Starch Derivatives that Contribute Significantly to the Bonding and Antibacterial Character of Recycled Fibers

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ABSTRACT: The objective of the current research was to fabricate and explore the ability of a renewable resource-based paper strength agent to enhance fiber–fiber bonding and introduce antibacterial properties to recycled fiber paper sheets. The agent corn starch, was modified with diethylenetriamine pentaacetic acid (DTPA), complexed with chitosan, and added to recycled furnish to provide a plethora of hydrogen bonding sites predicated by acid groups, hydroxyls, and amines. The goal was two-fold: (1) to not only increase interfiber bonding, but (2) afford antibacterial character. The modified corn starch was characterized in previous work by thermal gravimetric analysis, differential scanning calorimeter, and Fourier transform infrared spectroscopy. The recycled pulp slurry was mixed with a ∼1.5% modified starch/chitosan agent before manufacturing a two-dimensional paper substrate that was subjected to mechanical testing. The burst, STFI compressive strength, tensile, and interfiber bonding strength increased 48.8, 49.5, 49.9, and 176%, respectively, while significantly increased gloss was obtained despite slightly diminished tear and roughness. The antibacterial character of these substrates was confirmed by the substrates displaying a 97% bacteria kill rate.

INTRODUCTION

Corn starch (CS) is a carbohydrate widely acknowledged as one of the most abundant and useful biomaterials on the planet currently available in a variety of commercial forms. It typically occurs as a semicrystalline polymer characterized by glucose repeat units in linear chains composed of ∼25% amylose and 75% amylpectin by weight.1 It has sundry uses in a number of industries; in the pulp & paper industry, one is as a paper dry strength agent. Dry strength agents are multifunctional agents that not only enhance paper/paperboard mechanical properties such as burst, compression, and tensile, but also improve drainage and retention of fiber, fines, and filler. Typically, these agents are petroleum-derived agents such as derivatized polyacrylamides and, to a lesser extent, cationized or neat starch.

Starch has a number of molecular sites for derivatization owing to the multihydroxyl nature of the glucose ring. However, although starch is a biobased alternative to the petroleum agents that currently dominate the market, its ability to enhance mechanical properties is limited compared to its petroleum counterparts. Nevertheless, chemical derivatization opportunities, commercial availability, and low cost are all conducive for the development of more potent starch additives for paper strength applications.

Chitosan is a polysaccharide also composed of repeating glucose residues that, unlike starch, are glucosamine functionalities. More specifically, an amine functionality instead of a hydroxyl resides at the C2-position of a glucose ring and thereby provides a number of functional advantages in addition to hydrogen bonding; this work focused specifically on its ability to provide antibacterial activity.2,3 At present, chitosan is not known to be used in any operational sense for papermaking furnish.

Paper recycling is an important paradigm to address environmental concerns and reduce the need for energy and resource-intensive virgin fiber manufacture. Old corrugated containerboard (OCC), a major component of the recycled market, cannot be properly recycled without addressing the physically and chemically compromised fibers. Because it has been used at least two times, the fibers are hornified, that is, are

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much shorter, have reduced numbers of bonding sites, and are consequently weaker than virgin pulp fibers. Bonding between these shorter fibers is significantly weaker. OCC pulp fibers also suffer from anionic trash (dissolved polymeric and colloidal materials) that reduces its potential as a recycled furnish.\textsuperscript{4}

The United State uses $\sim$70 million tons of paper and paperboard per year (2011 MSW Characterization Reports) with a utilization rate for OCC of $\sim$92%. However, attempts to improve the strength of OCC typically result in mechanically inferior products relative to their virgin equivalents. Some early research identified that chemical treatments may improve bonding strength.\textsuperscript{5,6} A number of innovative studies demonstrated that chemical derivatization of waste fiber surfaces may prevent strength losses,\textsuperscript{7,8} while refining improves mechanical properties.\textsuperscript{9} The papermaking industry currently uses commercial dry strength agents that fall under the categories of cationic, anionic, amphoteric polyacrylamide, glyoxylate polyacrylamide, cationic starch, amphoteric starch, and carboxyl methyl cellulose, but strength improvement is still less than desirable relative to virgin pulp.\textsuperscript{9,10}

For decades, a number of studies have been conducted with nonrenewable petroleum-based additives for several applications including packaging, a high value sector of the pulp market.\textsuperscript{11} Increasing environmental concerns led to new biobased packaging materials based on renewable resources.\textsuperscript{11} In previous work from the authors, several biobased polymers including cellulose, soy-based polymers, and chitosan\textsuperscript{12–14} have been studied. However, these original approaches determined that having higher polysaccharide components was much more beneficial for dry strength purposes; therefore, diethylenetriamine pentaacetic acid (DTPA)/CS and DTPA/CS/chitosan additives comprise the core of this effort and represent a new approach to upgrade starch despite its ubiquitous nature in the paper industry. In the present investigation, chemical modification of CS was accomplished through the incorporation of DTPA and chitosan. This research focuses on the characterization of newly developed CS/chitosan-treated recycled OCC pulp sheets by examining interfiber bonding, mechanical, and antibacterial properties.

\section{RESULTS AND DISCUSSION}

\textbf{Characterization of Modified Corn Starch.} The carboxylic acid content of the modified CS increased from 0.0 meq/100 g to 380 meq/100 g. In addition to this measurement after the modification of CS, the degree of substitution and percent esterification were determined by titration. The degree of substitution and esterification percent were found to be 0.28 and 42%, respectively. The molecular weight was determined by intrinsic viscosity using an Ubbelohde-type viscometer.\textsuperscript{18} The molecular weight of CS and modified CS was found to be $12.96 \times 10^4$ and $16.84 \times 10^4$ Da, respectively, which is in agreement with grafting of the functional groups.

\textbf{Attenuated Total Reflectance FT-IR Analysis.} The attenuated total reflectance FT-IR (ATR-FTIR) spectra of the CS and modified corn starch (m-CS) were determined in Figure 1. A prominent peak at 3306 cm$^{-1}$ arises from the hydroxyl groups of CS, whereas no peak was found over 1720–1800 cm$^{-1}$, indicating the absence of carbonyl groups. However, when the CS reacted with DTPA, a peak was observed at 1740 cm$^{-1}$ which is attributable to the carbonyl group of the ester,\textsuperscript{15} indicating that DTPA has successfully grafted on to the CS surfaces.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure_1.png}
\caption{FT-IR spectra of CS (corn starch) and m-CS (modified corn starch).}
\end{figure}

\textbf{Thermal Behavior.} The thermogravimetric (TGA) behavior of the modified CS is depicted in Figure 2A. The weight loss below and near 100 °C can be attributed to water evaporation.\textsuperscript{23} However, weight loss above 100 °C was attributed to thermal decomposition of the modified CS.\textsuperscript{24} Both m-CS and m-CS/Ch showed a lower maximum weight loss temperature. This is because surface-modifying agents (DTPA) of CS which comprise the layer on the surface of the CS have a lower decomposition temperature.\textsuperscript{17,18} The differential thermogravimetry (DTG) curves are shown in Figure 2B. The modified CS (either m-CS or m-CS/Ch) exhibits a shift in the DTG peak temperature to lower temperatures, which is consistent with the results observed in thermal gravimetric analysis (TGA) curves. It should be noted that both m-CS and m-CS/Ch showed significantly higher residual mass. This was expected and attributed to the cross-linking by DTPA and/or chitosan. The order in the residue found for each of these three samples verifies cross-linking. Differential scanning calorimeter (DSC) analysis of the modified CS is shown in Figure 3. The endothermic peaks for the m-CS and m-CS/Ch were $\sim$200 °C, whereas the endothermic peak of CS is at 160 °C (Figure 3). Such increases are due to increased hydrogen and ester bonding in addition to plasticization arising from esterification.\textsuperscript{17} By comparing the DSC curves between m-CS and m-CS/Ch, the latter peak is sharper, a finding attributed to more hydrogen bonding introduced by the amino groups in chitosan.

\textbf{Application of m-CS/Ch. Effect of m-CS/Ch on Paper Strength Properties.} Physical strength is one of the most important properties of paper substrates. These substrates must
offer sufficient resistance to ensure high quality packaging, sealing, or wrapping applications. Typically, this gross resistance is attributed at the molecular level to adequate development of hydrogen bonds. After recycling, pulp fibers are irreversibly damaged, which affect final pulp strength properties. Figure 4 shows the tensile strength of recycled pulp sheet resulting after the addition of m-CS and m-CS/Ch.

The control sample was prepared from recycled pulp (CSF or Canadian Standard Freeness = 400). In tandem, a 1.5% modified CS/chitosan additive (on dry pulp weight) was mixed with the recycled pulp slurry. The tensile index of the 1.5% CS, 1.5% m-CS/Ch-treated recycled pulp sheet was 8.2 and 49.9% higher than the control pulp sheet. Similarly, the burst index and STFI compressive strength index increased by 15.0 and 48.8%, respectively, and 11.0 and 49.5%, respectively, compared to the control (Figures 5 and 6). The tear index of 1.5% m-CS/Ch-treated recycled pulp sheet decreased, but only 1.5% CS-treated recycled pulp sheet slightly increased compared to the control (Figure 7).

The interfiber bonding strength of the recycled pulp sheet (control) and additive-treated pulp sheets were measured by an Internal Bond Tester (Scott). The interfiber bonding strength increased by 176% for 1.5% m-CS/Ch-treated recycled pulp sheet compared to the control recycled paper sheet. This may be due to ester and amide bond formations between the pulp fibers and CS derivatives. 24−27

A high residual char was observed from 1.5% m-CS/Ch-treated recycled pulp sheet compared to the control recycled paper sheet after heating to 600 °C (Figure 8) which indicates that the modified CS/chitosan is cross-linking to the pulp fibers. 28
Dynamic Contact Angle of m-CS-/Ch-Treated Pulp Sheets.
The dynamic contact angle was determined to be 45° at 20 s for the OCC paper sheet (control). The water angle for the OCC paper sheet was significantly reduced to 4.5° at 200 s (Figure 9). In contrast, the dynamic contact angle for 1.5% m-CS-/Ch-treated OCC paper sheet was 102° at 20 s that dropped to 80° at 400 s, to 75° at 2200 s, and finally dropped to 45° at 2800 s. This may be because the m-CS/Ch additive contains chitosan that is strongly hydrophobic, producing a sticky gel under acidic pH conditions that adopts a plastic-like character under dry conditions.

Antimicrobial Activity of m-CS-/Ch-Treated Pulp Sheets.
The antimicrobial activity of different materials was tested according to the AATCC 147 test method. Figure 10 shows that unmodified CS significantly supported bacteria colony growth, but no bacteria or bacteria colony was observed for modified CS/chitosan. The nutritious properties of CS significantly promote bacteria growth versus modified CS/chitosan whose positively charged chitosan amine group likely plays a significant role in killing 97% of the bacteria. The less than 100% killing rate observed for the modified CS/chitosan sample may likely be due to incomplete exposure of the active bactericidal chitosan amine unit of the dry strength agent due to complexation with the acid functionalities of the DTPA and its reduced overall abundance in the composite system.

CONCLUSIONS
CS was modified with DTPA to increase the functionality of CS that leads to an enhancement of fiber–fiber bond formation in recycled pulp fibers. It was confirmed that carboxyl group content significantly increased. The modified CS was further coupled with chitosan to improve antimicrobial properties as well as increase interfiber bonding. The pulp slurry was blended with ~1.5% CS and related derivatives (m-CS and m-CS/Ch) before making a pulp sheet. The mechanical properties including tensile, burst, and STFI compressive strength index all increased by 8.2 and 49.9%, 15.0 and 48.8%, and 11.0 and 49.5%, respectively, whereas the interfiber bonding strength of m-CS-/Ch-treated pulp sheet increased 176%, in addition to a two-fold increase in gloss and 20% decrease in roughness. The antimicrobial activity of the CS derivative-treated pulp sheets was significantly increased as observed by the kill rate of ~97% of the bacteria.

EXPERIMENTAL SECTION
Materials. CS was supplied by Cargill Incorporated, Minneapolis, MN. The recycled pulp was supplied by Georgia Pacific, Atlanta, GA. Chemicals of reagent grade utilized were sodium hypophosphate (SHP), CAS registry number 123333-67-5, sodium hydroxide (NaOH), CAS registry number 1310-73-2, DTPA, CAS no. 67-43-6, and acetic acid, all of which were purchased from Fisher Scientific. Chitosan (Ch), CAS no. 9012-76-4, was purchased from Sigma-Aldrich. Deionized water was used for all experiments.

Modification of CS. CS (8 g) was boiled at 100 °C for 15 min and combined with 20 mL of solution of 2 g of DTPA and 0.4 g SHP in a 50 mL Petri dish and mixed vigorously with a glass rod. The mixture was placed in an air oven at 120 °C for 3 h, washed with DI water, and filtered several times to remove unreacted materials. The m-CS was air-dried at 50 °C in an air oven overnight. The reaction scheme is shown in Figure 11.

Complexation Reaction. Approximately 0.5 g Ch was dissolved into 50 mL of 1% acetic acid solution and added to a 50 mL solution of 1.2 g m-CS in a 250 mL round-bottom flask. The mixture was magnetically stirred at 80 °C for 90 min.

Figure 9. Contact angles for OCC pulp sheet and m-CS-/Ch-(modified CS/chitosan) treated OCC pulp sheets.

Figure 10. Antimicrobial activity of unmodified CS (corn starch), m-SC/Ch (modified corn starch/chitosan), and m-CS-/Ch (modified corn starch/chitosan additive)-treated OCC pulp sheets.
The reaction scheme is depicted in Figure 12. The resultant material is denoted as m-CS/Ch.

**Preparation of the Paper Sheet.** The paper sheet was prepared according to TAPPI Standard Method 205. In general, the additives (CS or modified-CS) were blended with the pulp slurry followed by pouring into the hand sheet molding machine. Water was further mixed with the pulp slurry and agitated a couple of times before drainage. The amounts of CS and modified-CS were 1.5 wt %. No white water was collected from the hand sheet molding machine because of the lack of adequate instrumentation systems.

**Testing Methods.**

**Determination of Carboxyl Content.** m-CS was dissolved in water and hydrolyzed with 0.1 N NaOH for 1 h. The excess amount of NaOH in m-CS solution was determined by titration with 0.1 N HCl using phenolphthalein as an indicator, and the carboxylic acid content in milliequivalents of acidity per 100 g was reported as follows:

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

where $W$ = weight of sample, $N$ = normality of HCl, $V_1$ = volume of HCl with sample, and $V_2$ = volume of HCl without sample.

**Determination of the Degree of Substitution and Degree of Esterification.** The m-CS was dissolved in DMSO to which 0.1 N NaOH was added to saponify the ester over 2 h. The unreacted NaOH was determined by titration with 0.1 N HCl. The percent esterification and the degree of substitution were determined according to following equation:

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

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

where $A$ % = degree of esterification, $W$ = weight of sample, $M$ = molecular weight of crosslinking agent, and $m$ = molecular weight of the cross-linking part of the cross-linking agent.

**Physical Properties of m-CS/Ch-Treated Recycled Paper Sheets.** The STFI compressive strength, burst, tensile, tear, roughness, and gloss of m-CS-treated recycled paper sheet were measured according to TAPPI T 826, TAPPI T 810, TAPPI T 220, TAPPI T 414, TAPPI T 538, and TAPPI T 480 test methods, respectively. The interfiber bonding strength of m-CS-/chitosan-treated recycled paper sheets was determined using a standard T 569 pm-00 (provisional method TAPPI 2000). For all runs, five samples were tested.

**Characterization.**

**ATR-FTIR Analysis.** ATR-FTIR spectra of m-CS/chitosan were recorded using a PerkinElmer FT-IR spectrophotometer.

**Thermal Gravimetric Analysis.** TGA (TA, Q500) was used for the thermogravimetric analysis of the sample in nitrogen atmosphere. The temperature range and the heating rate were 30–600 °C and 5 °C/min, respectively.

**Differential Scanning Calorimeter.** DSC (TA, Q100) was used with a hermetic pan (T 090127) for analysis. The temperature range and the heating rate were 40–240 °C and 2 °C/min, respectively. An empty pan was used as given in ref 22.

**Contact Angle.** Dynamic contact angles of m-CS-/Ch-treated OCC pulp sheets were obtained by a Phoenix 300 contact angle analyzer. Deionized water was used as the probe fluid.

**Antimicrobial Activity Test of m-CS and m-CS-Ch-Treated Recycled Paper Sheets.** The AATCC 147 test method was used to test the antimicrobial activity of unmodified and m-CS-Ch-treated OCC pulp sheets. Escherichia coli bacteria suspensions were inoculated into the peptone liquid. An air bath shaker was used for incubation at 37.8 °C for 12 h, and the culture broth was diluted. The peptone culture plates were prepared with mixtures of the bacteria suspension, CS, m-CS/Ch, and m-CS-Ch-treated OCC pulp sheet separately. A blank was also prepared for comparison. The plates were incubated at 37.8 °C for 24 h, and the inhibition rate was calculated according to the equation below.
\[ X = \frac{A - B}{A} \times 100\% \]

where A and B represent the number of colonies on the plates before and after inhibition.

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**Notes**

The authors declare no competing financial interest.

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