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Survey of Soy Protein Flour as a Novel Dry Strength Agent for Papermaking Furnishes

Haoyu Jin,[†] Lucian A. Lucia,[*,†] Orlando J. Rojas,[†,‡] Martin A. Hubbe,[†] and Joel J. Pawlak[†]

[†]Department of Forest Biomaterials (Wood & Paper Science), Laboratory of Soft Materials & Green Chemistry, North Carolina State University, Campus Box 8005, Raleigh, North Carolina 27695-8005, United States

[‡]School of Chemical Technology, Aalto University, P.O. Box 16100, 00076 Aalto, Finland

ABSTRACT: A series of experiments were conducted on recycled pulp samples for the novel purpose of determining the efficacy of employing soy protein flour to increase the strength of dry paper. Values of short span compression and tensile strength were the prime criteria for comparison based on industrial considerations. Various conditions were considered to uncover effective schemes for applying the soy proteins under industrial-like papermaking conditions including alkaline versus acidic as well as high or low ionic content papermaking conditions. A hybrid system of starch, a dry strength additive currently used in paper furnishes, and soy protein was considered to study the possible existence of any synergistic chemical effects. Results indicated that a 1 part (by mass) soy protein to 3 parts cationic starch hybrid system resulted in the highest strength increase in comparison to solely either the soy protein or the cationic starch as dry strength additives.

KEYWORDS: *soybean protein, papermaking, dry strength, mechanical properties*

INTRODUCTION

The soybean is a legume that has become one of the most important sources of vegetable protein in the world. There are various other applications for soybeans that include livestock feed, printing inks, adhesives, paper coatings, paints, fertilizers, sizing for textiles, insect sprays, and food substitutes. However, the application of soybean protein as a dry strength additive in papermaking has not been studied to any significant extent.

Dry strength additives are an important set of compounds that are essential for maximizing the mechanical integrity of the papermaking products. The purpose of any dry strength aid is to increase the strength properties of paper in its air-dried state while not compromising a host of other properties such as softness.[1] Dry strength additives 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.[2] Determining the right type of dry strength to balance costs and benefits is an important decision based on process set up. Various dry strength additives have been used throughout the years and include starch, carboxymethyl cellulose, guar gum, chitosan, and polyacrylamides.[3]

Studies have shown starch to be a cheap and effective dry strength additive for papermaking. One particular study used polyacrylamide as a retention aid and cationic starch as the dry strength aid while also reporting that cationic starch could have been used as the retention aid.[4] No actual conditions were stated besides the additional components included in the system and the preparation conditions for the cationic starch such as cooking the starch for 20 min in a 95 °C water bath and preparing a dilute solution for addition (usually the case for when starches are used). It is also known that a higher pH will promote the adsorptive function of cationic starch. It should also be noted that overdosing with cationic starch will provide a more concentrated effluent with a higher BOD rating and will also affect drainage and retention in a negative manner.[5] In Mohamed et al.'s study, the results showed a large variation range (a 8% improvement versus a 58% improvement) for the increase in tensile strength of paper from using cationic starch. This indicates that the conditions and other components mixed into the process can have a great influence on the overall effectiveness of the cationic starch additive.

A cursory study had been conducted by Fahmy et al. in applying soy protein as a dry strength additive, which showed some promise for papermaking.[6] Other studies have helped confirm the potential of soy protein as an effective strength additive in adhesives and blend membranes. Studies conducted by Liu and Li have shown soy protein adhesives to be a promising substitute to industrial petro-based adhesives, at least with respect to dry adhesion properties.[7] Thus, it would seem likely that because soy protein has a binding and adhesive nature, it would be desirable for increasing the dry strength of paper. Soy protein and cellulose membrane blends have also been researched for strength properties in studies conducted by Keskin et al. and Luo et al.[8,9] The results of the studies indicated increased tensile strength while decreasing the overall wet strength of the membranes. The main mechanism of interaction proposed by the researchers is that soy protein and cellulose engage in extensive hydrogen bonding networks, a result which is similar to that from the Zhang et al. studies dealing with soy protein plastic blends.[8,10] In these experiments, the soy protein content addition was extremely high, 40× higher than what would typically be used in papermaking (typically 1% m/m).

For this study, a series of trials were conducted to assess the application of soy protein as a putative dry strength additive by

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analyzing different conditions of pH and ionic strength while also testing a hybrid system of using both soy protein and starch. Results indicated a high potential of success for papermaking.

■ EXPERIMENTAL SECTION

Materials. Bakers soy flour (or 7B soy flour) was obtained from ADM (Archer Daniels Midland) Specialty Products-Oilseeds and was used for the majority of the soy protein application. It had a soy protein content of 53% by composition.[11] Pro-Fam 955 from ADM was used in a few trials at the start of the hybrid system studies with a soy protein content of 90% by composition.[12] Laboratory grade NaOH, $NaSO_4$, HCl, acetic acid, and Na_2CO_3 were used for pH and conductivity adjustments. A Pierce BCA Protein Assay kit was used for the determination of protein content in solutions. Parafilm was used to cover protein solutions when performing incubation for the assay. Unbleached virgin kraft pulp samples of samples (hardwood and softwood) were sent from Georgia Pacific for the papermaking trials.

Methods. Pulp samples were prepared with a Testing Machines Inc. disintegrator and then refined in a valley beater according to TAPPI test method T 200 at 1.67% consistency and 23 L using a virgin kraft fiber mix of 70% softwood fiber and 30% hardwood fiber. The Canadian Standard Freeness (method of relatively controlling fiber quality for its base strength) was then measured with a Testing Machines Inc. Canadian Standard Freeness Test according to TAPPI method T 227 to achieve approximately 600 CSF.

Starch solutions provided by National Starch, Opti-Pro 650 (high charge density cationic starch) and Opti-Plus 1030 (amphoteric starch) were prepared by cooking for 20 min in an Endurance mini double boiler with a 1% solution diluted with tap water over a Thermolyne Corporation Hot Plate adjusted to 550 W. Pregelatinized potato starch, aquajel 330AW, was provided by AquaSol Corporation, and a 1% solution was created with a drink mixer.

Soy protein solutions were made by mixing tap water with soy flour (Bakers 7B defatted soy flour) or soy protein isolate (Profam 955), pH was adjusted using NaOH or HCl, and conductivity was adjusted using Na_2SO_4. Foaming appeared in all trials when preparing the soy protein solutions. A Beckman Model J-21C Centrifuge was used to centrifuge soy protein solutions to remove insoluble particles at 12,000 rpms and 4 °C for 30 min. The concentration of soy protein in the solution was determined by the Pierce BCA Protein Assay method using reagents A and B by incubation in a Fischer Scientific Isotemp 228 hot water bath for 30 min at 37 °C and then measured with a Perkin-Elmer Lamda XLS spectrophotometer at 562 nm wavelength.

Conductivity was measured using an Oakton Con 6 Acorn Series conductivity meter. A Yamato Lab Stirrer was used to mix pulp slurries with additives for 5 min (30 min in early trials). Paper handsheets, 4 or 5 for each condition of interest, were made according to TAPPI method T205 sp-95 in a Robert Mitchell Inc. British Sheet Machine handsheet mold at a basis weight of 60 g/m^2 (with adjustment of conductivity in the mold to 1000 microsiemens if desired). Before making the handsheets, the screen was cleaned with a steam hose to ensure proper drainage. The handsheets were then pressed in a Testing Machines Inc. handsheet press.

Handsheets were measured for their basis weight first before test specimens were prepared at a 15 mm strip width using a Lorentzen & Wettre strip cutter. The specimens were tested for their tensile strength in a Lorentzen & Wettre tensile test and STFI short span compressive strength in a Lorentzen & Wettre STFI compression strength tester. Values at first are reported in units of N_{max} (newtons max or max force) and later as breaking length of km for tensile strength and lb_f for STFI values as displayed on the machine. Index values for each strength test were calculated by dividing each of the strength values by the corresponding basis weights. The error bars indicate the range of plus or minus one standard deviation. The details for the different abbreviated notations used for the various trials are shown in Table 1.

Table 1. Notation Legend

notation	description
control	normal pulp without any additives
soy #%	soy flour protein at #% dosage
soy pH #	soy flour protein at pH # and 1% dosage
P	soy protein at 1% dosage
S	cationic starch (Aquajel 330AW) at 1% dosage
P #:@	soy protein to cationic starch (Aquajel 330AW) ratio of # parts soy protein to @ parts starch at 1% dosage
PAS #:@	soy protein to amphoteric starch (Optiplus 1030) ratio of # parts soy protein to @ parts starch at 1% dosage
PCS #:@	soy protein to cationic starch (Optipro 650) ratio of # parts soy protein to @ parts starch at 1% dosage

An ANOVA single factor analysis was used to determine whether the data sets were significantly different with the assumption that the data sets have a normal distribution.

■ RESULTS AND DISCUSSION

Soy Flour Protein in a Direct Application. In order to thoroughly assess the potential of soy protein as a dry strength additive, the direct application of soy protein without any adjustments of pH and conductivity was executed in the first series of tests. Centrifugation was first done to ensure that the soy protein solution was homogeneous before application. Overdosing of the additive was also conducted to observe if there was a maximum in strength gained. Figures 1 and 2 demonstrate the tensile index and STFI index values for a direct application of soy flour protein (Bakers 7B soy flour) using no adjustments in pH or conductivity.

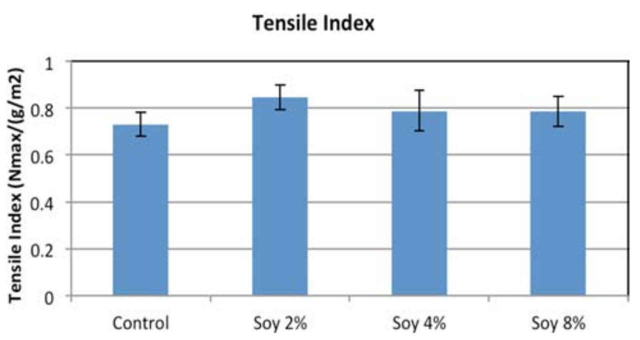

Figure 1. Tensile Index values for soy flour protein enhancement of dry strength from 0 to 8% dosage.

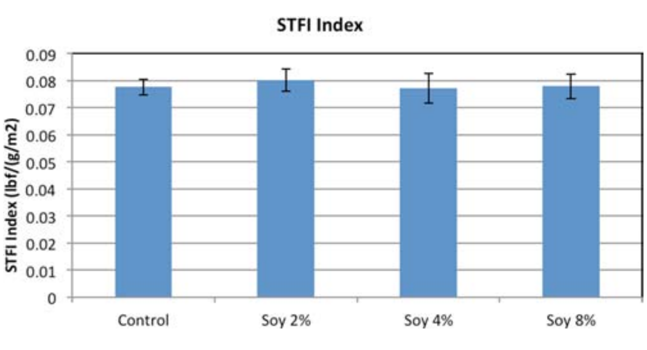

Figure 2. STFI Index values for soy flour protein enhancement of dry strength from 0 to 8% dosage.

The mixing time of these trials were 30 min, which was later determined to be more than necessary to ensure complete mixing. This was later reduced to 5 min of mixing time. As can be seen in the above Figures, the maximum appears to be at approximately 2% soy protein dosage. Further confirmation of this maximum was verified at dosage levels of 0.25%, 0.5%, and 1%. The soy protein beginning to self-aggregate may explain the trend of decreasing strength after the maximum.

Soy Flour Protein at Different pH Values with Conductivity Adjustments. The next step was to find better conditions of application of soy protein as a dry strength additive. The pH of the system and conductivity were monitored for their effects on the application of soy protein. A solubility analysis was conducted at pH values of 3, 5, 7, 9, and 11. Figure 3 shows the results for the solubility analysis of soy flour protein at the various pH values.

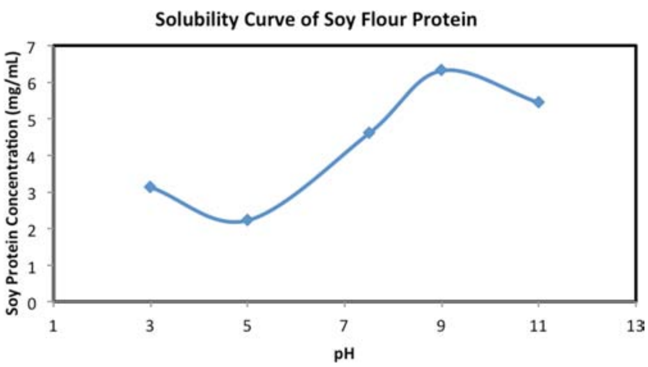

Figure 3. Soy flour protein solubility curve.

The isoelectric point (minimum solubility pH) from this curve appears to be at 4.8. The isoelectric point of the Achouri et al. study was approximately pH 4, but with modification (succinylation), it was approximately pH 5.[13] Ideally, the pH should be 9 to optimize solubility of the protein. In conjunction with the solubility study, two different papermaking conditions were tested (alkaline and acidic) at pH 9 and pH 5 using each of these solutions. Each trial was conducted with a 1% dosage level of soy flour protein based on the OD (oven-dried) weight of pulp. Alkaline and acidic papermaking results of tensile index values are shown in Figures 4 and 5 (STFI index graphs show similar trends); in general, the pH has an effect on the strength

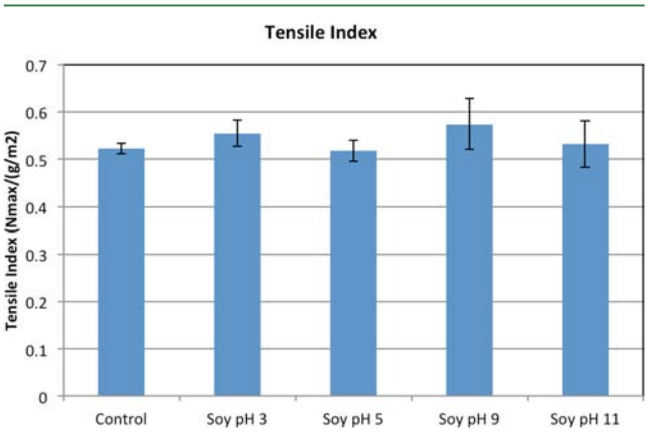

Figure 4. Tensile index values for soy flour protein enhancement of dry strength under alkaline papermaking conditions at pH 9.

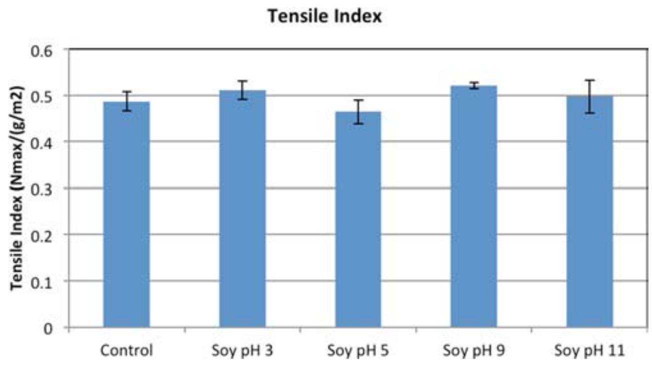

Figure 5. Tensile index values for soy flour protein enhancement of dry strength under acidic papermaking conditions at pH 5.

gains imparted on the paper depending on the pH of the solution and the papermaking conditions. Conductivity was adjusted to 1,000 microsiemens, and the soy solution pH was the variable in the trials.

The solubility was optimal at pH 9, and the strength increase was at a maximum at pH 9 in both alkaline and acidic conditions with the larger strength increase occurring under alkaline conditions. This may be attributed to the amphoteric nature of soy protein. At pH 9, the soy protein is anionic, and having salt in the system (for conductivity adjustments) may allow the soy protein to participate in ionic interactions as well as hydrogen bond with the cellulose. At pH 5, the protein may precipitate out of solution and be less inclined to form many bonds because the pH is near the soy protein isoelectric point. The soy flour protein may also have weaker bonds and overall less productive interactions because it is only slightly anionic after equilibrating to pH 5. This series of trials established the conditions that would be utilized for the next series of experiments in further magnifying the effects of soy protein. Acidic conditions for soy protein applications are typically nonideal based on these results. Although, no significant strength gains were discovered, the general trend still gives an idea of what conditions may promote the best results.

Soy Protein in a Hybrid System. Soy protein isolate (Profam 955), the highest grade/quality soy protein, was used in the next series of trials with the assumption that higher quality would enhance the overall mechanical properties of the furnish. A sample of Aquajel 330AW (pregelatinized cationic starch) from AquaSol Corporation was obtained for hybrid system studies with the soy protein isolate. The cationic starch is a noncommercialized product that was prepared using a high agitation drink mixer at a 1% concentration. The hybrid system was originally proposed to enhance the retention of the soy protein, and the interaction effects between the protein and starch are unknown.

A series of three experiments were conducted to confirm the trend that is illustrated in Figure 6 for the tensile index values (STFI index trend was similar). The trials were all conducted on a 1% total dosage at pH 9 papermaking conditions with conductivity adjusted to 1,000 microsiemens and with a pH 9 soy protein isolate solution (at 1,000 microsiemens). The latter conductivity of this solution was thus adjusted to better ensure the application of the soy protein at the desired conductivity level as well as the improvement of its solubility. The different trials conducted were a control (no additive), 1% soy protein isolate, P 3:1, P 1:1, P 1:3, and 1% cationic starch. The notation P #:# denotes a ratio of soy protein to cationic starch (e.g., P

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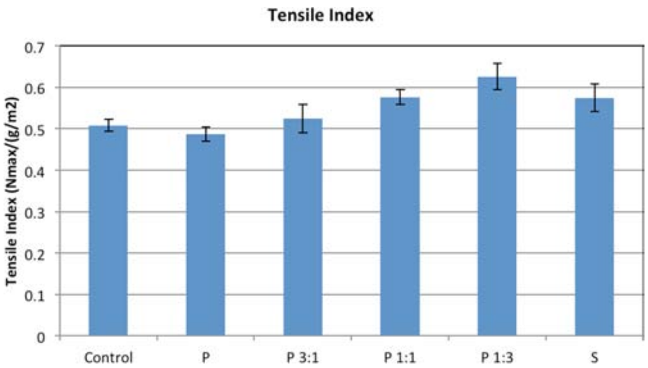

Figure 6. Tensile index values for soy protein isolate enhancement of dry strength in a hybrid system.

3:1 is 3 parts by mass soy protein to 1 part by mass cationic starch).

A major concern with using soy protein isolate is the cost. While deciding to use the best quality soy protein, the cost was neglected to favor what was expected to be better results. Soy flour protein was used in another experimental run to confirm the trends observed when using soy protein isolate because soy flour is much less costly. One additional modification was that the papermaking conditions were adjusted to pH 7. Figure 7

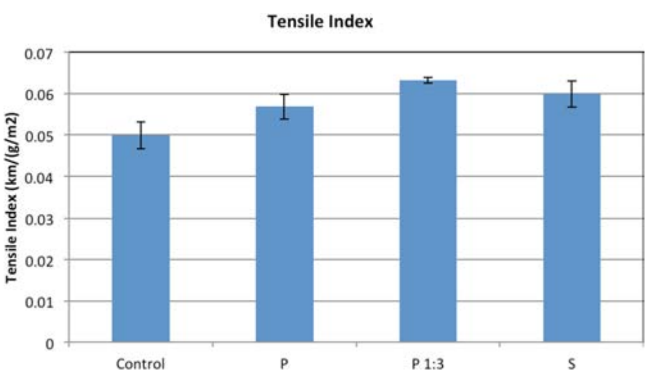

Figure 7. Tensile index values for soy flour protein enhancement of dry strength in a hybrid system.

shows an abbreviated trial run of the hybrid system to verify the strength gain trend for soy protein and cationic starch systems using soy flour protein instead of soy protein isolate. Take note that the units have changed between these two trials from N_{max} (max force in newtons) to km (breaking length), which was done to employ more conventional units.

On the basis of the results of these trials, soy flour protein appears to be the better choice for the hybrid system. The cost is much cheaper while still resulting in similar strength gains. Soy protein isolate by itself did not produce any tensile strength gains when dosed at 1%, while soy flour protein showed some improvement in tensile strength. Perhaps the carbohydrate content in the soy flour protein made the additive more compatible with cellulose interactions as reported in the study by Zhang et al. of soy protein-plastic blends.[10]

Only the P 1:3 ratio was tested for soy flour protein to confirm if it still had the same effect as soy protein isolate in the hybrid system because there was an observed maximum at that ratio in the series of conditions examined. One explanation of why the hybrid system works best at a ratio of 1 to 3 (protein to cationic starch) might be because of the distribution of charge or amount of charge in each additive. There may be more charged groups on soy protein than there is on cationic starch; therefore, there is a need for more starch to help anchor the protein on or in between the fibers. It has been shown that adding a cationic polymer followed by an anionic polymer yields better effects on strength gains.[14] Polymer bridging could be another reason why the hybrid system is effective.[14] A visual representation of polymer bridging is shown in Figure 8. The

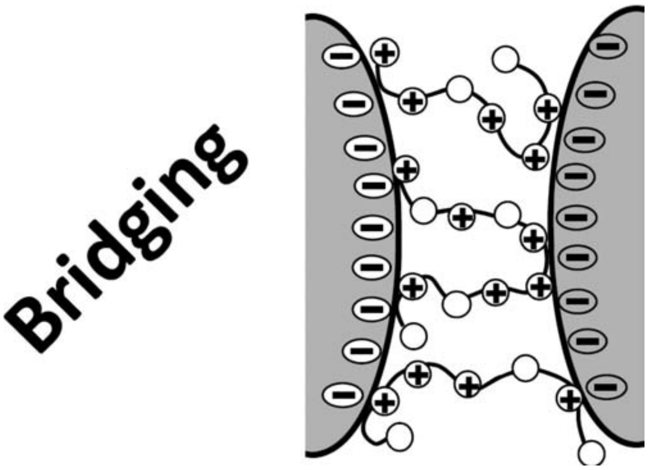

Figure 8. Polyelectrolyte bridging.[12]

cationic starch is a large molecular mass polymer that may attach a celluose fiber to the soy protein and then continue to attach the soy protein to another fiber. Furthermore, the soy protein could reinforce the bonds between the fibers and the starch. Nevertheless, there appears to be a synergistic effect between soy protein and cationic starch that will require further characterization.

Soy Flour Protein with Industrial Starches in a Hybrid System. An economic comparison could not be done with a noncommercialized cationic starch so two different corn starch products from National Starch were used for direct comparison. Opti-Plus 1030 is an amphoteric starch used in industrial recycle mills for strength improvement. Opti-Pro 650 is a high density cationic starch that is of interest because the results of the hybrid system needed to be reproducible. The trials were conducted with the same ratios as those in the previous hybrid system experiment but at the papermaking conditions of pH 7 and 1,000 microsiemens. The soy flour protein solution was adjusted to pH 9 with a conductivity of 1,000 microsiemens. The results are presented in Figures 9 and 10. The notation has been changed to accommodate the different starch samples. For example, PAS 3:1 means 3 parts soy protein to 1 part amphoteric starch, while PCS 1:3 means 1 part soy protein to 3 parts cationic starch. Likewise, AS denotes amphoteric starch, CS denotes cationic starch, and P denotes soy flour protein with the control being no additives.

With two amphoteric additives, the strength gained from the hybrid system of soy flour protein and amphoteric starch was worse than the soy flour protein with cationic starch. The amphoteric combination seemed to have a competitive trend where both the additives were fighting to attach onto the fibers. Ultimately, no matter what ratio of soy flour protein to amphoteric starch was used, the amphoteric starch alone performed the best in that set of hybrid trials. The tensile strength gains in the cationic starch and soy flour protein

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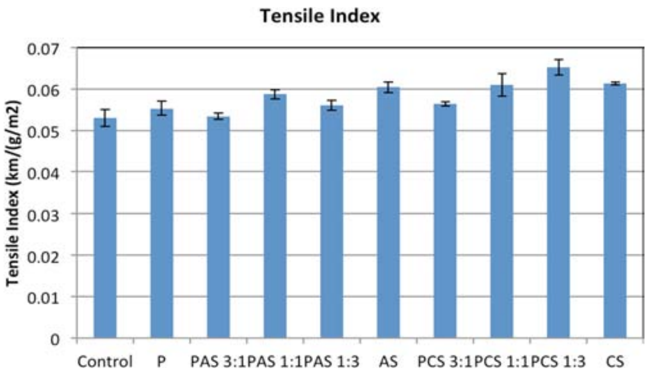

Figure 9. Tensile index values for soy flour protein enhancement of dry strength with industrial starches in a hybrid system.

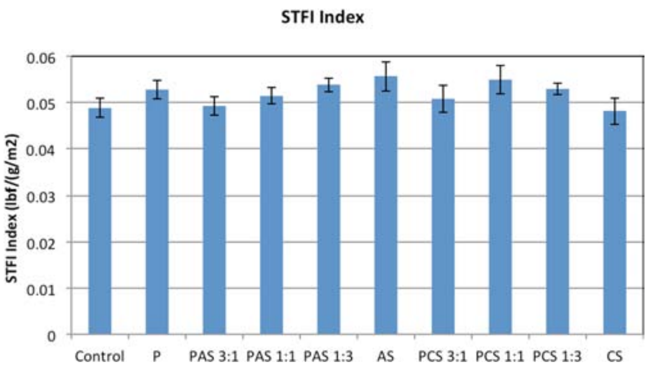

Figure 10. STFI index values for soy flour protein enhancement of dry strength with industrial starches in a hybrid system.

hybrid system were the best in this series of trials when compared to all of the additive runs. The STFI strength gains, however, were not so significant. STFI is the more important strength test when considering recycle packaging grade paper, but tensile strength still has its application in other grades.

Statistical Analysis. The results of the ANOVA single factor analyses are shown in Table 2. Of course, this analysis can only be performed under the assumption that the data is normally distributed. The most important key trials were tested to determine if the results were significantly different when compared to the control group. Each trial is labeled with the section and notation used for each graphical representation of the results. Each trial was compared to its corresponding control group. The *F* value indicates how different the data sets are from each other. A larger *F* value indicates a higher level of difference. As can be seen, different confidence levels were used to show at what point the two data sets were significantly different. The most important trials that indicate potential industrial applications showed a significant difference at the 99% confidence level. There were only two trials that showed significant difference only when considering the 90% confidence level. In general, the soy protein 1 part to 3 parts cationic starch trials resulted in fairly high *F* values that are a strong indication of significant difference between those values and the control values.

An industrial partner's experiments also found that cationic starch did not work very well for STFI strength, and that is why amphoteric starch was used. The most important conclusion that can be made from these results is that regardless of the cationic starch brand, the hybrid system at a 1 to 3 ratio of protein to starch imparts better strength than either the protein or cationic starch alone. The conditions in which these additives are applied can impact the efficiency of the strength increase and will require further research.

Table 2. Statistical Analysis Results

trial	confidence level	*F*-value	*F*-critical
Direct Application			
soy 2%	95%	9.83	5.99
pH and Conductivity			
alkaline (pH 9 soy protein solution)	90%	4.24	3.46
acidic (pH 9 soy protein solution)	95%	12.88	5.32
Hybrid System			
Soy Flour			
P (1% dosage)	90%	3.7	3.46
P 1:3	99%	24.49	11.26
Soy Protein Isolate			
P 1:1	99%	41.53	11.26
P 1:3	99%	57.36	11.26
Industrial Hybrid System			
PCS 3:1	90%	4.76	3.46
PCS 1:1	99%	17.96	11.26
PCS 1:3	99%	64.06	11.26

AUTHOR INFORMATION

Corresponding Author

*E-mail: lalucia@NCSU.edu.

Notes

Finally, portions of P.J.'s M.Sc. degree were fulfilled by the accomplishment of the work described herein.

The authors declare no competing financial interest.

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