the (1) process water, (2) pulp slurry, and the (3) paper sheet formed.

The results show that cPAM, chitosan solution, and glyoxylate chitosan significantly reduces bacteria colony count in all three samples; (1) process water, (2) pulp slurry, and the (3) paper sheet formed. However, it is worth noting that the glyoxylate chitosan-treated samples reduced the bacteria colony count to a more significant extent than cPAM and chitosan solution. This observation is consistent throughout all samples; (1) process water, (2) pulp slurry, and the (3) paper sheet formed, and agrees with both the transformation observation result and odor intensity results. See figures 48-50.



Untreated Process Water With E.coli

cPAM-treated Process Water With E.coli

Chitosan Solution-treated Process Water With E.coli

Glyoxylate Chitosan-treated Process Water With E.coli

Untreated Process Water With S.aureus

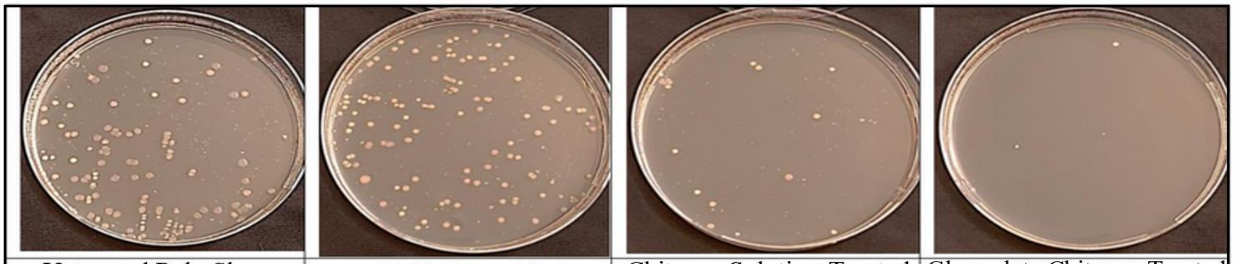
cPAM-treated Process Water With S.aureus

Chitosan Solution-treated Process Water With S.aureus

Glyoxylate Chitosan-treated Process Water With S.aureus

Note: E.coli (gram-negative), S.aureus (gram-positive)

Figure 48: Antimicrobial activity of untreated and additive-treated process water.

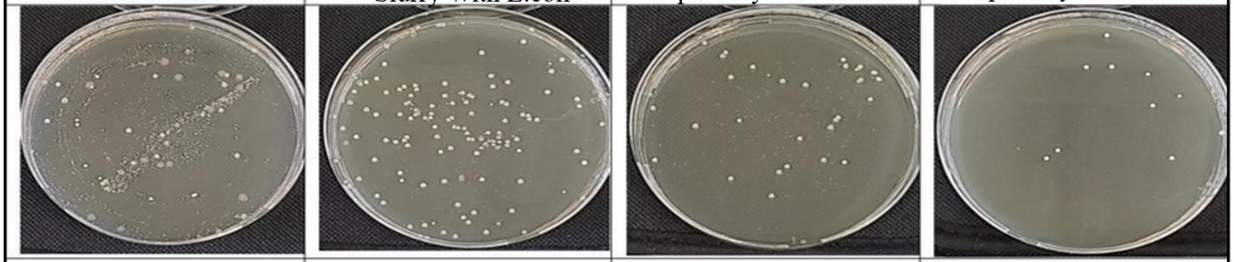


Untreated Pulp Slurry With E.coli

cPAM-Treated Pulp Slurry With E.coli

Chitosan Solution-Treated Pulp Slurry With E.coli

Glyoxylate Chitosan-Treated Pulp Slurry With E.coli



Untreated Pulp Slurry With S.aureus

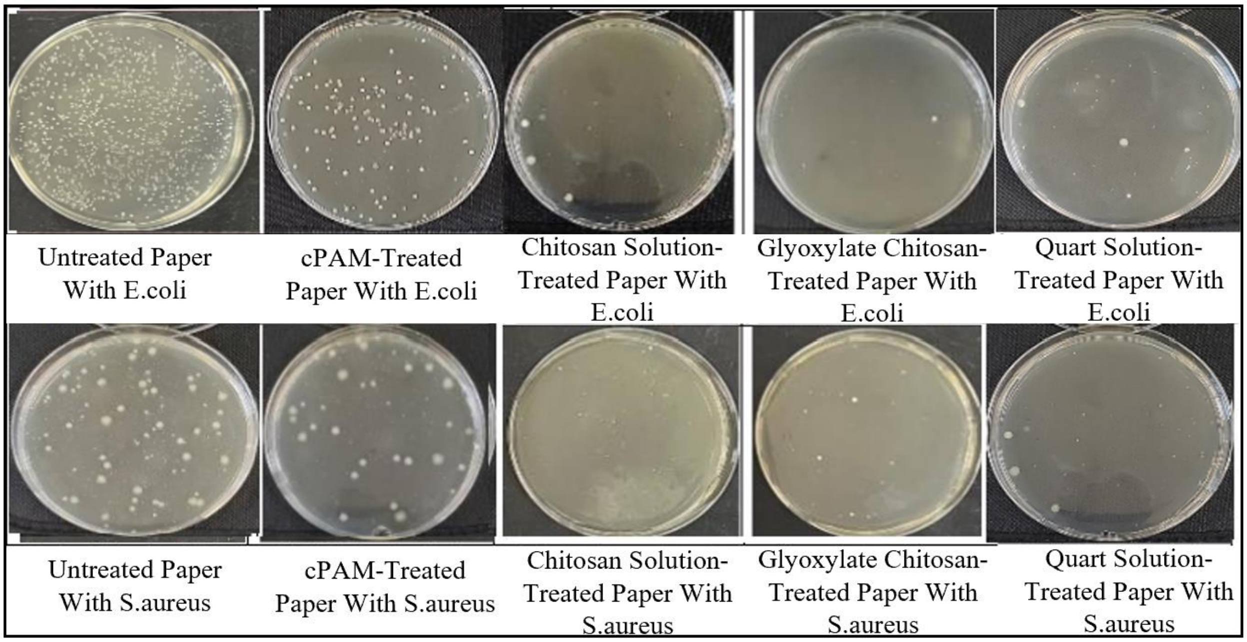
cPAM-Treated Pulp Slurry With S.aureus

Chitosan Solution-Treated Pulp Slurry With S.aureus

Glyoxylate Chitosan-Treated Pulp Slurry With S.aureus

Note: E.coli (gram-negative), S.aureus (gram-positive)

Figure 49: Antimicrobial activity of untreated and additive-treated pulp slurry.



Note: E.coli (gram-negative), S.aureus (gram-positive)

Figure 50: Antimicrobial activity of untreated and additive-treated paper sheet.

6.5 Conclusions

A synthesized bio-based paper strength additive was prepared from chitosan. Chitosan was dissolved in an aqueous medium in the presence of hydrochloric acid, to incorporate positively charged amine functional group into chitosan for further reaction with glyoxal. 0.5% of GPAM, PAE, chitosan solution, and glyoxylate chitosan additive were separately blended with OCC pulp slurry prior to making paper hand sheets for testing of physical properties. The wet tensile index of OCC paper treated separately with GPAM, PAE, chitosan solution, and glyoxylate chitosan increased by approximately 31%, 33%, 65%, and 429% respectively compared to the control. Similarly, the dry tensile index increased by approximately 15%, 14%, 31%, and 36% respectively compared to the control sample.

In addition, the pilot-trial results showed that cPAM, chitosan solution, and glyoxylate chitosan increased the wet tensile index of 150 GSM OCC paper by approximately 76%, 279% and 582% respectively. Similarly for dry tensile index, burst index, and STFI, glyoxylate chitosan increased these properties by approximately 100%, 99% and 76% respectively which are all significantly higher than that of cPAM-treated OCC paper. The antimicrobial study also showed that glyoxylate chitosan-treated OCC paper had significantly lower bacteria growth on the agar plate, 90-95% less than control OCC paper, and the glyoxylate chitosan-treated slurry had only odor intensity levels of around 1 over approximately a 11-week observation period.

7. A SYNTHESIZED STARCH-BASED COATING TO PROVIDE PAPER WITH HIGH BARRIER PROPERTIES FOR PACKAGING APPLICATIONS

7.1 Abstract

The aim of the research work is to develop environment-friendly and biodegradable bio-based coating materials from glyoxylate starch-amide and N-hydroxyl methyl starch-amide with hydrophobic agents to replace the petroleum-based non-biodegradable plastic. Three different types of hydrophobic agents – alkyl ketene dimer (AKD), zein, and poly dimethyl siloxane (PDMS) were separately blended with the glyoxylate starch-amide and N-hydroxyl methyl starch-amide separately. Further, hydrophobic agent-blended glyoxylate starch-amide or N-hydroxyl methyl starch-amide based additives were applied on paper their barrier properties were studied. Initial results showed that both AKD-blended glyoxylate starch-amide and N-hydroxyl methyl starch-amide based coating additives has the highest barrier properties.

Keywords: glyoxylate starch-amide, N-hydroxymethyl starch-amide, hydrophobic agent, bio-based coating, packaging, barrier properties, dynamic contact angle.

7.2 Experimental section

7.2.1 Materials

Glyoxylate starch-amide and N-hydroxymethyl starch-amide were prepared at polymer lab in the department of Chemical and Paper Engineering at WMU. Alkyl ketene dimer (AKD) was manufactured by Solenis. Zein was purchased from Sigma Aldrich, CAS number 9010-66-6. Poly-dimethyl siloxane was purchased from Sigma Aldrich, CAS number 9016-00-6.

7.2.2 Preparation of synthesized starch-based coating

The synthesized starch-based coating was prepared by the blending of hydrophobic agents into N-hydroxymethyl starch-amide and glyoxylate starch-amide separately. The three hydrophobic agents used in this study such as alkyl ketene dimer (AKD), zein, and polydimethylsiloxane (PDMS). The dosage of the hydrophobic agent was optimized as well. The dosage percentages studied were 0, 1, 3, 5, 7, 9, 11, 15, 20, 25, 30, and 50 respectively. The liquid bioplastic was applied on a blotter paper as a coating agent by using a bar applicator with 6 mils thickness. The resulting paper heat dried and then cured at 105°C for 10 minutes. The steps are shown in figure 51.

Figure 51: Synthesis of synthesized starch-based coating from cornstarch.

7.2.3 Determination of viscosity and hi-shear data

The viscosity of the prepared coating was measured using a Brookfield Ametek Viscometer, spindle #6, 100 RPM, and read at 25°C. It was found that each cross-linking agent significantly affects the viscosity of the coating. The viscosity of cornstarch solution was found to be 500cP. The viscosity of the glyoxal starch-amide with AKD bioplastic coating is 5500cP. While the viscosity of the N-hydroxymethyl acrylamide starch-amide with AKD is 2160cP. Viscosity results are summarized in table 13. To further understand the characteristics of the developed coatings, the shear behavior was analyzed using a Hercules Hi-shear viscometer. The Hi-shear curves are shown in Figure 52. The figures generated showed that all kinds of coating exhibited a thixotropic behavior. This means that the coatings will undergo shear thinning when high pressure is applied to it.

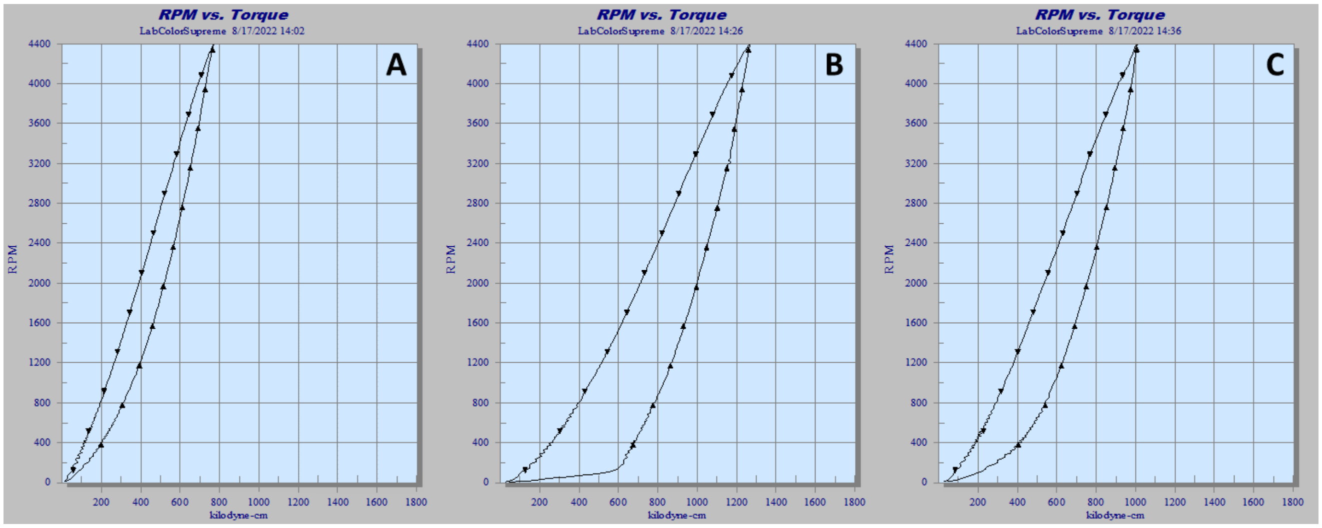


Figure 52: Hi-shear curve of (A) cornstarch, (B) glyoxylate starch-amide with AKD, (C) N-hydroxymethyl starch-amide with AKD.

Table 13: Viscosity of synthesized starch-based bioplastic coating additive.

Label	**Material**	**Viscosity Range (cP)**	**Average Viscosity (cP)**
A	Cornstarch	480-520	500
B	Glyoxylate starch-amide with AKD	5460-5540	5500
C	N-hydroxymethyl starch-amide with AKD	2130-2190	2160

7.2.4 Optimization of hydrophobic agent concentration

After investigating the different dosage of AKD, it was determined that 5% dosage provides the highest surface barrier properties. Figure 53 below shows a representation of how the contact angle of the water droplet changes over time. A dixie plate is used as a reference to compare the water barrier property of the bioplastic-coated paper. Figure 53 also shows that the synthesized starch-based coated paper showed a higher contact angle (about 100°) and was holding the water droplet for a longer time compared to a market product, the dixie plate.

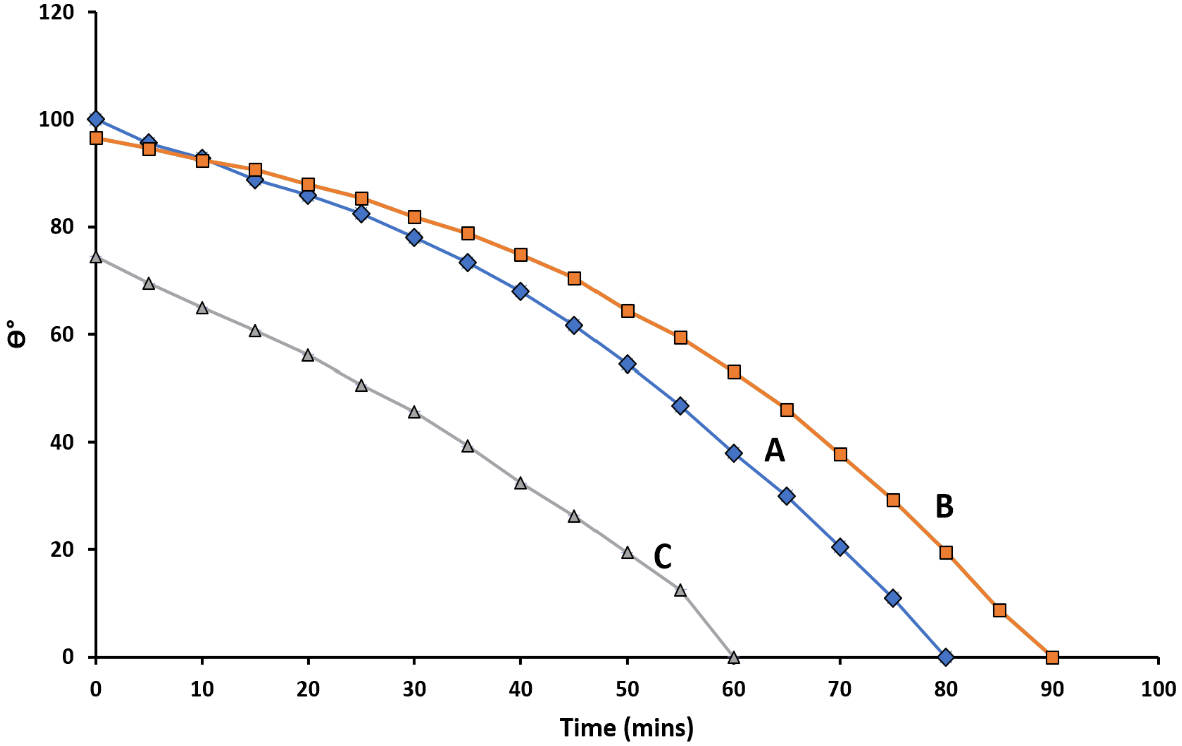


Figure 53: Contact angle of (A) N-hydroxymethyl starch amide with AKD, (B) glyoxylate starch amide with AKD, and (C) dixie plate.

7.2.5 Dynamic contact angle (DCA)

The dynamic contact angle was tested by using an FTA32 software and camera setup. The images captured by the camera show the different initial contact angles of the different hydrophobic agents. A commercial product such as Dixie plate was used as a benchmark to compare the synthesized starch-based coating-coated paper hydrophobicity. It is observed from the image (Fig. 54) that starch-based coating-coated paper sheet has a higher initial contact angle (>90°) than the polyethylene laminated dixie plate.

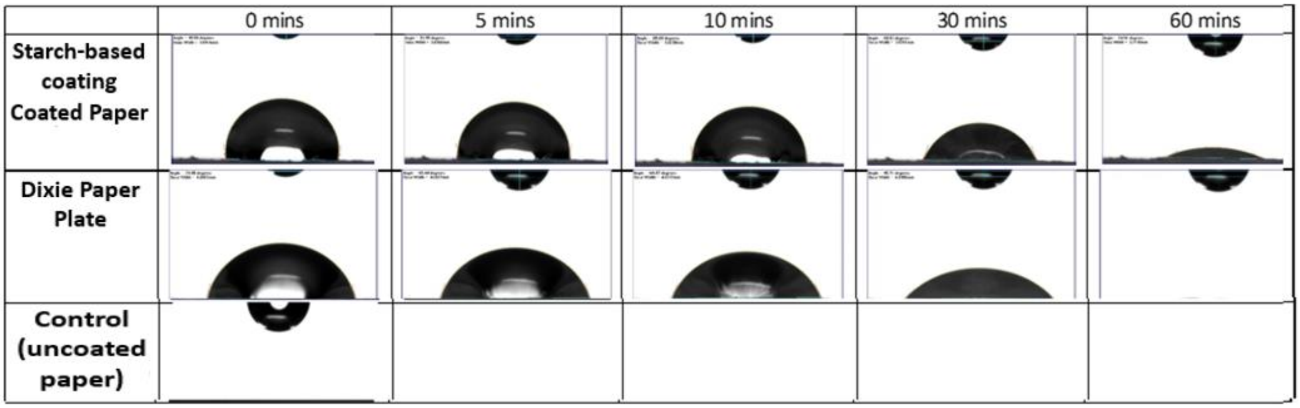


Figure 54: Contact angle images captured by the FTA32 software and camera set up.

7.2.6 Surface water barrier

Figure 55 shows the water barrier property of the synthesized starch-based coating coated paper. Image **A** shows water absorbed into uncoated paper, Image **B** shows a water droplet beading on the highly hydrophobic surface of the starch-based coating-coated liner board, **C**-**E** (brown packaging paper) shows that the starch-based coating-coated paper substrate prevents water absorption for longer times (~5 minutes). Image **F** shows a paper cup substrate holding water (~5 minutes). Although the coated paper substrates were not exposed to water for extended duration, the figure below illustrates that water beads on the paper surface, providing it with some extent of hydrophobic surface,

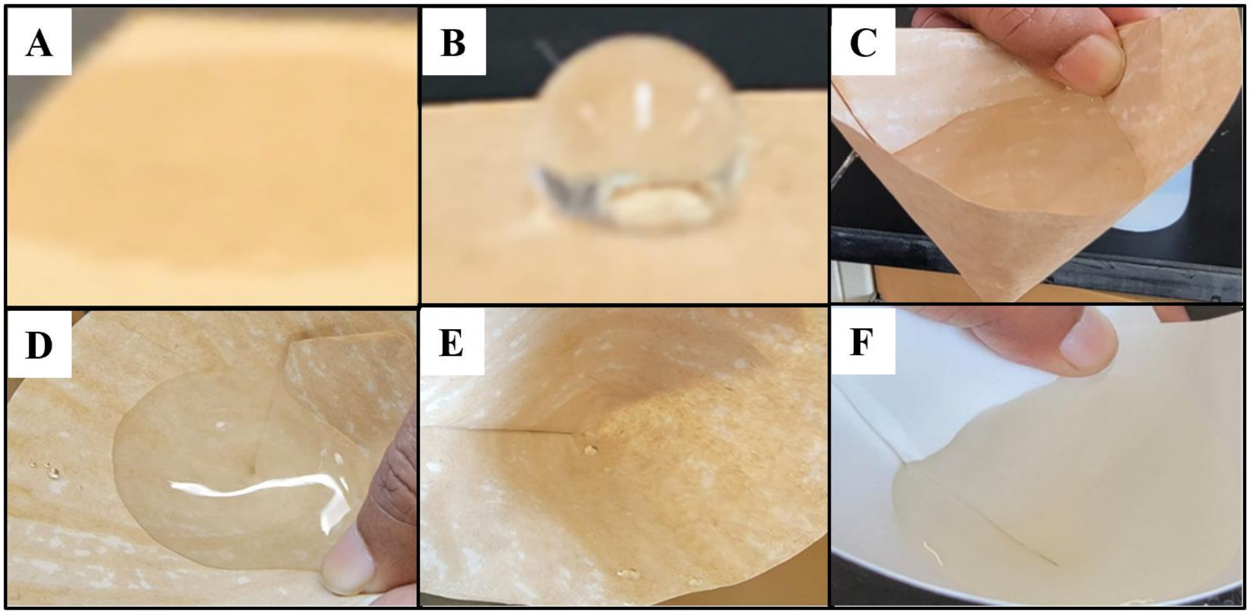
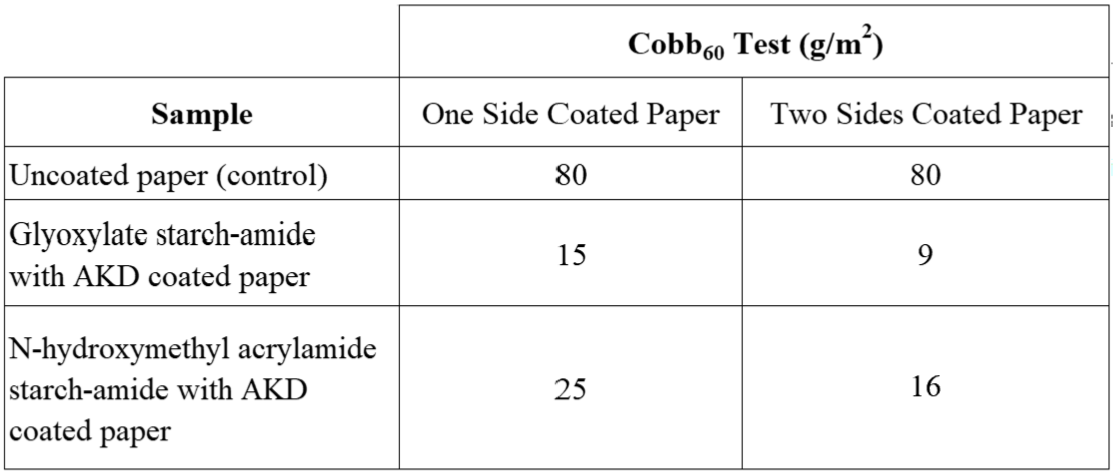


Figure 55: (A) uncoated packaging paper, (B) synthesized-starch coated liner board (C-E) synthesized-starch coated packaging paper, (F) paper cup paper.

7.2.7 Cobb test

The cobb test was carried out in accordance to T 441 om-09. It was found that the synthesized starch-based coating significantly increased the water barrier property of the surface of the coated paper. A one side coating with glyoxal starch-amide with AKD reduced the $Cobb_{60}$ from 80 to 15, while coating on both sides of the paper further reduced the $Cobb_{60}$ result to 9. Similarly, coating one side of the paper with N-hydroxymethyl acrylamide starch-amide with AKD reduced the $Cobb_{60}$ result from 80 to 25, and two-sided coating resulted in $Cobb_{60}$ result of 18. See table 14. The combination of glyoxylate starch-amide with AKD was further tested for longer durations (5 minutes and 10 minutes). Although the coated paper showed significantly less Cobb values, it is observed that with increased time, the Cobb value increases. The results are shown in Table 15.

Table 14: $Cobb_{60}$ test result of glyoxylate starch-amide with AKD and N-hydroxyl methyl starch-amide with AKD-coated paper.



	$Cobb_{60}$ Test (g/m^2)	
Sample	One Side Coated Paper	Two Sides Coated Paper
Uncoated paper (control)	80	80
Glyoxylate starch-amide with AKD coated paper	15	9
N-hydroxymethyl acrylamide starch-amide with AKD coated paper	25	16

Table 15: Cobb test result glyoxylate starch-amide with AKD, one-side coated paper.

Sample	**Cobb$_{60}$**	**Cobb$_{300}$**	**Cobb$_{600}$**
Uncoated paper (control)	80	88	106
Glyoxylate starch-amide with AKD coated paper	15	37	54

7.2.8 Mechanical properties of casted starch-based coating film

It is observed from figures 56 & 57 that the synthesized starch-based coating film displays flexibility and moldability. The manufacturing process is casting or molding, and thus scalable. It is also observed from Table 16 that the tensile strength of bioplastic film is much stronger than synthetic polyethylene (PE) film but shows lower elongation. However, on its own, the casted starch-based film can only withstand water for approximately 2 minutes before showing signs of absorption. In-depth analysis and more significant work are still required to further develop the starch-based film to become hydrophobic.

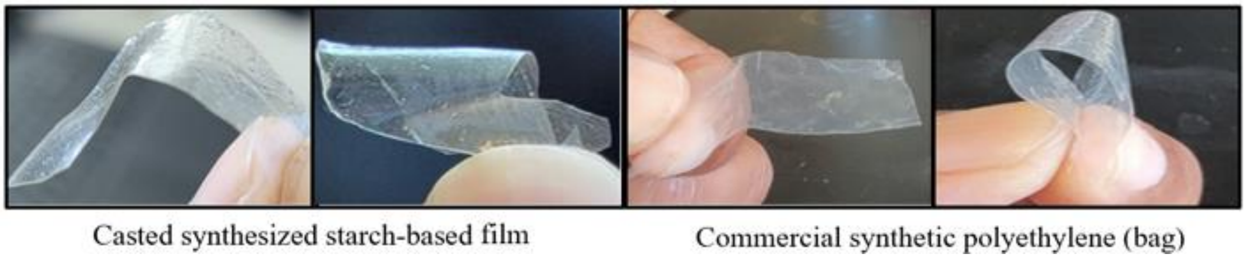
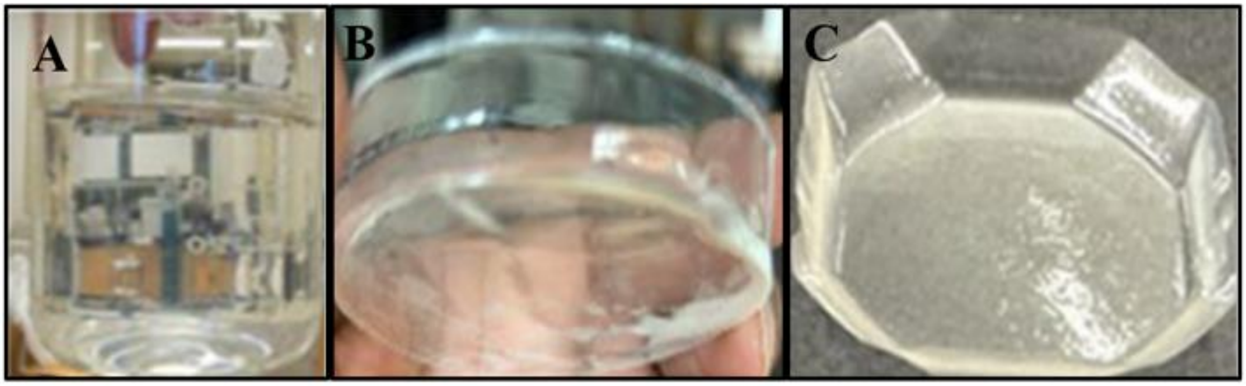


Figure 56: Flexibility of casted starch-based film compared to polyethylene bag.



Liquid synthesized starch-based coating

Casted synthesized starch-based coating film

Figure 57: Image of (A) liquid synthesized starch-based coating, and casted starch-based films (B and C).

Table 16: Mechanical properties of synthesized starch-based film.

Sample	**Width (mm)**	**Thickness (mm)**	**Load (kgf)**	**Extension (mm)**	**Load/Thickness (kgf/mm)**	**Extension/Thickness**
Synthesized starch-based film	7	0.06	1.442	1.37	24.03	22.83
Polyethylene (bag)	7	0.05	0.8	10.78	16	215.6

7.3 Conclusions

The synthesized starch-based coating developed from glyoxylate starch-amide, and N-hydroxymethyl starch amide with AKD, showed promising water barrier properties in reference to a market product, the Dixie paper bowl. The $Cobb_{60}$ test result showed that both starch-based coatings significantly reduced the water absorption/retention of the paper substrate. Casting of the synthesized starch-based coating resulted in a film which is transparent, flexible, high tensile, but does not possess high elongation properties. Although these initial test results show that the synthesized starch-based film may have the potential to be further developed into a bioplastic, more work is still required to further enhance its water barrier properties, flexibility, and elongation characteristics.

8. CONCLUSIONS

8.1 Overall conclusions

The first study aims to develop a starch-based paper strengthening agent which possess temporary wet strength properties to replace GPAM. Experiments were carried out to optimize and synthesize glyoxylate starch amide. Upon application to OCC pulp fibers, it was found that glyoxylate starch amide significantly increases wet strength, dry strength, tear, burst resistance and inter-fiber bonding between fibers. When compared to GPAM, it showed very similar results which means that it has the potential to replace GPAM in the future, providing a more environment friendly alternative.

The second study is very similar but uses cationic starch instead of cornstarch. The positive charge on the cationic starch molecule provides it with better retention on to the net negatively charged cellulose fibers. This allows N-hydroxymethyl starch amide to be a permanent wet strength additive. Upon testing, N-hydroxymethyl starch amide significantly increases wet strength, dry strength, tear, burst resistance and inter-fiber bonding between fibers. It also exhibits very similar characteristics to PAE. The results showed that it has the potential to replace PAE as a permanent wet strength agent in the future.

The third study aims to develop a dual-function polysaccharide-based additive to provide paper with increased mechanical properties and anti-microbial properties. It was observed that glyoxylate chitosan was able to noticeable enhance paper strength while also exhibiting anti-microbial properties by reducing/minimizing decay in process water, pulp slurry, and reduced bacteria count.

In addition to developing bio-based strength additives, this study also investigated the potential of making bioplastic from the synthesized starches, glyoxylate starch amide and N-hydroxymethyl starch amide. Both of which were blended with AKD and showed potential water barrier properties when used as a coating on a paper surface. Upon casting, it is observed that the synthesized starch-based coating film showed high tensile but low elongation. This causes the film to be brittle. The film by itself absorbs water over time when exposed to water. This means that it is not yet ready to be considered as a bioplastic. Results showed good potential and more work is required to fully evaluate the potential of the synthesized starch-based coating if to be further developed into a bioplastic.

8.2 Future work

Future studies should focus in the evaluation of shelf-life, recyclability, stability, and environmental impacts of glyoxylate starch amide, N-hydroxymethyl starch amide, and glyoxylate chitosan additives. Since most of the tests were done in the lab, a larger scale study would provide insightful information regarding the potential of these bio-based additives to be used in an actual paper manufacturing plant. In addition to these studies, a more comprehensive comparison between these bio-based additives to their commercial counterparts, such as GPAM and PAE, should be evaluated as well.

To further develop the synthesized starch-based coating film, several more hydrophobic agents should be evaluated as it may provide it with even better water barrier properties. It is also recommended to incorporate plasticizers to increase the flexibility, smoothness, and elongation of the synthesized starch-based coating film. Until then, it is still not ready to be considered as a replacement for polyethylene.

REFERENCES

1. Suzano. (2022, September). Paper consumption worldwide from 2021 to 2032. Retrieved from statista.com: https://www.statista.com/statistics/1089078/demand-paper-globally-until-2030/
2. FAO. (2022, December). Total production of paper and paperboard in the United States from 1961 to 2021. Retrieved from statista.com: https://www.statista.com/statistics/252708/total-us-production-of-paper-and-board-2001-2010/
3. AFANDA. (2022). Unpacking Continuously High Paper Recycling Rates. American Forest & Paper Association.
4. Hubbe, M. A., Venditti, & Rojas, O. J. (2007). What happens to cellulosic fibers during papermaking and recycling? A review. BioRes, 739-788.
5. A.M. Scallan and G.V. Laivins. The mechanism of hornification of wood pulps. In Products of Papermaking, Trans. of the 10th Fund. Res. Symp. Oxford, 1993, (C.F. Baker, ed.), pp 1235–1260, FRC, Manchester, 2018.
6. Minor, L. J.; Atalla, H. R. (1992). Strength loss in recycled fibers and methods of restoration. Materials Research Society. Symp. Proc. Vol. 266.

7. Mohammad, N.; Nima, S.; Ahmad, S.; Mohammad, J. S. Studying the effect of chemical additives on strength properties of recycled paper. J. Basic. Appl. Sci. Res. 2011, 1, 2314-2318.
8. Gruber, E.; Weigert, J. Chemical modification of cellulose pulps to reduce their tendency for hornification. Papier 1998, 52, 20−26.
9. Salam, A.; Lucia, L; Jameel, H. Starch derivatives that contribute significantly to the bonding and antibacterial character of recycled fibers. ACS Omega 2018, 3(5), 5260–5265. DOI: 10.1021/acsomega.8b00307
10. Laivins, J. V.; Scallan, A. M. The influence of drying and beating on the swelling of fines. J. Pulp Paper Sci. 1996, 22, 178.
11. Yuan, Z.Y; Hu, H. Preparation and characterization of crosslinked glyoxalated polyacrylamide paper-strengthening agent. Journal of Applied Polymer Science 2012, 459-469. DOI: 10.1002/app.36779
12. Obokata, T.; Isogai, A. The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine-epichlorohydrin (PAE) resin. Colloids and Surfaces A Physicochemical and Engineering Aspects 2007, 302(1), 525-531. DOI: 10.1016/j.colsurfa.2007.03.025
13. Corre, D. L.; Bras, J.; Dufresne, A. Starch Nanoparticles: A Review. Biomacromolecules 2010, 11, 5, 1139-1153. DOI: 10.1021/bm901428y
14. PlasticsEurope. (2021, 10). Plastics - the Facts 2017. Retrieved from plasticeseurope.org: https://plasticseurope.org/wp-content/uploads/2021/10/2017-Plastics-the-facts.pdf
15. PlasticsEurope. (2021, 10). Plastics - the Facts 2019. Retrieved from plasticeseurope.org: https://plasticseurope.org/wp-content/uploads/2021/10/2019-Plastics-the-facts.pdf

16. Hopewell, J.; Dvorak, R.; Kosior, E. (2009) Plastic recycling: challenges and opportunities. Philos Trans Soc B. 364:2115–2126
17. Cole, M. et al (2011). Microplastics as contaminants in the marine environment: A review. Marine Pollution Bulletin.
18. Isobe; et al (n.d). Selective transport of microplastics and mesoplastics by drifting in coastal waters. Marine Pollution Bulletin
19. Ekta, B. J.; Mahipal, S. S.; Rouf, A. B.; Bhagat, D.S. Microplastics from food packaging: An overview of human consumption, health threats, and alternative solutions. Journal of Environmental Nanotechnology, Monitoring & Management, Vol. 16, Dec 2021, 100608
20. T. Brautaset, T.E. Ellingsen, in Comprehensive Biotechnology (Second Edition), 2011
21. Salim, H. (2016). Basics of Paper Manufacturing. OKSUFAPC.
22. Suzano; AFRY. (2023, January). Paper consumption worldwide from 2021 to 2032. Retrieved from statista.com: https://www.statista.com/statistics/1089078/demand-paper-globally-until-2030/
23. China, H. (2017). What is OCC and how to make profit from old corrugated cardboard recycling. Qingdao.
24. Singh, S. P.; Burgess (November 2001). "Package Specifications for Corrugated Boxes with Heavy Flowable Products in Single Parcel Shipments". Journal of Testing and Evaluation. 29 (6): 570. doi:10.1520/JTE12403J.
25. Jenkins, P. J.; Donald, A. M. J. The influence of amylose on starch granule structures. Biol. Macromol. 1995, 17, 315–321

26. Haq, F.; Yu, H. J.; Wang, L.; Teng, L.; Haroon, M.; Khan, U. R.; Mehmood, S.; Bilal-Ul-Amin; Ullah, R. S.; Khan, A.; Nazir, A. Advances in chemical modifications of starches and their applications. Carbohydrate Research 2019, 476, 12-35.
27. Sharma, M.; Aguado, R.; Murtinho, D.; Valente, A. J. M.; Mendes De Sousa, A. P.; Ferreira, P. J. T. A review on cationic starch and nanocellulose as paper coating components. International Journal of Biological Macromolecules 2020, 162, 578-598
28. Muhd, A. A.; Farhana, A. Chitosan Nanocomposite Application in Wastewater Treatments. Journal of Nanotechnology in Water and Wastewater Treatment, 2019, 243-265.
29. Zhaoping, S.; Guodong, L.; Feixiang, G.; Wenxia, L. Application of Chitin/Chitosan and Their Derivatives in the Papermaking Industry. Polymers (Basel). 2018 Apr 1;10(4):389. doi: 10.3390/polym10040389. PMID: 30966425; PMCID: PMC6415250.
30. Anahita, R. S.; Mina, S.; Azadeh, B. Recent advances in application of chitosan and its derivatives in functional finishing of textiles. The Impact and Prospects of Green Chemistry for Textile Technology, 2019.
31. Rohan, S. D.; Sanjit, A.; Noureddine, A. Biopolymer-Based Materials from Polysaccharides: Properties, Processing, Characterization and Sorption Applications. Advanced Sorption Process Application, Nov 5, 2018. DOI: 10.5772/intechopen.80898
32. Cornel, H. (2004). US Patent No. US7119148B2.
33. Herth G, Schornick G, Buchholz F (2015). "Polyacrylamides and Poly(Acrylic Acids)". Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH. pp. 1–16. doi:10.1002/14356007.a21_143.pub2

34. Nyyssölä, Antti; Ahlgren, Jonni (April 2019). "Microbial degradation of polyacrylamide and the deamination product polyacrylate". International Biodeterioration & Biodegradation. 139: 24–33. doi:10.1016/j.ibiod.2019.02.005.
35. Chan, L.L. (1991). EU Patent No. 0515750A2.
36. Marton, J. (1996). Dry-strength additives. In: Roberts, J.C. (eds) Paper Chemistry. Springer, Dordrecht. https://doi.org/10.1007/978-94-011-0605-4_6
37. Neimo, Leo, ed. (1999). "13". Papermaking Chemistry. Papermaking Science and Technology. Vol. 4. Helsinki, Finland: Fapet OY. pp. 289–301. ISBN 952-5216-04-7.
38. Harshita, G. Plastic Container Market, By Material (PET, PP, HDPE, PVC, LDPE, and others), By product (Bottles & Jars, Cups & bowls, Bags & Pouches, and others), By Application (Food & Beverages, Personal Care, Pharmaceutical, Consumer goods, and others) - Forecast 2030.
39. PlasticsEurope, 2020. Plastics-the facts 2020. An Analysis of European Plastics Production, Demand and Waste Data. URL: https://www.plasticseurope.org/application/files/5716/0752/4286/AF_Plastics_the_facts-WEB-2020-ING_FINAL.pdf
40. Vladimir, G. Kimmo, S. Mikko, H. & Matti, H. Strength chemistry for board and tissue production: Scientific outlook and end applications. PAP-FOR, Kemira (2012).
41. P. Jariyasakoolroj, P. Leelaphiwat, N. Harnkarnsujarit Advances in research and development of bioplastic for food packaging J. Sci. Food Agric., 100 (14) (2020), pp. 5032-5045

42. R. Grujić, D. Vujadinović, D. Savanović. Biopolymers as food packaging materials Advances in Applications of Industrial Biomaterials, Springer International Publishing, Cham (2017), pp. 139-160
43. H. Chen, J. Wang, Y. Cheng, C. Wang, H. Liu, H. Bian, Y. Pan, J. Sun, W. Han Application of protein-based films and coatings for food packaging: a review. Polymers (Basel), 11 (12) (2019), p. 2039
44. Environment Canada; Health Canada (August 2009). "Screening Assessment for the Challenge: 2-Propenamide (Acrylamide)". Environment and Climate Change Canada. Government of Canada.
45. Dotson, G.S., April 2011). "NIOSH skin notation (SK) profile: acrylamide [CAS No. 79-06-1]" DHHS (NIOSH) Publication No. 2011-139. National Institute for Occupational Safety and Health (NIOSH)
46. Environment Canada; Health Canada (November 2008). "Screening Assessment for the Challenge: Oxirane, (chloromethyl)-(Epichlorohydrin)". Environment and Climate Change Canada. Government of Canada.
47. M. Cherif Lahimer, N. Ayed, J. Horriche, S. Belgaied. Characterization of plastic packaging additives: food contact, stability and toxicity. Arab. J. Chem., 10 (2017), pp. S1938-S1954
48. Brasselet, C.; Pierre, G.; Dubessay, P.; Dols-Lafargue, M.; Coulon, J.; Maupeu, J.; Vallet-Courbin, A.; de Baynast, H.; Doco, T.; Michaud, P.; Delattre, C. Modification of Chitosan for the Generation of Functional Derivatives. Appl. Sci. 2019, 9, 1321. https://doi.org/10.3390/app9071321

49. Li, S.; Mujyambere, J. M. V.; Liu, M. Synthesis of carboxymethyl starch with high degree of substitution by a modified dry process. Advanced Materials Research 2011, 233-235, 306-310. DOI: 10.4028/www.scientific.net/AMR.233-235.306
50. Yuan, Z.Y; Hu, H. Preparation and characterization of crosslinked glyoxalated polyacrylamide paper-strengthening agent. Journal of Applied Polymer Science 2012, 459-469. DOI: 10.1002/app.36779
51. Sweidan, K.; Jaber, M. A.; Jbour, N. A.; Obaidat, R.; Rimawi, M.; Badwan, R. A. Further investigation on the degree of deacetylation of chitosan determined by potentiometric titration. J. Excipients and Food Chem. 2011, 2 (1), 16. DOI: N/A)
52. Sawant, N.; Salam, A.; Lucia, L. Esterified polysaccharide composites that display super absorbency from highly favorable hydrogen and Ionic interactions. Industrial; Engineering Chemistry Research 2020, 59(32), 14234–14241. DOI: 10.1021/acs.iecr.0c02823
53. Zhang, H.; Wu, J.; Zhang, He, J. 1-Allyl-3-methylimidazolium Chloride Room Temperature Ionic Liquid: A New and Powerful Nonderivatizing Solvent for Cellulose. Macromolecules 2005, 38,8272-8277. DOI: 10.1021/ma0505676
54. Salam, A.; Venditti, R. A.; Pawlak, J. J.; El-Tahlawy, K. Crosslinked hemicellulose citrate–Chitosan aerogel foams. Carbohydrate Polymers 2011, 84(4), 1221–1229. DOI: 10.1016/j.carbpol.2011.01.008
55. Tian, Y.; Li, Y.; Xu, X.; Jin, Z. Y. Starch retrogradation studied by thermogravimetric analysis (TGA). Carbohydrate Polymers 2011, 84(3), 1165-1168. DOI: 10.1016/j.carbpol.2011.01.006

56. Christian, D.; Roberta, D. S.; Francesca, S.; Alessandro, S.; Giuseppe, V.; Alfonso, M.; Luigi, N. Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. J. Appl. Polym. Sci. 2008, 110, 2453−2460. DOI: 10.1002/app.28660

57. Alonso, D.; Gimeno, M.; Olayo, R.; Vazquez-Torres, H.; Sepulveda-Sanchez, D. J.; Shirai, K. Cross-Linking Chitosan into UV-Irradiated Cellulose Fibers for the Preparation of Antimicrobial-Finished Textiles. Carbohydr. Polym. 2009, 77, 536−543. DOI: 10.1016/j.carbpol.2009.01.027

58. Shi, R.; Zhang, Z.; Liu, Q.; Han, Y.; Zhang, L.; Chen, D.; Tian, W. Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. Carbohydr. Polym. 2007, 69, 748− 755. DOI: 10.1016/j.carbpol.2007.02.010

59. Salam, A.; Lucia, L. A.; Jameel, H. A novel cellulose nanocrystals-based approach to improve the mechanical properties of recycled paper. ACS Sustainable Chemistry; Engineering 2013, 1(12), 1584–1592. DOI: 10.1021/sc400226m

60. Liu, X.; Yu, L.; Liu, H.; Chen, L.; Li, L. In situ thermal decomposition of starch with constant moisture. Polym. Degrad. Stab. 2008, 93, 260−262. DOI: 10.1016/j.polymdegradstab.2007.09.004

61. Menzel, C.; Gonzalez-Martinez, C.; Vilaplana, F.; Diretto, G.; Chiralt, A. Incorporation of natural antioxidants from rice straw into renewable starch films. International Journal of Biological Macromolecules 2020, 146, 976-986. DOI: 10.1016/j.ijbiomac.2019.09.222

62. Li, S.; Mujyambere, J. M. V.; Liu, M. Synthesis of carboxymethyl starch with high degree of substitution by a modified dry process. Advanced Materials Research 2011, 233-235, 306-310. DOI: 10.4028/www.scientific.net/AMR.233-235.306

63. Yuan, Z.Y; Hu, H. Preparation, and characterization of crosslinked glyoxalated polyacrylamide paper-strengthening agent. Journal of Applied Polymer Science 2012, 459-469. DOI: 10.1002/app.36779
64. Fotie, G.; Limbo, S.; Piergiovanni, L. Manufacturing of food packaging based on nanocellulose: Current advances and challenges. Nanomaterials 2020, 10(9), 1726. DOI: 10.3390/nano10091726
65. Miglierini, G. The many benefits of wet strength resins. 2017, Paper Industry World. https://www.paperindustryworld.com/many-benefits-wet-strength-resins/ (accessed 17 March, 2022
66. Lu, C.; Rosencrance, S.; Swales, D.; Covarrubias, R.; Hubbe, M. A. Dry Strength: Strategies for Stronger Paper. TAPPI Press. 2020, 7, 155-196. DOI: N/A
67. Zhang, H., Zhao, C., Li, Z. et al. The fiber charge measurement depending on the poly-DADMAC accessibility to cellulose fibers. Cellulose 23, 163–173 (2016). https://doi.org/10.1007/s10570-015-0793-x
68. Paulsson, B., Grawe, J., & Törnqvist, M. (2002). Hemoglobin adducts and micronucleus frequencies in mouse and rat after acrylamide or N-methylolacrylamide treatment. Mutation Research/Genetic Toxicology and Environmental Mutagenesis, 516, 101-111.
69. Christian, D., Roberta, D. S., Francesca, S., Alessandro, S., Giuseppe, V., Alfonso, M., & Luigi, N. (2008). Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. J. Appl. Polym. Sci., 110, 2453−2460.
70. Salam, A., Lucia, L., & Jameel, H. (2014.) Fluorine-based surface decorated cellulose nanocrystals as potential hydrophobic and oleophobic materials. Cellulose, 22(1), 397–406.

71. Salam, A.; Pawlak, P. P.; Venditti, R. A.; El-tahlawy, K. Synthesis and Characterization of Starch Citrate-Chitosan Foam with Superior Water and Saline Absorbance Properties. Biomacromolecules, 2010, 11(6), 1453-1459. DOI: 10.1021/bm1000235
72. Alonso, D., Gimeno, M., Olayo, R., Vazquez-Torres, H., Sepulveda-Sanchez, D. J., & Shirai, K. (2009). Cross-Linking Chitosan into UV-Irradiated Cellulose Fibers for the Preparation of Antimicrobial-Finished Textiles. Carbohydr. Polym., 77, 536−543.
73. Shi; Zhang; Liu; Han; Zhang; Chen. (2007). Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. Carbohydr. Polym., 69, 748−755.
74. Salam, A., Lucia, L. A., & Jameel, H. (2013). A novel cellulose nanocrystals-based approach to improve the mechanical properties of recycled paper. ACS Sustainable Chemistry; Engineering, 1(12), 1584–1592.
75. Dome, K., Podgorbunskikh, E., Bychkov, A., & Lomovsky, O. (2020) Changes in the crystallinity degree of starch having different types of crystal structure after mechanical pretreatment. Polymers, 12(3), 641.
76. Bernabe, P., Peniche, C., & Arguelles-Monal, W. (2005). Swelling behavior of chitosan/pectin polyelectrolyte complex membranes. Effect of thermal cross-linking. Polym. Bull., 55, 367−375.
77. Salam, A., Venditti, R. A., Pawlak, J. J., & El-Tahlawy, K. (2010). Synthesis and characterization of starch citrate-chitosan foam with superior water and saline absorbance properties. Biomacromolecules, 11 (6), 1453–9.

78. Salam, A., Venditti, R. A., Pawlak, J. J., & El-Tahlawy, K. (2011). Crosslinked hemicellulose citrate–Chitosan aerogel foams. Carbohydrate Polymers, 84(4), 1221–1229.
79. Howard, R. C., & Jowsay, C. J. (1989). Effect of cationic starch on the tensile strength of paper. J. Pulp Pap. Sci., 15, 225.
80. Miglierini, G. (2017). The many benefits of wet strength resins. Paper Industry World Staff.
81. Bates, N. A. (1969). Polyamide-epichlorohydrin wet-strength resin. 2. A study of mechanism of wet-strength development in paper. Tappi, 52(6), 1162-1169.
82. Khwaldia K, Arab-Tehrany E, Desobry S. Biopolymer Coatings on Paper Packaging Materials. Compr Rev Food Sci Food Saf. 2010 Jan;9(1):82-91. doi: 10.1111/j.1541-4337.2009.00095.x. PMID: 33467805.
83. Lillian, L. Bioplastics in Food Packaging: Innovative Technologies for Biodegradable Packaging. San Jose State University, 2006.
84. Baxter, A.; Dillon, M.; Taylor, K. D.; Roberts, G. A. Improved method for i.r. determination of the degree of N-acetylation of chitosan. Int J Biol Macromol. 1992 Jun;14(3):166-9. doi: 10.1016/s0141-8130(05)80007-8. PMID: 1390449.
85. Chariya, K.; Bunla, R.; Chanokporn, A.; Mantana, O.; Paiboon, S.; Pakorn, O. Preparation of Water-Based Alkyl Ketene Dimer (AKD) Nanoparticles and Their Use in Superhydrophobic Treatments of Value-Added Teakwood Products. ACS Omega 2022, 7(31), 27400-27409, DOI: 10.1021/acsomega.2c02420
86. Mocchiutti et al. (2007). “Colloidal titration, polyelectrolytes,” BioResources 2(3), 399-407.

87. Zhang, H., Zhao, C., Li, Z. et al. The fiber charge measurement depending on the poly-DADMAC accessibility to cellulose fibers. Cellulose 23, 163–173 (2016). https://doi.org/10.1007/s10570-015-0793-x
88. Wang, L., Abbasi, N. M., Abdin, ul Z., & Saleem, M. (2016). Chemical modification of cornstarch and its applications. RSC Advances. DOI: 10.1039/C6RA16795K
89. Q. Chen, H. Yu, L. Wang, Z. ul Abdin, Y. Chen, J. Wang, W. Zhou, X. Yang, R. U. Khan and H. Zhang, (2015). Recent Progress in Chemical Modification of Starch. RSC Advances.,5, 67459–67474.
90. Arora B, Tandon R, Attri P, Bhatia R. Chemical Crosslinking: Role in Protein and Peptide Science. Curr Protein Pept Sci. (2017) ;18(9):946-955. DOI: 0.2174/1389203717666160724202806. PMID: 27455969.
91. A. N. Jyothi, S. N. Moorthy and K. N. Rajasekharan, Starch/Staerke, 2006, 58, 292–299.
92. A. V. Singh and L. K. Nath, Int. J. Biol. Macromol., 2012, 50, 14–18.
93. N. Reddy and Y. Yang, Food Chem., 2010, 118, 702–711.
94. L. Guo, G. Li, J. Liu, Y. Meng and Y. Tang, Carbohydrate Polymer, 2013, 93, 374–379.
95. A. Zarski, S. Ptak, P. Siemion and J. Kapusniak, Carbohydrate Polymer, 2016, 137, 657–663.
96. Y. F. Zuo, J. Gu, Z. Qiao, H. Tan, J. Cao and Y. Zhang, Int. J. Biol. Macromol., 2015, 72, 391–402.
97. H. Gran¨o, J. Y. Kauhaluoma, T. Suortti, J. K¨aki and K. Nurmi, Carbohydr. Polym., 2000, 41, 277–283.
98. Y. Shi, B. Ju and S. Zhang, Carbohydr. Polym., 2012, 88, 132–138.
99. O. B. Wurzburg, Modifed starches-properties and uses, CRC Press Inc., 1986.

100. W. Yanli, G. Wenyuan and L. Xia, Carbohydr. Res., 2009, 344, 1764–1769.

101. Lertsutthiwong P., Chandrkrachang S., Nazhad M.M., Stevens W.F. Chitosan as a dry strength agent for paper. Appita J. 2002;55:208–212.

102. Ashori A., Cordeiro N., Faria M., Hamzeh Y. Effect of chitosan and cationic starch on the surface chemistry properties of bagasse paper. Int. J. Biol. Macromol. 2013;58:343–348. doi: 10.1016/j.ijbiomac.2013.04.056.

103. Mocchiutti P., Schnell C.N., Rossi G.D., Peresin M.S., Zanuttini M.A., Galvan M.V. Cationic and anionic polyelectrolyte complexes of xylan and chitosan. Interaction with lignocellulosic surfaces. Carbohydr. Polym. 2016;150:89–98. doi: 10.1016/j.carbpol.2016.04.111.

104. Wu T., Farnood R. Cellulose fibre networks reinforced with carboxymethyl cellulose/chitosan complex layer-by-layer. Carbohydr. Polym. 2014;114:500–505. doi: 10.1016/j.carbpol.2014.08.053.

105. Arboleda J.C., Niemi N., Kumpunen J., Lucia L.A., Rojas O.J. Soy protein-based polyelectrolyte complexes as biobased wood fiber dry strength agents. ACS Sustain. Chem. Eng. 2014;2:2267–2274. doi: 10.1021/sc500399d.

106. Adel A.M., Dupont A.L., Abou-Yousef H., El-Gendy A., Paris S., El-Shinnawy N. A study of wet and dry strength properties of unaged and hygrothermally aged paper sheets reinforced with biopolymer composites. J. Appl. Polym. Sci. 2014;131:14–20. doi: 10.1002/app.40761.

107. Amended final report on the safety assessment of polyacrylamide and acrylamide residues in cosmetics. Int J Toxicol. 2005;24 Suppl 2:21-50. doi: 10.1080/10915810590953842. PMID: 16154914.

108. John I. Brauman and Larry K. Blair, Gas-phase acidities of alcohols, Journal of the American Chemical Society 1970 92 (20), 5986-5992. DOI: 10.1021/ja00723a029.

109. Tomasik, P.; Schilling, C.H. Chemical modification of starch. Adv. Carbohydr. Chem. Biochem. 2004, 59, 175–204

110. Abdel-Latif, Ehab & Mohammed Fahad, Mustafa & Ismail, Mohamed. (2019). Synthesis of N -aryl 2-chloroacetamides and their chemical reactivity towards various types of nucleophiles. Synthetic Communications. 50. 1-26. 10.1080/00397911.2019.1692225.

LIST OF PUBLICATIONS AND CONFERENCES

PUBLICATIONS

1. Cornellius Marcello, Abdus Salam, A biobased synthesized N-hydroxymethyl starch-amide for enhancing the wet and dry strength of paper products, Carbohydrate Polymers, Volume 299, 2023, 120194, ISSN 0144-8617, Https://doi.org/10.1016/j.carbpol.2022.120194.
2. Cornellius Marcello, Abdus Salam, Synthesis, Characterization, and Application of Glyoxylate Starch-Amide for Enhancing Wet and Dry Paper Strength, ACS Sustainable Chemistry & Engineering 2022 10 (43), 14262-14270. DOI: 10.1021/acssuschemeng.2c04285

PENDING SUBMISSION MANUSCRIPTS

1. Cornellius Marcello, Kecheng Li, Abdus Salam, A Synthesized Starch- based Liquid Bioplastic for High Barrier Coating Additive of Papers, Journal of Advanced Materials.
2. Cornellius Marcello, Neha Sawant, Jason Wang, Kecheng Li, Abdus Salam. Synthesis and Evaluation of Glyoxylate Chitosan as an Antimicrobial Wet and Dry- Dry-Strengthening Agent of Pulp Products, ACS Sustainable Chem. Eng.

CONFERENCES

1. Cornellius Marcello, Abdus Salam, (2022), Synthesis of starch-based bioplastic coating for packaging material, ACS Sustainability in a Changing World.