

# Soy Protein-Based Polyelectrolyte Complexes as Biobased Wood Fiber Dry Strength Agents

Julio C. Arboleda,<sup>†</sup> Niko Niemi,<sup>†</sup> Juha Kumpunen,<sup>†</sup> Lucian A. Lucia,<sup>\*,†,‡,§</sup> and Orlando J. Rojas<sup>\*,†,||,⊥</sup>

<sup>†</sup>Department of Forest Biomaterials, North Carolina State University, Raleigh, North Carolina 27695-8005, United States

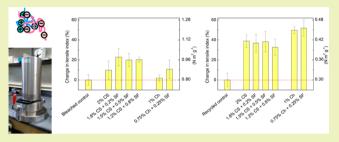
<sup>‡</sup>Key Laboratory of Pulp & Paper Science and Technology of the Ministry of Education, Qilu University of Technology, Jinan 250353, P.R. China

<sup>§</sup>Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States

<sup>II</sup>Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, United States

<sup>1</sup>School of Chemical Technology, Department of Forest Products Technology, Aalto University, Aalto 00076, Finland

**ABSTRACT:** Soy protein flour, isolate, and their derivatives were investigated to enhance the dry strength properties of paper. The soy systems were applied in aqueous suspensions consisting of lignin-free and recycled fibers to investigate their adsorption and interaction effects. Experiments using soy flour, soy protein isolate and its hydrolysates, cationized soy flour, and dual systems consisting of soy flour combined with cationic starch or chitosan were pursued. Improved paper strength was obtained when soy protein flour was utilized in combination with conventional treatments based on cationic



polymers. For example, increases in ultimate tensile and compressive strength of lignin-free fiber paper of 23% and 10%, respectively, were measured when dual systems consisting of soy flour and cationic starch were applied relative to the fibers with no additive. In the case of lignin-containing recycled fibers, improvements of 52% and 56%, respectively, were obtained for a soy flour—chitosan dual system (compared to fibers without additive). The results confirm that an opportunity exists to valorize residual soy products that are inexpensive, environmentally friendly, and offer an alternative sustainable option for paper performance enhancements relative to conventional (nonsustainable) dry strength additives.

KEYWORDS: Soy protein, Ionic complexes, Dry strength, Wood fibers, Papermaking, Mechanical properties, Polyelectrolyte complexes

# INTRODUCTION

A wide range of chemical additives have been applied to papermaking furnishes to facilitate the formation of wet webs and potentially enhance the mechanical strength of the final dry fiber network. Although on average approximately 10% of the total cost of papermaking can be attributed to the broad class of paper strength additives, they nonetheless achieve significant enhancements in both chemical and physical properties that are otherwise not attainable if fibers only were used.<sup>1</sup> Among the conventional chemicals in papermaking, dry strength agents maximize the mechanical robustness of the final products while preserving other properties such as opacity, bulk, and printability; indeed, they have attracted wide consideration in view of the increased use of recycled fibers, which display compromised mechanical properties when compared to virgin fibers. In addition, their application continues to be attractive because they allow for a reduction in the weight per unit volume (basis weight) for a given dry strength target (lower weight material that retains the same mechanical performance) and thus lower operational and production costs.

The most conventional papermaking dry strength additives on the market are based on starches (unmodified, cationic, and anionic derivatives), polyacrylamides, guar gums, carboxymethyl cellulose, and methyl cellulose.<sup>2,3</sup> Even though these widely used polymers generally exhibit good performance, other macromolecules have been considered for economic and performance reasons, including soy proteins (SPs) and residuals from soy oil production when used alone or in combination with other polymers.<sup>4,5</sup> Additives for papermaking applications must be chosen with regard to a number of factors that dictate final paper performance and include economics, government compliance (if required for food/contact grades), biodegradation, environmental compatibility, and overall physicochemical performance of the final dry web.

Soy-derived products constitute a low cost, sustainable, and environmentally friendly option that find high value applications in the formulation of adhesives,<sup>6–8</sup> films,<sup>9–12</sup> gels,<sup>13,14</sup> foams,<sup>15–18</sup> emulsions,<sup>19–21</sup> and aerogels.<sup>22</sup> On average, soy beans are composed of proteins (36%), carbohydrates (28%), oil (19%), moisture (13%), and minerals (4%). After soy oil extraction (defatting), the main byproduct is a protein-rich

Received: March 3, 2014 Published: August 28, 2014

#### ACS Sustainable Chemistry & Engineering

mixture that can be further purified into soy flour (about 50% protein), soy protein concentrate (about 70% protein), and soy protein isolate (about 90% protein).<sup>23</sup> Obtaining high purity protein products requires extensive purification methods and can be quite cumbersome and economically demanding, and as a consequence, soy flour is often the most attractive product for deployment in industry due in part to its relatively low manufacturing and processing costs.

In the current formulation of dry strength agents, two soy grades have been used so far: (1) denatured soy protein isolates (SPIs), which can augment up to 26% of the dry strength of paper produced from sugar cane bagasse fibers<sup>4</sup> and (2) soy flour (SF) and SPI soluble fractions (after centrifugation, yielding about 10% of the total product mass) that have shown improvements in dry strength of up to 15% and exhibit a synergistic effect when combined with cationic starch (dry strength gains up to 26%).<sup>5</sup>

It is already known that although SPs can interact with both hydrophobic and hydrophilic materials, they adsorb onto lignin to a higher extent as compared to cellulose;<sup>24</sup> therefore, different performances are expected if fibers with different amounts of lignin are used. Thus, a fundamentally exciting part of the current research was investigating the dynamics of the surface interactions of soy flour with lignin and how such interactions could ultimately affect fiber—fiber bondability. Dry strength additive experiments were therefore done on bleached and lignin-containing *recycled* fibers, an important class of papermaking furnish that is seeing increased usage on a global market due to a relatively scarcity of virgin fiber.

From a fundamental molecularity perspective, the use of polyelectrolyte complexes (PECs), obtained by a mixture of cationic and anionic polymers, have been shown to improve the mechanical properties of paper through increased electrostatic networking mechanisms among the PECs and fiber charged surfaces.<sup>25–29</sup> The synergistic effect observed from SP and cationic starch suggest the formation of polyelectrolyte structures and motivated the current study of systems where SPs are combined with cationic macromolecules.

Other proteins have been used in papermaking in the past; the use of casein in particular for coatings since the 1890s is well known and still in use today.<sup>30,31</sup> Although proteins constitute a wide family of products that have the ability to interact with different substrates and improve bonding, they have not been used in wet-end chemistry to any high extent.

Several engineered proteins with induced cellulose binding domains have been used for protein immobilization to produce sensors, catalyzers, and purification systems,<sup>32,33</sup> and although similar products rich in cellulose binding domains have been used to improve the mechanical properties of paper,<sup>34</sup> the high cost of these alternatives is still too prohibitive to be able to feasibly consider their application within the papermaking industry.

The current contribution to the literature is principally focused on the characterization and rigorous analysis of the properties of SP-based formulations for their potential in papermaking dry strength applications. Thus, SF without further purification was used alone or in combination with cationic polymers and other SPs derivatives, as a potentially new generation of dry strength agents for papermaking.

### MATERIALS AND METHODS

Two different wood fiber sources were used, namely, lignin-free virgin bleached softwood and recycled liner with 8% residual lignin (kappa number of 53). Commercial soy flour, SF (7B defatted, > 53% protein and 32% carbohydrates) and soy protein isolate, SPI (Pro Fam 955, > 90% protein) were generously supplied by ADM (Decatur, IL). SF is typically produced by milling dehulled and defatted soy beans or soy meal, while SPI is produced by alkaline extraction followed by precipitation at a mildly acidic pH of dehulled and defatted soybean flakes.

A 60% solution of (3-chloro-2-hydroxypropyl) trimethylammonium chloride (CTA) in water from Aldrich was used for SF cationization. Cationic starch "Charge+310", generously supplied by Cargill (Minneapolis, MN), was used after cooking at 4% solid concentration (95 °C, 15 min). Polyaluminum chloride (PAC) Eka ATC 8210 with a 10.2% active content ( $Al_2O_3$ ) was kindly supplied by Akzo-Nobel (Arnhem, The Netherlands). Low molecular weight chitosan with a degree of acetylation between 75% and 85% (Sigma-Aldrich) was used after dissolution in 1% acetic acid solution (8 h mixing at room temperature) at 1% solid concentration.

A 20% solution of poly(diallyldimethylammonium chloride) (poly-DADMAC) with a  $M_w$  between 100 and 200 kDa (charge density on dry basis: 6.19 mequiv/g) from Sigma-Aldrich was used to prepare 0.001 N solutions and later to perform charge demand titrations as a polycationic titrant. A 0.0025 N poly(vinyl sulfate) potassium salt (PVSK) with a  $M_w$  of about 200 kDa (charge density on dry basis: 6.16 mequiv/g) was obtained from Nalco and was used as an anionic titrant for charge demand titrations.

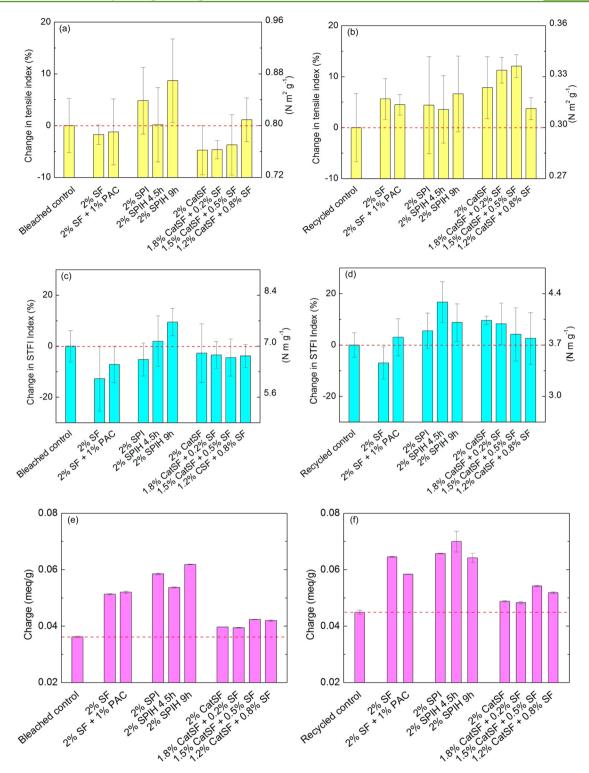
**Protein Quaternization.** A total of 200 g of SF dispersion (15%) was loaded in a closed glass reactor equipped with a mechanical stirrer and temperature control to which 67.6 g of CTA solution (60%) was added and was stirred, while 24.25 g of NaOH solution (50%) was incorporated. The temperature was raised to 60 °C for 30 h to obtain a homogeneous, yellow, and turbid solution.

**Hydrolysis.** The SPI aqueous dispersion (5% solids) was subjected to acid hydrolysis with 0.1 N HCl at 70 °C. Samples were removed from the hydrolysis reaction at different times to obtain SP hydrolysates at different degrees of hydrolysis. The samples obtained were cooled to room temperature, neutralized to pH 7 using 1N NaOH, and subsequently freeze-dried for further use.

**Recycled Fiber Furnish Preparation.** Linerboard clippings were soaked in water for 30 min and disintegrated in a standard TAPPI disintegrator (Testing Machines, Inc., New Castle, U.S.A.) for 15,000 cycles at 3000 rpm at 2% solids content according to TAPPI standard T-205. A furnish with a final Canadian standard freeness (CSF) of 550 mL was obtained. Approximately 2% calcium carbonate based on dry fiber was added, and the conductivity was adjusted to 1000  $\mu$ S/cm using sodium sulfate. The pH was adjusted to 8.

**Bleached Pulp Furnish Preparation.** A Valley beater (Valley Iron Works, Wisconsin, U.S.A.) was used to beat the pulp at 2% solids content following the TAPPI-200 standard method. The CSF of the furnish was monitored during the process according to TAPPI-227 standard method until a final CSF of  $\cong$ 550 mL. Calcium carbonate (2% based on dry fiber) was added to the furnish, and the conductivity was adjusted to 1000  $\mu$ S/cm using sodium sulfate. The pH was adjusted to 8.

Handsheet Making. At least five handsheets were prepared for each condition using both bleached and recycled fibers following TAPPI standard method T205 sp-95 (cylinder mold Robert Mitchell, Inc., Quebec, Canada). Approximately 450 g of suspension of fibers at 2% solids were diluted to 0.3% with water, and the additives were added and stirred for 15 min, after which the pH was adjusted to 8-8.5. The resultant suspension was titrated for polyelectrolyte concentration and poured into a forming cylinder half filled with water. The resultant handsheets of 60 g/m<sup>2</sup> dry basis weight were pressed (Herman Manufacturing Co. Press, Ohio, U.S.A.) for 5 min first and then for 2 min at 50 psig. After pressing, the handsheets were dried using a Formax 12 in. drum dryer from Adirondack Machine Corp. (New York, U.S.A.), operating at 105 °C at a residence time of 1 min 45 s. The handsheets were conditioned under controlled conditions (50  $\pm$  1% relative humidity and of 23  $\pm$  2 °C) overnight before testing. At least five handsheets were prepared using recycled



**Figure 1.** Effect on the mechanical properties of handsheets from the addition of soy flour (SF), SF + polyaluminum chloride (PAC), soy protein isolate (SPI), SPI hydrolysates (SPIH) obtained at two different hydrolysis times, and cationic soy flour (CatSF) used in combination with SF. Different mechanical tensile indices (a,b) and STFI (c,d) are presented. The electrostatic charge obtained by polyelectrolyte titration is shown in panels (e,f). The "control" represents a handsheet in the absence of any of the additives.

and bleached fibers without any additives (controls) and different SPderived products alone and in combination with other additives.

**Charge Demand.** The negative charge density on the surface of the fibers in the given furnish was determined by reverse titration using streaming current to determine the end neutralization point. A total of 100 g of fiber suspension was used to prepare the handsheets (after additive addition) and was mixed with approximately 25 mL of 0.001N poly-DADMAC solution; after mixing for 5 min, the solution was centrifuged (30 min, 10000 rpm). Finally, 10 g of the supernatant was titrated revealing an excess of poly-DADMAC in solution and thus the density of negative charges on the original fibers.

**Mechanical Properties.** The tensile properties of the handsheets were determined using the TAPPI-494 standard method. To evaluate the tensile strength, an Alwetron TH1 manufactured by Lorentzen &

#### ACS Sustainable Chemistry & Engineering

Wettre (Kista, Sweeden) was used. Probes (105 mm  $\times$  15 mm) were placed between the clamps with an initial gap of 100 mm and pulled until failure. The force was recorded as a function of elongation, and the ultimate tensile strength was determined. In order to evaluate the short span compression strength (STFI), a compression strength tester (App, 52; Type, 3-2) manufactured by Lorentzen & Wettre (Kista, Sweeden) was used. Samples of 70 mm  $\times$  15 mm were placed between two clamps at a 0.7 mm gap and operated under compression mode until failure caused by disruption of the internal structure of the sheet. For each condition, at least one sample from the five different handsheets was tested.

# RESULTS AND DISCUSSION

Soy flour (SF) and soy protein isolate (SPI) are not completely water soluble, but aggregate in aqueous media, depending on pH. In earlier work, it was observed that when SF and SPI were added to a furnish in which no control of the aggregation behavior was exerted, lower mechanical properties of the handsheets resulted compared to control samples (fiber furnish with no additive). The particular behavior witnessed arises from poor intermolecular interactions between the agglomerated soy derivatives and cellulosic fibers,<sup>3</sup> thus resulting in poor sheet formation. It was incumbent, therefore, at the onset of the research, to centrifuge SP dispersions to remove the aggregated components before any application of the soy as a dry strength additive.<sup>5</sup> These centrifugations, however, resulted in an unfortunate ~90% of the soy product being discarded.

A simple solution to avoid wasting SPs during the purification processes was realized through a meticulous analysis of the soy composition. The high intrinsic levels of aspartic and glutamic acid in the soy amino acid composition ( $\approx$  31% of the total soy protein mass) are able to dramatically reorganize the protein macromolecular structure upon increasing pH, a finding that resulted in substantially increased SP solubility. Thus, the solution to minimizing SP aggregation was to generate an alkaline condition (pH 12, 2% concentration), giving rise to a translucent dispersion that was adequate for addition to fiber furnishes and thus avoid agglomeration and resultant poor sheet formation. However, addition of the translucent dispersion to the already basic (pH 8-8.5) initial fiber slurry caused an unacceptable increase in final pH; thus, HCl (0.5 N) was necessary to maintain the pH of the fiber slurry.

A series of physical testing methods ascertain various product-specific properties that included burst, folding endurance, tear strength, bending stiffness, and breaking length, among others. The two principal physical methods to evaluate the effect of the additives are *tensile strength index*, a quotient of the maximum stress a material can sustain prior to ultimate failure divided by its basis weight (*vide supra*), and *short span compression strength* (STFI), an important physical property for packaging useful to predict the delamination of corrugated boxes when they are stacked.

The tensile indices and STFI values of handsheets that were consequently obtained are presented in Figure 1(a-d). Though the obtained results are very similar, several trends can be observed. In the case of lignin-free fibers (Figure 1(a)), only SPI addition appears to improve the tensile strength, whereas a modest improvement in the tensile indices of paper from recycled fibers was observed in Figure 1(b). Interestingly, the STFI of handsheets from lignin-free fibers was reduced after using both soy derivatives. SF application also resulted in a reduced STFI value in the case of recycled fibers, while SPI improved the STFI for the same fiber system. The results are in

agreement with earlier work that indicated that SPs interact strongly with lignin<sup>24</sup> and consequently interfere with maximum fiber–fiber bonding. The change in anionic charge of the furnish was characterized after the addition of SF and SPI; as expected, the addition of anionic SP derivatives increased the anionic charge density of the fiber suspension (Figure 1(e,f)).

The concept of introducing two opposing charged polyelectrolytes to improve fiber bonding is useful to implement for achieving maximum benefits for sheet formation.<sup>26,27,35</sup> Therefore, to improve fiber affinity with the anionic additives, polyaluminum chloride (PAC), a polycationic flocculant, was added to both fiber systems before protein addition. The strong flocculating effect of PAC induced poor paper formation, and as a result, no major improvement in the mechanical properties of the handsheets was obtained (Figure 1).

SPI hydrolysis is a technique that has been shown in this laboratory to improve the protein water solubility and their rate of sorption.<sup>36</sup> SPI hydrolysates (SPIH) were therefore generated after 4.5 and 9 h of acid hydrolysis and were added to examine if such an approach could be of benefit. It appears in all cases (Figure 1) that the 9 h SPIH were more beneficial for tensile strength than the 4.5 h hydrolysates, demonstrating a higher surface activity.<sup>17</sup> Hydrolysis improves the STFI performance in both fibers, while compared to nonhydrolyzed SPI, the best results were obtained when 9 h SPIH were used on bleached fibers. In the case of lignin-containing recycled fibers, optimal results were obtained with 4.5 h SPIH, exhibiting higher surface hydrophobicity and thereby better interactions with lignin.

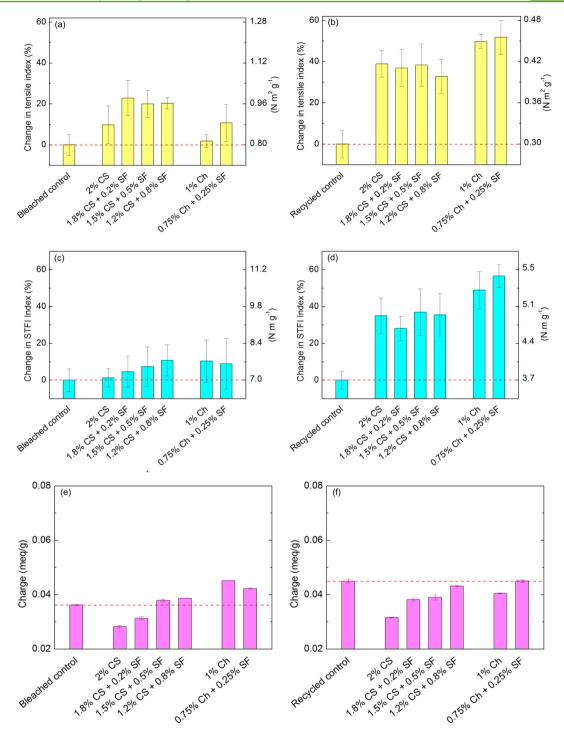
Cationic Soy Flour. SF was cationized by allowing the epoxide form (right structure, Figure 2(a)) of 3-chloro-2-

OH I CICH₂ CHCH₂N⁺(CH₃)₃Cŀ	+	NaOH	$\longrightarrow$	O CH₂CHCH₂N⁺(CH₃)₃Cl <sup>-</sup> + NaCl	(a)
,O CH₂CHCH₂N⁺(CH₃)₃Cl⁻	+	ROH	$\longrightarrow$	OH I ROCH₂CHCH₂N⁺(CH₃)₃CI <sup>-</sup>	(b)
_O CH₂CHCH₂N⁺(CH₃)₃Cl⁻	+	RNH <sub>2</sub>	$\longrightarrow$	OH I RNHCH₂CHCH₂N⁺(CH₃)₃CI⁻	(c)

**Figure 2.** Protein cationization using CTA. CTA (a, left) is activated to form an epoxide ring in alkaline conditions (a, right). The resulting epoxide can react with amino acids with hydroxyl (b) and amine (c) groups.

hydroxypropyl trimethyl ammonium chloride (CTA) to react with the hydroxyl (Figure 2(b)) and amine groups (Figure 2(c)) in proteins. The charge demand for the various products that resulted from the epoxide ring opening reaction was determined by polyelectrolyte titrations that yielded 0.078 and 0.085 mequiv/g at pH 10.5 and 8.2, respectively. The pH dependence of SP surface charge is explained by the presence of reactive carboxylic and amino groups in SP whose state of protonation (and hence, charge) is pH dependent. Compared with starch cationization, commonly used for papermaking, SF cationization displays several fundamental differences: (1) SF exhibits anionic behavior before being modified; therefore, the derivatization has to generate enough positive charges to neutralize the initial negative charges before the material exhibits a net cationic behavior. (2) Not all residues in SF have

Research Article



**Figure 3.** Effect of the addition of cationic starch (CS) used alone or in combination with soy flour (SF) and chitosan (Ch). The effect on the tensile index is illustrated in panels (a,b). The effect on STFI is illustrated in panels (c,d), and the charge of the system is illustrated in panels (e,f).

cationizable groups, while starch is abundant in reactive hydroxyl groups. For these reasons, a high degree of cationization is more difficult to obtain in SPs compared to carbohydrates. The charge of the CatSF used was 0.347 mequiv/g.

The mechanical properties of the handsheets prepared using CatSF are shown in Figure 1. It is easily observed that CatSF gave rise to improved handsheet dry strength for the recycled fibers but not for lignin-free fibers, a result highlighting the importance of nonionic interactions when SP derivatives are used "that is" in agreement with the results obtained when SF and SPI were used in recycled fibers.

**Complexes of Cationic Starch and SPs.** In previous reports, SF and SPI soluble fractions were obtained by centrifugation and later used as dry strength additives, showing synergistic effects with cationic starch (CS).<sup>5</sup> Mixtures of SF and cationic starch were prepared and evaluated as dry strength additives to evaluate if nonpurified SF exhibits the same behavior. After preparation of the mixtures, it was found that SF can be easily dispersed in cooked CS suspensions, likely because of formation of polyelectrolyte complexes (PECs) and

## ACS Sustainable Chemistry & Engineering

protein rearrangement induced in the anionic SF by the cationic media.  $^{\rm 28}$ 

The properties of the handsheets obtained using CS and SF at various ratios are observed in Figure 3. A synergy was observed from using SF and CS in the handsheets of lignin-free fibers (a 23% increase in tensile index was observed), whereas in recycled fibers no appreciable effect was observed, although the addition of SF is not detrimental, i.e., up to 25% of CS can be replaced with SF, which lowers the cost of the wet-end additive.

Compared with other additives, the use of CS reduced the surface anionic charge of the fiber considerably (Figure 3e). The addition of SF tends to increase the surface anionic charge because in the formation of CS–SF complexes, the cationic groups of CS are partially neutralized. It is interesting to note that the best results for mechanical properties do not coincide with the minimum surface charge, as often happens when PECs are used in papermaking, a result opposed to conventional dry strength additives.<sup>35</sup>

PECs have been intensively studied since their discovery in the 1930s.<sup>37</sup> These structures, resulting from the mixture of polyanions and polycations, possess intriguing physical, chemical, and electrostatic properties between those of ionic crystalline solids and amorphous organic polymers, which can be exploited over a host of practical applications like drug delivery, filtration membranes, and dry strength additives in papermaking. Specifically, they act as bonding agents when the paper is dried forming nonuniform distributions of charged segments with maximum effectiveness when one of the charges is in excess, generating attractive collisions between PEC and the fibers.<sup>35</sup> The synergistic effect observed when CS and SF are used in combination can be explained by the formation of PECs that are especially operative in bleached fibers that exhibit the highest obtained improvement.

**Complexes of Chitosan and SPs.** Chitosan is a biomacromolecule that has drawn significant attention as of late because of its antibacterial effects, hemostatic properties, composites, hydrogels, etc.<sup>38</sup> In essence, it fulfils several of the primary requirements of a paper dry strength additive because it is composed of linear molecules, has a high molecular mass, can form films, is polycationic, and is capable of forming hydrogen bonds with cellulosic fibers. Moreover, it possesses low toxicity, is biodegradable and biocompatible, and acts as an antimicrobial and antifungal agent.<sup>39</sup>

Chitosan is characterized as a linear polymer chain of  $\beta$ -(1-4)-D-glucosamine and N-acetyl-D-glucosamine residues. The amine group in the D-glucosamine becomes cationic at low pH and thus is water soluble and has a good affinity for anionic cellulosic fibers ultimately manifesting good performance as dry strength agent. Nevertheless, its performance is not optimal when it is applied in alkaline conditions typical in industrial papermaking.<sup>139,40</sup> An acidic solution of 1% of chitosan in 1% acetic acid was added to the fiber furnish, and later the pH was adjusted with 1 N NaOH to 8-8.5 to prepare the handsheets. A total of 2% of chitosan based on the dry weight of fiber was used. The obtained handsheets were very adhesive and were damaged when they were removed from the screen used in paper formation and metallic plates used in pressing. Compared to the case of recycle fibers, this behavior was more pronounced when lignin-free fibers were used. It is well known that chitosan has adhesive properties.<sup>41</sup> Nevertheless, stickiness in papermaking has not been reported in the past. At an industrial scale, this behavior may potentially lead to sheet break, downtime,

and consequently, inefficient operation. When the chitosan dosage was reduced, the stickiness of the paper was also reduced such that experiments using 1% chitosan as a dry strength additive could be carried out without considerable sheet damage. The obtained results can be observed in Figure 3. Complexes of chitosan-SF were also used after adding SF and chitosan solutions to the fiber suspension at 0.75% and 0.25%, respectively. In the case of the chitosan-SF complexes, the results for handsheets from lignin-free and recycled fibers were very different but both demonstrated important improvements in the mechanical strength of the handsheets. The addition of SF reduced the adhesiveness of the handsheets on the papermaking screens and press plates. This effect was particularly pronounced when lignin-free fibers were used. Such reduction in stickiness prevented damage of the sheet during formation and therefore preserved the mechanical properties of the paper obtained using the mixed additives. In the case of lignin-containing recycled fibers in which the stickiness problem was less pronounced, the addition of chitosan improved the mechanical properties (improvements of 50% and 57% TI and STFI, respectively). When SF was added as a complex with chitosan, further improvements were observed in the mechanical properties.

The charge of SF and chitosan in the fiber suspension should be highly dependent on the pH of the media, and in turn, the formation and behavior of formed PECs will be determined by the charge of the individual molecules. At pH 8, chitosan is not charged and thus loses its water solubility. Therefore, it is expected that chitosan would precipitate onto the surface of the fibers, even though the adsorption of chitosan in these conditions is not necessarily driven by electrostatic interactions. Chitosan and its gel-forming abilities can coagulate fibers improving interactions among them to increase the mechanical properties. Unfortunately, the swollen state of chitosan on the fiber surfaces also promotes their adhesion to other surfaces. It is expected that when chitosan and SF are in contact with the furnish, before pH adjustment, PECs can be formed, forming less swollen compact structures that adsorb easily on the fibers to avoid adhesion onto other materials. This effect is particularly pronounced in lignin-containing recycled fibers that have a high affinity toward SF, which obtain improvements in tensile indices up to 57%, the highest improvement obtained.

#### CONCLUSIONS

Soy protein (SP) and its derivatives constitute effective dry strength additives that exhibit good performance and synergistic effects when combined with cationic polymers such as chitosan or cationic starch. It is not necessary to have a highly purified product for improved fiber—fiber bonding; nevertheless, some fiber qualities such as the lignin content highly affect the additive performance. The obtained results highlight the promising performance that can be attained when SP-based polyelectrolyte complexes are used as dry strength agents in papermaking.

## AUTHOR INFORMATION

#### **Corresponding Authors**

\*E-mail: lucian.lucia@ncsu.edu. Tel.: +1-919-515-7707 (L.A.L.).

\*E-mail: orlando.rojas@aalto.fi. Tel.: +1-919-515-7707 (O.J.R.).

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors are thankful for funding support provided by the United Soybean Board (USB) under Projects 2490 and 2466.

# ABBREVIATIONS

SPs, Soy proteins; SPI, Soy protein isolate; SF, Soy flour; PEC, Polyelectrolyte complex; CTA, (3-chloro-2-hydroxypropyl)trimethylammonium chloride; PAC, Polyalluminum chloride; DADMAC, Diallyldimethylammonium chloride; PVSK, Poly-(vinyl sulfate) potassium salt; CSF, Canadian standard freeness; STFI, Short span compression strength; SPIH, Soy protein isolate hydrolyzate; CS, Cationic starch; Ch, Chitosan; CatSF, Cationic soy flour

## **REFERENCES**

(1) Smook, G. A. *Handbook for Pulp & Paper Technologists*; Angus Wilde Publications: Bellingham, WA, 2002.

(2) Biermann, C. J. Handbook of Pulping and Papermaking; Academic Press: San Diego, CA, 1996.

(3) Pelton, R. On the design of polymers for increased paper dry strength – A Review. Appita J. 2004, 57, 181–190.

(4) Fahmy, Y.; El-Wakil, N. A.; El-Gendy, A. A.; Abou-Zeid, R. E.; Youssef, M. A. Plant proteins as binders in cellulosic paper composites. *Int. J. Biol. Macromol.* **2010**, *47*, 82–85.

(5) Jin, H.; Lucia, L. A.; Rojas, O. J.; Hubbe, M. A.; Pawlak, J. J. Survey of soy protein hour as a novel dry strength agent for papermaking furnishes. J. Agric. Food Chem. **2012**, 60, 9828–9833.

(6) Wang, Y.; Mo, X.; Sun, X. S.; Wang, D. Soy protein adhesion enhanced by glutaraldehyde crosslink. *J. Appl. Polym. Sci.* 2007, 104, 130–136.

(7) Qi, G.; Li, N.; Wang, D.; Sun, X. S. Adhesion and physicochemical properties of soy protein modified by sodium bisulfite. *J. Am. Oil Chem. Soc.* **2013**, *90*, 1917–1926.

(8) Hettiarachchy, N.; Kalapathy, U.; Myers, D. Alkali-modified soy protein with improved adhesive and hydrophobic properties. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1461–1464.

(9) Gennadios, A.; Weller, C. Edible films and coatings from soymilk and soy protein. *Cereal Foods World* **1991**, *36*, 1004–1009.

(10) Kim, K.; Weller, C.; Hanna, M.; Gennadios, A. Heat curing of soy protein films at selected temperatures and pressures. *LWT-Food Sci. Technol.* **2002**, 35, 140–145.

(11) Bai, H.; Xu, J.; Liao, P.; Liu, X. Mechanical and water barrier properties of soy protein isolate film incorporated with gelatin. *J. Plast. Film Sheeting* **2013**, *29*, 174–188.

(12) Zhou, X.; Mohanty, A.; Misra, M. A new biodegradable injection moulded bioplastic from modified soy meal and poly(butylene adipateco-terephthalate): Effect of plasticizer and denaturant. *J. Polym. Environ.* **2013**, *21*, 615–622.

(13) Hua, Y.; Cui, S.; Wang, Q.; Mine, Y.; Poysa, V. Heat induced gelling properties of soy protein isolates prepared from different defatted soybean flours. *Food Res. Int.* **2005**, *38*, 377–385.

(14) Adachi, T.; Otani, Y.; Inoshita, M.; Hirotsuka, M. Patent JP236623,September 30, 1994.

(15) Wagner, J.; Gueguen, J. Surface functional properties of native, acid-treated, and reduced soy glycinin. 1. Foaming properties. *J. Agric. Food Chem.* **1999**, *47*, 2173–2180.

(16) Matsudomi, N.; Sasaki, T.; Kato, A.; KobayashI, K. Conformational changes and functional properties of acid-modified soy protein. *Agric. Biol. Chem.* **1985**, *49*, 1251–1256.

(17) Martinez, K. D.; Carrera Sanchez, C.; Rodriguez Patino, J. M.; Pilosof, A. M. R. Interfacial and foaming properties of soy protein and their hydrolysates. *Food Hydrocoll.* **2009**, *23*, 2149–2157.

(18) Park, S.; Hettiarachchy, N. Physical and mechanical properties of soy protein-based plastic foams. J. Am. Oil Chem. Soc. 1999, 76, 1201–1205.

(19) Wagner, J.; Gueguen, J. Surface functional properties of native, acid-treated, and reduced soy glycinin. 2. Emulsifying properties. *J. Agric. Food Chem.* **1999**, *47*, 2181–2187.

(20) Ray, M.; Rousseau, D. Stabilization of oil-in-water emulsions using mixtures of denatured soy whey proteins and soluble soybean polysaccharides. *Food Res. Int.* **2013**, *52*, 298–307.

(21) Pui Yeu, P.; Martin-Gonzalez, M. F. S.; Narsimhan, G. Effect of hydrolysis of soy beta-conglycinin on the oxidative stability of O/W emulsions. *Food Hydrocoll.* **2014**, *35*, 429–443.

(22) Arboleda, J. C.; Hughes, M.; Lucia, L. A.; Laine, J.; Ekman, K.; Rojas, O. J. Soy protein-nanocellulose composite aerogels. *Cellulose* **2013**, *20*, 2417–2426.

(23) Damodaran, S.; Paraf, A. Food Proteins and Their Applications; Marcel Dekker: New York, 1997.

(24) Salas, C.; Rojas, O. J.; Lucia, L. A.; Hubbe, M. A.; Genzer, J. On the surface interactions of proteins with lignin. *ACS Appl. Mater. Interfaces* **2013**, *5*, 199–206.

(25) Heath, H.; Ernst, A.; Hofreite, B. T.; Philips, B.; Rusell, C. Flocculating agent starch blends for interfiber bonding and filler retention – Comparative performance with cationic starches. *Tappi* **1974**, *57*, 109–111.

(26) Gardlund, L.; Wagberg, L.; Gernandt, R. Polyelectrolyte complexes for surface modification of wood fibres II. Influence of complexes on wet and dry strength of paper. *Colloids Surf., A* 2003, 218, 137–149.

(27) Gardlund, L.; Forsstrom, J.; Andreasson, B.; Wagberg, L. Influence of polyelectrolyte complexes on the strength properties of papers from unbleached kraft pulps with different yields. *Nord. Pulp Paper Res. J.* **2005**, *20*, 36–42.

(28) Hubbe, M. Dry-strength development by polyelectrolyte complex deposition onto non-bonding glass fibres. *J. Pulp Paper Sci.* **2005**, *31*, 159–166.

(29) Hubbe, M. A. Bonding between cellulosic fibers in the absence and presence of dry-strength agents – A review. *BioResources* 2006, *1*, 281–318.

(30) Morsy, F. Dielectric properties of coated paper and the effect of various soluble thickeners. *Polym. Plast. Technol. Eng.* **2005**, 44, 351–362.

(31) Paulson, J.; Moore, R. Characterization of proteins in coated papers by SDS polyacrylamide-gel electrophoresis. *Tappi J.* **1993**, *76*, 102–104.

(32) Hernandez, K.; Fernandez-Lafuente, R. Control of protein immobilization: coupling immobilization and site-directed mutagenesis to improve biocatalyst or biosensor performance. *Enzyme Microb. Technol.* **2011**, *48*, 107–122.

(33) Levy, I.; Shoseyov, O. Cellulose-binding domains biotechnological applications. *Biotechnol. Adv.* **2002**, *20*, 191–213.

(34) Levy, I.; Nussinovitch, A.; Shpigel, E.; Shoseyov, O. Recombinant cellulose crosslinking protein: A novel paper-modification biomaterial. *Cellulose* **2002**, *9*, 91–98.

(35) Hubbe, M.; Moore, S.; Lee, S. Effects of charge ratios and cationic polymer nature on polyelectrolyte complex deposition onto cellulose. *Ind. Eng. Chem. Res.* **2005**, *44*, 3068–3074.

(36) Arboleda, J. C.; Rojas, O. J.; Lucia, L. A. Monitoring soy protein hydrolysis and its physicochemical behavior on model surfaces. *Biomacromolecules* **2014**.

(37) Michaels, A. Polyelectrolyte complexes. Ind. Eng. Chem. 1965, 57, 32-&.

(38) Kaur, S.; Dhillon, G. S. The versatile biopolymer chitosan: Potential sources, evaluation of extraction methods and applications. *Crit. Rev. Microbiol.* **2014**, 40, 155–175.

(39) Lertsutthiwong, P.; Chandrkrachang, S.; Nazhad, M.; Stevens, W. Chitosan as a dry strength agent for paper. *Appita J.* **2002**, *55*, 208–212.

(40) Ashori, A.; Harun, J.; Zin, W.; Yusoff, M. Enhancing drystrength properties of kenaf (*Hibiscus cannabinus*) paper through chitosan. *Polym. Plast. Technol. Eng.* **2006**, *45*, 125–129.

(41) Khanlari, S.; Dube, M. A. Bioadhesives: A review. Macromol. React. Eng. 2013, 7, 573-587.

2274