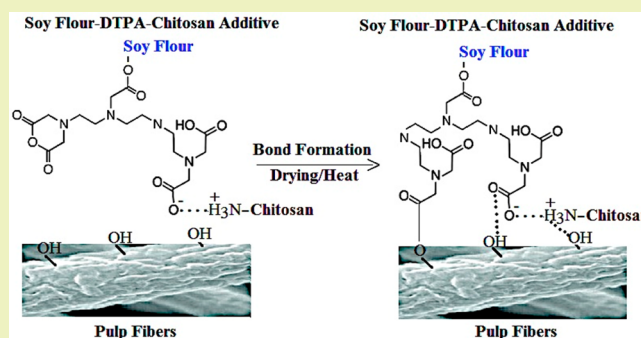


# A New Class of Biobased Paper Dry Strength Agents: Synthesis and Characterization of Soy-Based Polymers

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**ABSTRACT:** The goal of the current effort was to develop a new soy-based (soy flour) derivative to impart high fiber–fiber strength improvements to two-dimensional paper sheets. The success of the research hinged on successful proliferation of carboxylic and/or amine functionalities onto the polymeric backbone of the soy flour to significantly contribute to improved interfiber bonding of the paper–fiber sheets. Diethylenetriaminepentaacetic acid (DTPA) was reacted with soy flour in the presence of sodium hypophosphite and complexed with chitosan for the development of a new class of dry strength agents to improve integration into pulp fibers and thus increase interfiber bonding. The synthetic conditions including surface modifier concentration, time, temperature, pH, and material-to-liquor ratio were optimized. The paper materials incorporating the DTPA cross-linked (modified) soy flour agent demonstrated unprecedented tensile strength increases. A 1% soy protein flour–DTPA–chitosan agent by mass of pulp-based slurry was thoroughly mixed before generating two-dimensional hand sheets whose tensile indices increased 52.6%, 53%, and 57.8% for recovered (OCC, old corrugated containerboard), NSSC (virgin) pulp, and kraft (virgin) pulp sheets, respectively. The modified soy flour agent-treated pulp sheets also provided significantly increased gloss and water repellency with diminished surface roughness.

**KEYWORDS:** Soy flour, Cross-linking/synthesis, Dry strength agents, Recovered fibers, Kraft pulp, Interfiber bonding, Mechanical properties



## INTRODUCTION

Pulp is a lignocellulosic-based fibrous material that is generally prepared by chemically or mechanically separating predominantly cellulose fibers from their natural bundled state in crops, waste paper, or wood. Their morphology, mechanical or chemical stability, and/or optical properties can change significantly when formed into a wet web of paper and subsequently subjected to processes such as pressing, drying, printing, storage, repulping, or deinking.<sup>1</sup> Typically, the responses of various paper blends or materials to different external stresses vary, but generally, “virgin” or never-reclaimed fibers tend to significantly outperform reclaimed (or recycled) fibers. Paper reclamation has been practiced for many years as a means to demonstrate good environmental stewardship practices and address national/regional energy concerns. Often, it is possible to substitute reclaimed fibers in place of virgin fibers for the production of equivalent paper or paperboard. It has been reported that the utilization rate of OCC (old corrugated containerboard), a popular and widely used grade of paper, in 1963 was 21.1% in the United States,

whereas it increased to 67% during the early part of the past decade with a concomitant reclamation rate of nearly 70%.<sup>2</sup> Recently, the American Forest and Paper Association (AF&PA) divulged a reclamation rate for OCC of over 91%.

The major problem with attaining the goal set by AF&PA for paper reclamation is the inherent loss of strength that occurs from changes in basic fiber qualities such as length, flexibility, swelling, bonding, and purity (contamination).<sup>3</sup> The reduced interfiber bonding of reclaimed fibers relative to virgin wood pulp fibers is generally attributed to the drying phase of the first papermaking cycle.<sup>4</sup> Drying is a *de facto* papermaking protocol accompanied by partially irreversible lamination of fiber components, especially fibrils in the fiber wall (“hornification”), as well as increased resistance to swelling during rewetting.<sup>1</sup> Additionally, when hornification occurs within the pores of the fiber, the loss in swelling capacity results in stiffer fibers, which

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lack the conformability of virgin fibers and thus have a reduced opportunity to maximize bonding strength.<sup>4,5</sup> The most universally acknowledged property loss in reclaimed paper fibers is mechanical, manifested as a loss of interfiber bonding measured by tensile and burst strengths. Interfiber bonding is characterized primarily by hydrogen bonding between surface carbohydrate macromolecules of neighboring fibers. The strength of interfiber bonding critically depends on the chemical nature of the polysaccharide molecules with particular emphasis on functional groups such as hydroxyl, carbonyl, and carboxyl. Not surprisingly, it also depends upon the extent of surface contact among fibers.<sup>4</sup>

Therefore, a number of research efforts have attempted to improve the strength of reclaimed paper by addressing either one or both of the latter aspects given that reclaimed fibers are mechanically inferior to their virgin equivalents. Past research has demonstrated that high intensity (PFI) refining increases tensile and bursting strength of reclaimed paper, but at the expense of the production of a high level of fines (typically, submillimeter-sized particles from the S2 layer of wood fibers) that tend to slow down dewatering of the wet web of paper. A loss of fiber length and coarseness can lead to compromises in tear strength and folding endurance.<sup>6,7</sup> Earlier research efforts have identified several chemical treatments that contributed to significant improvements in the interfiber bonding strength of a recycled pulp sheet.<sup>8</sup> Among those studies, a few have demonstrated that chemical modification of pulp fibers may eliminate strength losses.<sup>9,10</sup>

The interest in chemical derivatization continues unabated with much research devoted toward discovering agents that can augment fiber–fiber bonding. Soybean-based byproducts have recently been identified by our group as potentially viable agents or the next generation (biobased) of additives for paper dry strength enhancements.<sup>11</sup> The United States produced nearly 88 million metric tons of soybeans in 2013<sup>12</sup> of which soy flour is the second pass byproduct (after defatting the soybeans), that can be characterized as a complex carbohydrate made by roasting the soybean, removing the coat, and grinding it into flour. Defatted soy flour is commercially available and contains approximately 32% carbohydrates, 51% soy protein, 3% fat, and a host of other components such as water, vitamins, and minerals.<sup>13</sup>

Soy protein is a long polymer chain consisting of 18 different polar and nonpolar amino acids; the polar amino acids can be used as chemical juncture sites to cross-link the protein and thus improve its mechanical, thermal, and physical properties, as well as reduce water sensitivity and hydrophilicity.<sup>14</sup> Earlier research has related that soy proteins can be cross-linked by incorporation of aldehydes such as glyceraldehyde, formaldehyde, and glutaraldehyde by *Maillard* reactions.<sup>15</sup> Cross-linked isolated soy protein has previously been used to develop biodegradable polymers that possess enhanced mechanical properties.<sup>16</sup> A cursory study conducted by Jin et al.<sup>11</sup> applying soy bean protein flour as a dry strength additive showed promise for papermaking. The results of such studies showed increased tensile strength from hydrogen-bonding networks between soy protein and pulp fibers. However, to date, the strength improvement has not been comparable to commercial dry strength agents likely due to the very low density of hydrogen bonding functionalities on the soy flour.

Dry strength additives are very important as a class of chemical reagents because they allow for a reduction in the overall basis weight of the paper product to achieve the same

dry strength and thus save on the cost of cellulosic raw materials. Selecting the correct dry strength agent to minimize costs is key for success in papermaking. Different types of dry strength additives such as native starch, cationic starch, carboxymethyl cellulose, guar gum, and polyacrylamides have been used. These types of commercial dry strength agents, however, have not been able to increase the strength properties of reclaimed pulp furnish to levels comparable to virgin pulp. The key to dry strength enhancements is a complex function of successful homogeneous blending of a reagent with hornified fibers, surfaces for interfacial bonding, and economics.

DTPA (diethylenetriaminepentaacetic acid) is a reagent that could provide successful cross-linking because it contains five carboxyl groups and two amine groups. At sufficiently high temperatures, its carboxyl groups can condense to form anhydrides and form amides or esters with the amine or hydroxyl groups, respectively, on the polar amino acid residues (or carbohydrates, the only hydroxyl groups in this case) of soy flour. These available functionalities may form hydrogen, ionic, or covalent bonding networks within the pulp fibers and improve interfiber bonding strength.

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

## ■ EXPERIMENTAL SECTION

**Materials.** Soy flour was provided by Archer Daniel Midland (ADM, Decatur, IL). Starch was supplied by Cargill Incorporated, Minneapolis, MN. Reclaimed OCC, NSSC (virgin), and kraft (virgin) pulp were supplied by Georgia-Pacific Innovation Research Institute, Norcross, GA. Cross-linking agents, i.e., diethylenetriaminepentaacetic acid (DTPA) and chitosan, were purchased from Sigma-Aldrich. Chemicals of reagent grade utilized were sodium hypophosphate (SHP), CAS registry number 123333-67-5; polyDADMAC, catalog no.: NC0175667; and sodium hydroxide, CAS registry number 1310-73-2. Denatured alcohol and acetic acid were purchased from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water.

**Chemical Modification of Soy Flour.** Approximately 5 g of the modifying agent (DTPA) was dissolved into 20 mL of alkali solution in a 50 mL Petri dish to which 1 g of sodium hypophosphite (SHP) was added. Soy flour (5 g) was added to the Petri dish and vigorously mixed with a glass rod. The mixture was placed in an air oven set at 130 °C over a time course of 4 h. Reaction products were washed with DI water and filtered several times to remove any unreacted materials. The product obtained was a modified soy flour that was air oven-dried at 50 °C overnight. Thereupon, the modified soy flour was complexed with chitosan using a previously described procedure.<sup>17</sup> Briefly, 1 g of chitosan was dissolved into 50 mL of a 1.5% acetic acid solution. Modified soy flour (1 g) was also dissolved into 50 mL of water and then added to the existing 50 mL of chitosan solution previously placed within a 250 mL round-bottomed flask. The reaction mixture

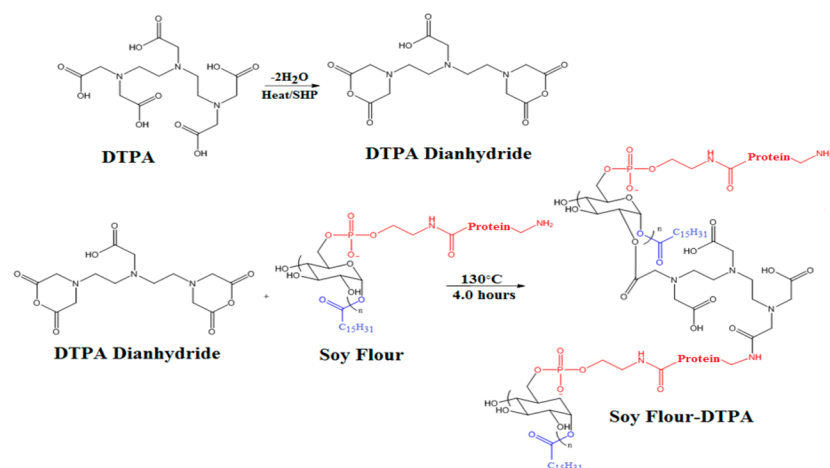


Figure 1. Suggested esterification route for soy flour and DTPA.

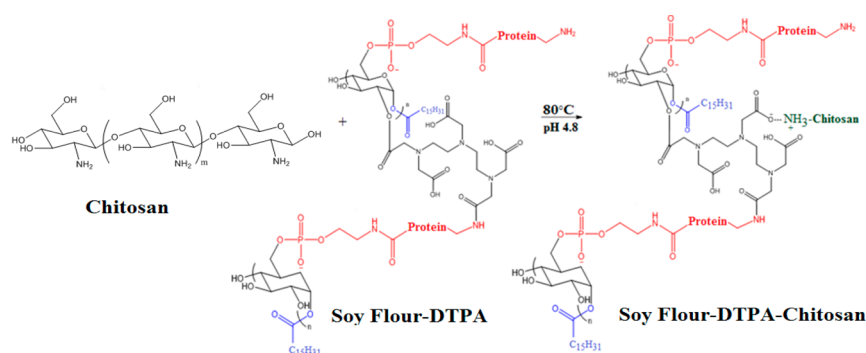


Figure 2. Suggested complexation reaction of the soy flour–DTPA reagent with chitosan.

was stirred using a magnetic stirrer at 80 °C for 90 min.<sup>18</sup> The proposed reaction schemes for the reactions with DTPA are shown in Figures 1 and 2.

**Characterization. Determination of Carboxylic Acid Content.** A fixed amount of soy flour–DTPA was dissolved into 20 mL of 0.1 N NaOH and hydrolyzed for 1 h. The excess NaOH was determined by titration with 0.1 N HCl and phenolphthalein as the indicator<sup>19</sup> in which the carboxyl content in milliequivalents of acidity per 100 g was calculated by the following equation:

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

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

**FT-IR Analyses.** IR spectra of all modified soy flour samples were recorded on a PerkinElmer FT-IR spectrophotometer.<sup>20</sup>

**Thermal Gravimetric Analyses (TGA).** The TGA used in this study was a TGA Q500. A nitrogen atmosphere was used. The temperature range and heating rate were 30–600 and 5 °C/min, respectively, followed by isothermal heating at 600 °C.<sup>21</sup>

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

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

**Contact Angles.** Dynamic contact angle measurements were performed with a Phoenix 300 Contact Angle Analyzer (Seo Co., Ltd., Korea). Deionized water was used as the probe fluid.<sup>19</sup>

**Scanning Electron Microscopy (SEM).** Morphological characterization of modified soy protein flour additive-treated OCC pulp hand sheets was performed using images acquired using a scanning electron microscope (SEM), Hitachi S-3200N.<sup>17</sup>

**Preparation and Characterizations of OCC Pulp Hand Sheets.** The sheet was prepared according to TAPPI Standard Method T 205 using a 900 mL pulp slurry (2.7 g OCC having a freeness of 400 CSF) in a sheet molder in the presence or absence of a modified soy flour additive. The pulp slurry was diluted with 10 L of water to produce a uniform sheet. The sheet was dried in a condition room and subsequently cured at 25–110 °C for 1 h.<sup>18</sup> In addition, the additive dosage percentage and pH were optimized based on the tensile strength of the additive-treated OCC pulp sheet.

**Physical Properties Test of Additive-Treated Recycled OCC Pulp Hand Sheets.** The tensile, burst, STFI, gloss, and roughness of additive-treated OCC pulp hand sheets were tested according to TAPPI T 220, TAPPI T 810, TAPPI T826, TAPPI T 480, and TAPPI T 538 test methods, respectively.

**Interfiber Bonding Strength of Additive-Treated Reclaimed OCC Pulp Sheets.** The interfiber bonding strength of additive-treated OCC pulp hand sheets was obtained using a standard T 569 pm-00 (provisional method-2000@ 2000 TAPPI) testing protocol.

**Quantification of Amounts and Types of Chemical Bonds.** The total unbound carboxylic acid contents of additive-treated OCC pulp sheets were determined by the methylene blue adsorption method.<sup>24</sup> Approximately 1 g of pulp was suspended in 25 mL flask of aqueous methylene blue chloride with the addition of 25 mL of borate buffer solution and filtered through sintered glass. Approximately 10 mL of the filtrate was transferred to a 100 mL calibrated flask to which 10 mL of 0.1 N HCl was added. The flask was filled to 100 mL with DI water, and the methylene blue in the solution was determined



photometrically using a calibration curve. The free dye concentration was determined from experimental results ( $X$ , see below). A PerkinElmer UV/vis spectrophotometer was employed to determine the dye concentration in solution. The carboxyl group content of the sample was obtained according to the following equation:

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

where  $X$  is the total amount of free methylene blue (mg), and  $Z$  is the weight of the oven-dry sample (g). In addition, the total carboxylic acid content (bonded and unbound) of additive-treated OCC pulp sheets was determined by acid–base titration.<sup>20</sup> (Note: The ester bond between the additive and the OCC pulp fiber can be cleaved by saponification with sodium hydroxide to allow measurement).

**Calculations.** The total esterification degree (bonds formed) was ascertained by applying the following equation:

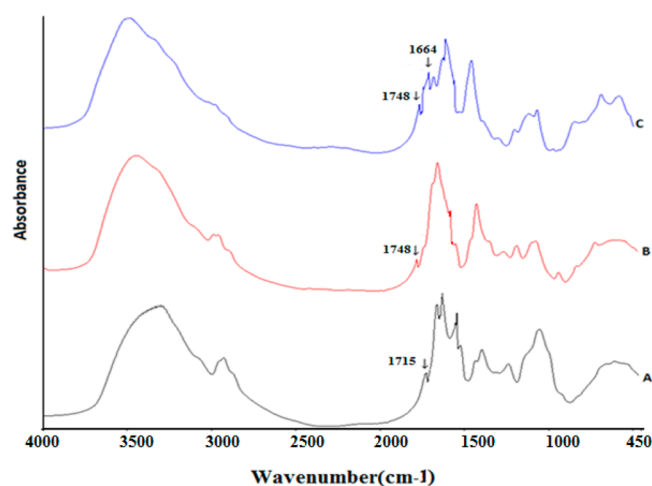
$$\begin{aligned} &\text{Total ester bonds formed} \\ &= (A - B) \text{ of additive-treated OCC pulp sheets} \end{aligned}$$

where  $A$  is the total carboxyl content (unbound and bonded) of additive-treated OCC pulp sheets (mmol/g), and  $B$  is the total unbound carboxyl content of additive-treated OCC pulp sheets (mmol/g).

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Soy Flour–DTAP–Chitosan Additive.** Soy flour is a complex glycoprotein that is replete with functional groups such as alcohols, carboxamides, thiols, thioethers, carboxylic acids, and a great diversity of amino acids. These functional groups are excellent chemical juncture sites for surface modification through reactions with a variety of modifying agents, especially those described in the current study. The driving hypothesis for this work is that significantly increasing the sites for hydrogen bonding will cause a significant enhancement in the interfiber bonding of the final product. This latter goal was accomplished by the modification of soy flour with DTPA via an esterification reaction in the presence of sodium hypophosphite and followed by subsequent complexation with chitosan. For the purposes of clarity and simplicity, the characterization of the DTPA-based complex will be representative of the modifying agent reactions. The carboxyl content of the DTPA cross-linked soy flour increased from 260 mequiv/100 g to 450 mequiv/100 g. It was found that the OCC fiber–fiber bonding as a result of the DTPA cross-linked soy flour was much better than the control as demonstrated by a comparison of the tensile strength indices.

**FT-IR Spectral Support.** The FT-IR spectra of soy flour (A), soy flour–DTPA (B), and soy flour–DTPA–chitosan (C) are shown in Figure 3. The spectrum of soy flour shows a prominent peak at 1715  $\text{cm}^{-1}$ , which can be attributed to a carboxyl group from the soy protein. Not surprisingly, when the soy flour reacts with the DTPA, an additional peak is observed at 1748  $\text{cm}^{-1}$ , while after further complexation with chitosan, signature peaks appeared at 1748  $\text{cm}^{-1}$  and 1664  $\text{cm}^{-1}$  attributable to the ester carbonyl functionality and amide of the chitosan, respectively. Amide bands in the spectrum appeared because the soy flour–DTPA derivatives undergo a complexation with chitosan followed by an amide reaction that occurs from drying the sample to over 105  $^{\circ}\text{C}$ . This latter result implicates the linking of the soy flour–DTPA to chitosan by a coupling reaction between the amino groups of chitosan and the carboxylic groups of soy flour–DTPA derivatives.



**Figure 3.** FT-IR spectra of soy flour (A), soy flour–DTPA (B), and soy flour–DTPA–chitosan (C). The prominent 1748  $\text{cm}^{-1}$  band derives from the ester carbonyl stretch (after DTPA tethering).

**Thermal Analysis.** The thermogravimetric behavior of the soy flour derivatives is shown in Table 1. For several of the

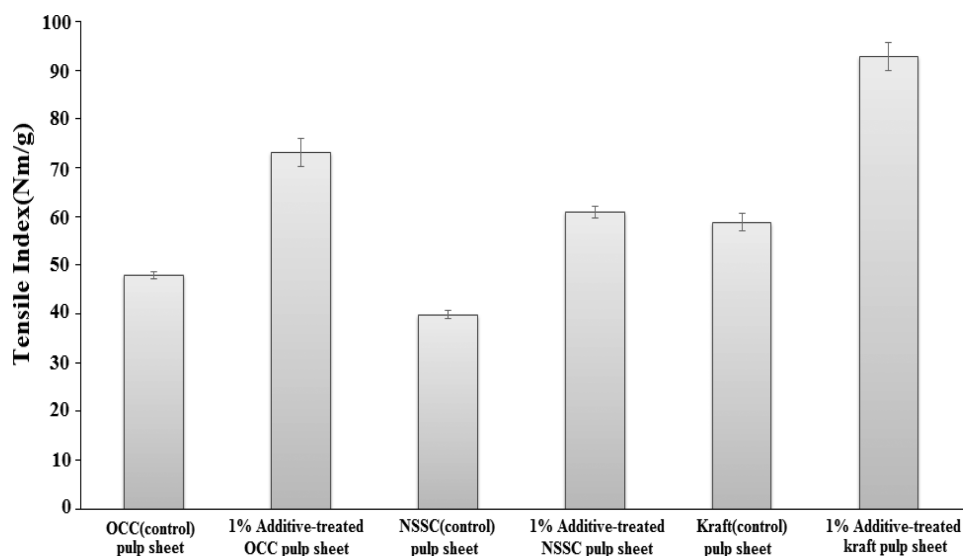
**Table 1.** Thermal Analysis of Soy Flour and Derivatives

sample	TGA maximum (DTG) degradation temp ( $^{\circ}\text{C}$ )	Residual char at 600 $^{\circ}\text{C}$ (%)	DSC endothermic peak ( $^{\circ}\text{C}$ )
DTPA	280.3	25.1	217.5
soy flour	310.2	23.4	188.6
soy flour–DTPA	300.3	27.1	199.2
soy flour–DTPA–chitosan	293.8	29.0	200.5
chitosan	290.0	26.0	268.4

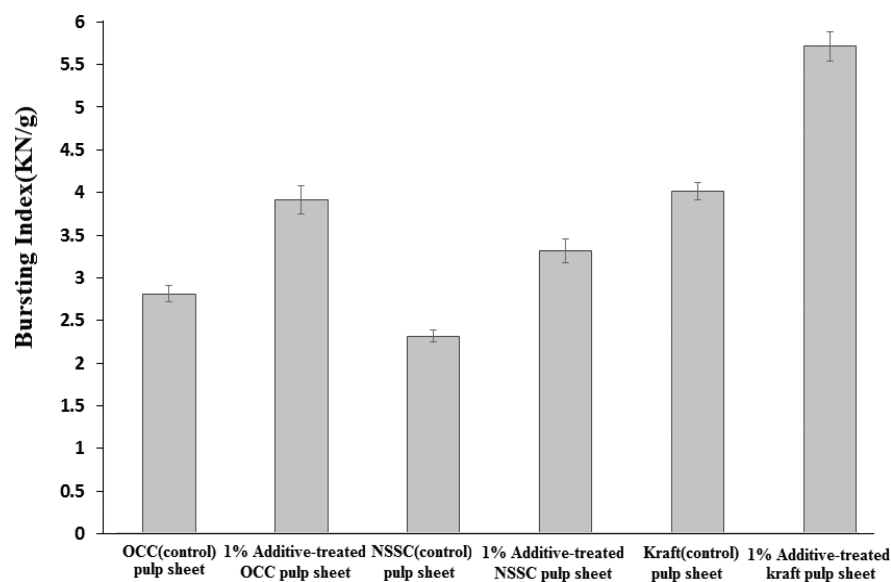
samples, a weight loss about 100  $^{\circ}\text{C}$  was attributable to water evaporation.<sup>19</sup> However, weight loss above 100  $^{\circ}\text{C}$  was likely caused by the thermal decomposition of the soy flour and its derivatives.<sup>17</sup> DTPA had a single sharp decomposition peak at 280.3  $^{\circ}\text{C}$ , whereas the soy flour had a single weight loss peak at 310.2  $^{\circ}\text{C}$ ; however, all derivatives of soy protein flour display a decrease in the maximum weight loss temperature and a concomitant significantly higher residual mass after heating to 600  $^{\circ}\text{C}$ . The latter result may be explained by soy flour surface-modifying agents possessing a lower decomposition temperature that is on the surface of the soy flour and the materials derived from the esterification possessing a lower temperature of degradation.<sup>15,16</sup>

The thermal behavior obtained from a differential scanning calorimetric analysis of the soy flour derivatives are shown in Table 1. DTPA displays a very sharp endothermic peak at 217.5  $^{\circ}\text{C}$ , whereas for the soy flour an endothermic peak was observed at 188.6  $^{\circ}\text{C}$ . The endothermic peak increased for the reaction products as illustrated in Table 1. The increase in the magnitude of the endothermic peak may originate from changes in chemical composition characterized by increased hydrogen bonding, plasticization, and an increase in molecular organization arising from esterification.<sup>22</sup>

**Application of Soy Flour–DTAP–Chitosan Additive to Reclaimed and Virgin Pulp Furnishes for Mechanical Property Improvements.** High mechanical properties in a two-dimensional paper sheet are likely the most important criteria for generating paper sheets. The sheets must display



**Figure 4.** Tensile indices of the controls and respective modified soy flour additive-treated pulp handsheets (margin of error was calculated at the 95% confidence interval).

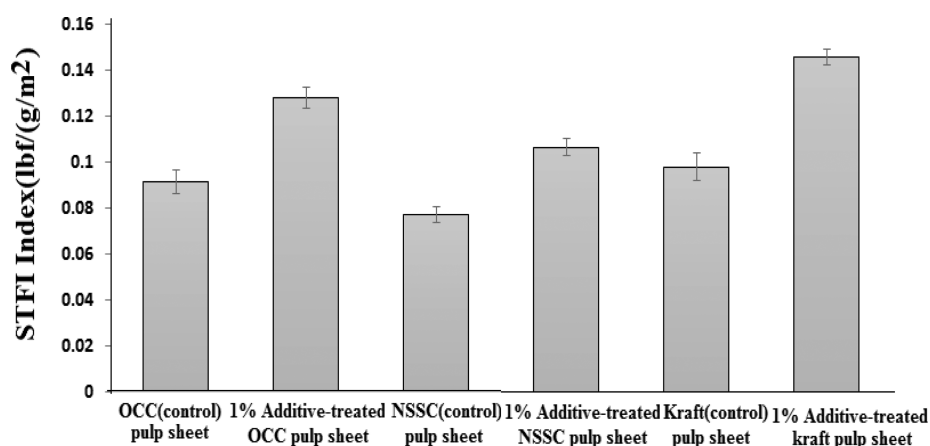


**Figure 5.** Bursting indices of the controls and respective modified soy flour additive-treated pulp hand sheets (margin of error was calculated at the 95% confidence interval).

sufficient resistance to tolerate stresses introduced by packaging (e.g., boxes), wrapping (e.g., linerboard), or sealing (e.g., liquid packaging). In general, macroscopic resistance is ascribed at the molecular level to a hydrogen-bonding network. More specifically, it is dependent on the quantity and surface area of the bonding sites. Reclaimed fibers have been irreversibly damaged by usage and thus diminish final paper strength properties. Figure 4 shows the tensile indices of OCC (reclaimed), NSSC (virgin), and kraft (virgin) pulp hand sheets before and after the addition the soy flour–DTPA–chitosan additive. It can be observed that the tensile index of soy flour–DTPA–chitosan additive-treated OCC, NSSC, and kraft pulp sheets increased by about 52.6%, 53.0%, and 57.8%, respectively. Similarly, the bursting index and STFI (compression) index of soy flour–DTPA–chitosan additive-treated OCC, NSSC, and kraft pulp increased 39.2%, 43.5%, and 42.5%, respectively, and 39.9%, 38.1%, and 48.6%, respectively (Figures 5 and 6). The increased strength properties are likely

to have resulted from higher interfiber bonding between the fibers and the soy flour–DTPA–chitosan additive. Soy flour–DTPA–chitosan contains a very large quantity of free  $-\text{OH}$ ,  $-\text{COOH}$ , and  $-\text{NH}_2$  functional groups. These groups are intimately involved in hydrogen and ionic bonding with pulp fibers that possess sizable quantities of  $-\text{OH}$  groups (both cellulose and lignin), which significantly contribute to the relative bonded area between fibers and additive. In addition, when the additive-treated pulp sheet is dried at  $T > 105^\circ\text{C}$ , the  $-\text{COOH}$  groups of the soy flour–DTPA–chitosan additive form anhydrides that react with the hydroxyl groups of pulp fibers to generate esters.<sup>20</sup> The combination of hydrogen bonding and esterification accounts for the increased bonding phenomena between the fiber and additive during sheet formation as manifested by increased mechanical properties.

The *t*-test of paired samples (for the mean) was measured to confirm the significance of the improvements in tensile indices of the additive-treated pulp hand sheets. In each of the cases, an



**Figure 6.** STFI indices of the controls and respective modified soy flour additive-treated pulp hand sheets (margin of error was calculated at the 95% confidence interval).

untreated sheet was compared to a sheet formed from the treated fibers. The *t*-test values for the OCC (control and additive-treated OCC pulp sheets), NSSC (control and additive-treated NSSC pulp sheets), and kraft (control and additive-treated kraft pulp sheets) samples were 15.23,  $-23.56$ , and  $-30.08$ , respectively. *p* values were 0.0000012, 0.00000063, and 0.000000016, respectively. Because these *p* values were significantly lower than the  $\alpha$  value 0.05 ( $p < 0.05$ ), there was a basis to posit significant differences between the test performances results (tensile indices) between the control and soy flour–DTPA–chitosan additive-treated pulp sheet samples.

A comparative study of the mechanical properties of OCC pulp hand sheet results using the soy flour–DTPA–chitosan dry strength additive and several commercial dry strength additives is shown in Table 2. In comparison to the commercial

**Table 2. Mechanical Properties of Reclaimed OCC Pulp Hand Sheets with Different Dry Strength Reagents<sup>a</sup>**

dry strength additive	tensile index (Nm/g)	bursting index (KN/g)	STFI index (lbf/(g/m <sup>2</sup> ))
no additive	47.9	2.8	0.091
soy flour–DTPA–chitosan	73.1	3.9	0.128
soy flour–chitosan	52.8	3.4	0.109
soy protein flour–DTPA–chitosan	71.25	4.0	0.130
soy protein flour–chitosan	57.00	3.3	0.110
soy protein flour	49.28	2.7	0.093
acid hydrolyzed soy protein flour	48.5	2.8	0.091
soy flour (commercial)	50.29	2.9	0.096
native starch (commercial)	51.73	3.0	0.098
cationic starch (commercial)	55.1	3.1	0.102
cationic polyacrylamide (commercial)	56.0	3.2	0.107
anionic polyacrylamide (commercial)	50.7	2.9	0.092

<sup>a</sup>At 1.5% addition level, dried at room temperature, and cured at 105 °C.

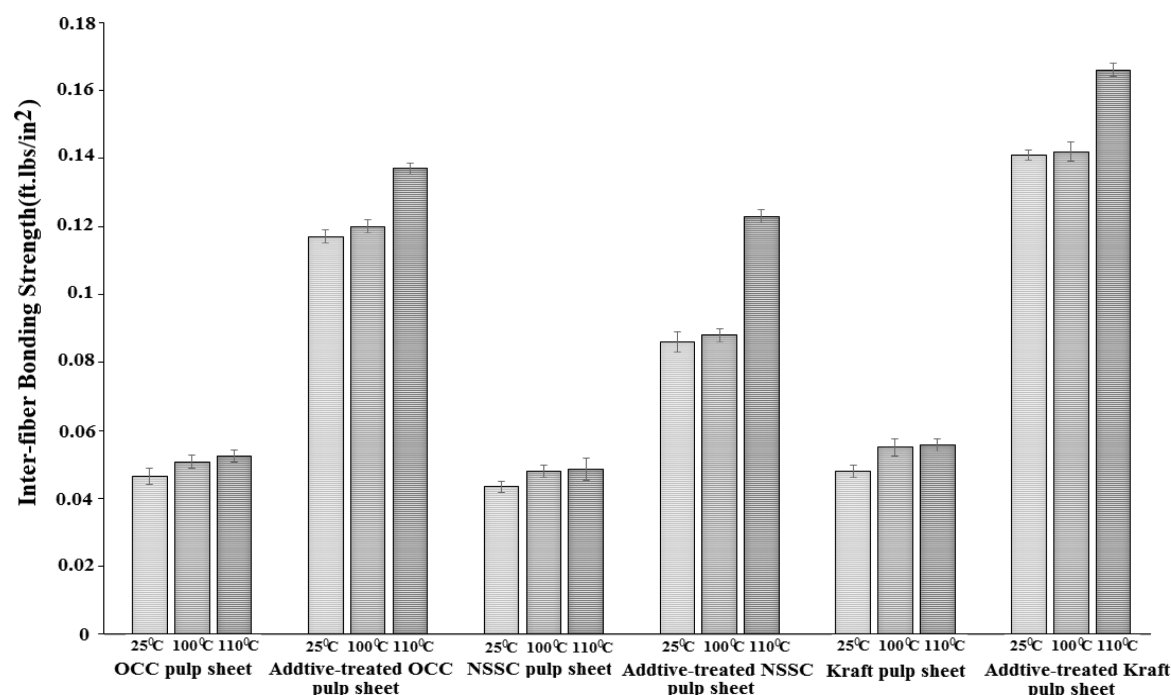
dry strength additive results, the soy flour–DTPA–chitosan additive results convincingly demonstrate improved performance in tensile, bursting, and STFI (compression) indices. These latter findings indicate that the chemistry introduced into the soy flour–DTPA–chitosan enhances bonding between pulp fibers. Thus, it appears that soy flour–DTPA–chitosan provides a viable alternative as a dry strength agent; moreover,

soy flour and chitosan are renewable materials, extremely cheap, readily abundant, and environmentally compatible that offset the use of the more relatively expensive starch reagent as a dry strength agent (millions of tons/year) so that starch may be used for human consumption.

The optimum dosage for the soy flour–DTPA–chitosan additive was 1%, while the optimal pH was found to be 4 and 8 to yield the maxima tensile indices of the additive-treated OCC pulp hand sheets. The basis for the latter phenomena is firmly grounded in pH-dependent electrostatics; at pH 4, the amine groups of the additive are nearly all protonated (their  $pK_a$  is about 1 unit higher), while at pH 8, the carboxylic groups ( $pK_a$  4.75) are also nearly all deprotonated. The charged species are therefore much more likely to interact favorably with the diversity of groups and charges on pulp fibers via electrostatics.

The mechanical properties of the modified polysaccharide additive-treated pulp sheets were compared to a set of commercial dry strength additive-treated pulp sheets as shown in Table 2 and were found to be significantly higher.

**Bond Formation with Reclaimed OCC and Virgin Pulps.** The interfiber bonding strength was measured by an internal bond tester (Scott). Each pulp hand sheet (control and additive-treated) was cured at three different temperatures (25, 90, and 110 °C) for 1 h. The interfiber bonding strength for the control OCC, NSSC, and kraft pulp handsheets increased approximately 10–12% when they were cured at 90 or 110 °C versus 25 °C. The interfiber bonding strength of soy flour–DTPA–chitosan additive-treated OCC, NSSC, and kraft pulp hand sheets showed nearly the same results when the samples were cured at 25 and 90 °C, but their strengths were significantly lower versus the soy flour–DTPA–chitosan additive-treated pulp sheets cured at 110 °C (Figure 7). The temperature dependence, nature of the system, and ensuing chemistry dictate that condensation (anhydride) reactions are occurring; at 110 °C, two carboxylic acid groups condense to form an anhydride. Anhydrides can lead to other chemical reactions (e.g., esterifications, amidations) that additionally improve interfiber bonding strength. However, curing temperatures between 25 and 90 °C are not sufficient to thermodynamically induce esterification or amidation because it has been reported that at temperatures below 100 °C carboxylic acid groups do not yield anhydrides likely because of equilibrium effects from excess moisture.<sup>20</sup>



**Figure 7.** Interfiber bonding strength for 25, 90, and 110 °C cured controls and additive-treated pulp hand sheets (margin of error was obtained at the 95% confidence interval).

It may be observed from Figure 7 that the interfiber bonding strength of all cured (25–110 °C) soy flour–DTPA–chitosan additive-treated OCC, NSSC, and kraft pulp hand sheets increased about 2.5–3 times relative to their respective controls. The significantly increased interfiber bonding strength, which ultimately increases the relative bonded area between fibers, can be attributed to electrostatic interactions and hydrogen bonding within the paper fibers during the paper making process.<sup>18</sup> The combined interactive effects also contributed to an increase in macroscopic tensile strength.

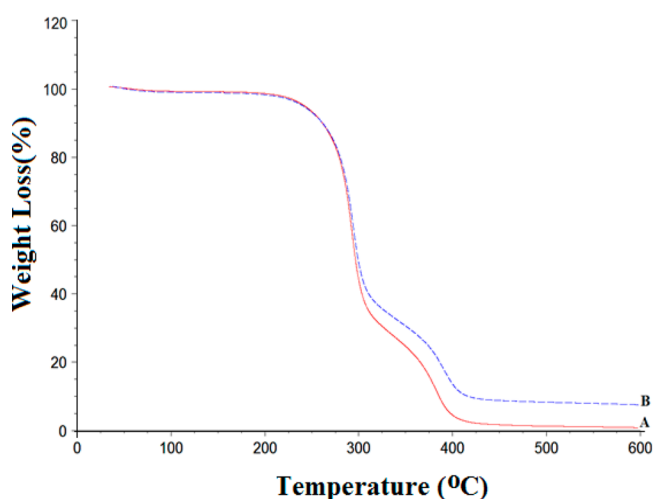
The ester bonds as measured by titration (see Experimental Section for details) are shown in Table 3. The totals were found

**Table 3.** Quantity of Ester Bonds in Additive-Treated Pulp Hand Sheets

curing temperature (°C)	ester bonds formed (mmol/100 g) in the additive-treated pulp sheets		
	additive-treated OCC pulp hand sheets	additive-treated NSSC pulp hand sheets	additive-treated kraft pulp hand sheets
25	0.0	0.0	0.0
90	0.0	0.0	0.0
110	1.82	1.96	1.90

to be 1.82, 1.96, and 1.90 mmol/100 g, respectively, when soy flour–DTPA–chitosan additive-treated pulp hand sheets were cured at 110 °C for 1.0 h. The anhydrides formed at this temperature lead to esters.<sup>18</sup> However, as already noted, for curing temperatures between 25 and 90 °C, no esters formed. This is because no anhydrides formed at curing temperatures below 100 °C. Further evidence for the presence of ester linkages between reclaimed OCC pulp fibers and dry strength reagent was obtained by ATR. A peak was observed at 1734  $\text{cm}^{-1}$  at 110 °C cured soy flour–DTPA–chitosan additive-treated pulp hand sheets NOT present at the lower temperatures. The peak observed is not large in magnitude

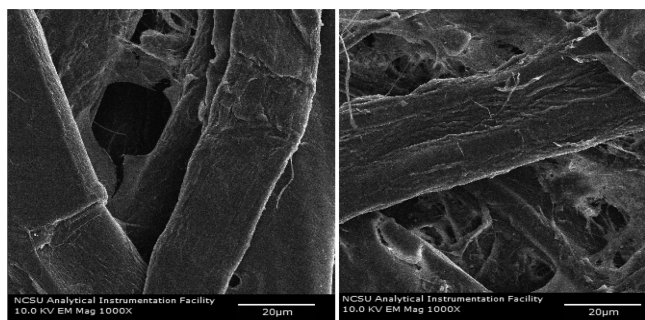
because a low quantity of carboxylic acid groups is present in OCC pulp because the applied level of additive (1%) was low. In addition, a high residual char value was observed in the soy flour–DTPA–chitosan-treated OCC pulp sheet compared to the control (OCC pulp sheet) after heating at 600 °C (Figure 8), which originates from strong and intransigent soy flour–



**Figure 8.** Thermogravimetric analyses of OCC (A) and soy flour–DTPA–chitosan-treated OCC pulp sheets (B).

DTPA–chitosan cross-linking (covalent linkages) to the OCC pulp fibers. The SEM (scanning electron microscopy) photomicrographs of OCC hand sheets and soy flour–DTPA–chitosan-treated OCC recycle pulp hand sheets are shown in Figure 9. The OCC control has a continuous smooth pore structure that contains plate-like solid pore walls, whereas the soy flour–DTPA–chitosan-treated OCC pulp hand sheet sample reveals a rougher surface with smaller irregular fragments on the fiber surfaces. It may be that these are





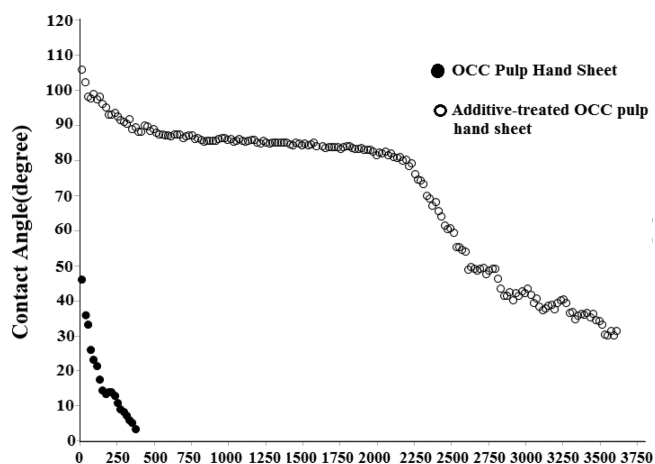
**Figure 9.** SEM image of OCC (left) and soy flour–DTPA–chitosan additive-treated OCC pulp sheets (right).

aggregations of modified soy flour–DTPA–chitosan additive and fines/fibrils increasing the bonded area among the OCC pulp fibers to provide more compact fiber assemblies.

A dynamic mechanical analysis of OCC pulp sheets and soy flour–DTPA–chitosan additive-treated OCC pulp sheets were performed in tension mode, and the results are illustrated in Figure 10. The storage modulus and loss storage modulus of the OCC pulp sheet and soy flour–DTPA–chitosan additive-treated OCC pulp sheet both decreased with increasing temperature. It is also observed from Figure 10 that the storage modulus of soy flour–DTPA–chitosan additive-treated OCC pulp sheets increased 135.9% (2.35 times) at 30 °C but decreased 135.9% to 128.87% when the sample was heated to 245 °C over 5 min isotherms relative to the control OCC pulp sheet. This latter result reflected increased bonding likely from cross-linking between fibers and the additive.<sup>17</sup> However, the loss modulus for the OCC pulp hand sheet from 30 to 245 °C decreased about 34%, and the soy flour–DTPA–chitosan additive-treated OCC pulp sheet decreased about 21%. These results implicate a soy flour–DTPA–chitosan additive cross-linking within the OCC pulp fibers.

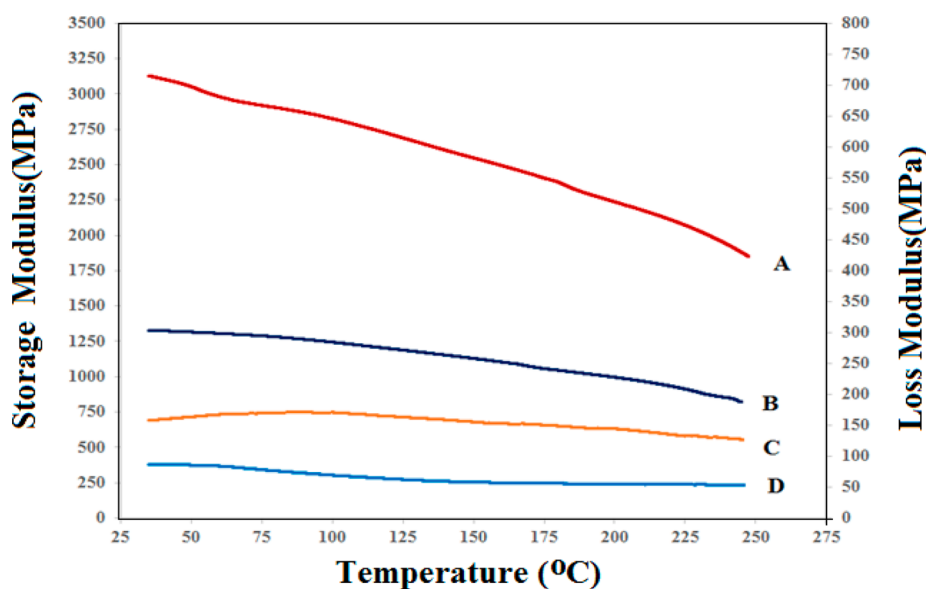
**Interactions with Water.** The dynamic contact angle of DI water droplets at 20 s was determined to be 46° for OCC pulp

sheet hand sheets (control), although it significantly dropped to 4.5° after approximately 380 s (Figure 11). In contrast, the



**Figure 11.** Contact angle of OCC pulp hand sheets (●) and soy flour–DTPA–chitosan-treated OCC pulp hand sheets (○).

dynamic contact angles at 20 s for CNs (cellulose nanocrystals)–DTPA–chitosan-treated OCC pulp sheet were 106°, which later dropped to approximately 85° after 2000 s and finally reached 31° after approximately 3700 s. This reflects the significantly decreased water absorbency of the soy flour–DTPA–chitosan additive-treated OCC relative to the control pulp sheet. Although the control OCC has an irregular surface and is quite hydrophilic, the soy flour–DTPA–chitosan contains chitosan that is hydrophobic and generates a sticky gel under wet acidic pHs that presents a plastic-like character under dry conditions. When a pulp sheet with the additive is produced under pressing, it distributes very evenly over the rough surface to cover it uniformly and produce a paper surface that is smooth with increased gloss (Figure 11). Thus, because the additive-treated sheet surface is hydrophobic due to the



**Figure 10.** DMA of curve A, storage modulus of soy flour–DTPA–chitosan-treated OCC pulp hand sheets; curve B, storage modulus of OCC pulp hand sheets; curve C, loss modulus of soy flour–DTPA–chitosan-treated OCC pulp hand sheets; and curve D, loss modulus of OCC pulp hand sheets.



plastic-like chitosan under dry conditions, the contact angle increases.

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### Notes

The authors declare no competing financial interest.

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