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A preliminary assay of the potential of soy protein isolate and its hydrolysates to provide interfiber bonding enhancements in lignocellulosic furnishes

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ABSTRACT

Soy protein isolate (SPI) was extracted from soy flour and hydrolyzed with hydrochloric acid, sodium hydroxide, and enzyme, separately, to provide a series of hydrolysates. The SPI and its hydrolysis products were later cross-linked with ethylendiaminetetraacetic acid (EDTA) in the presence of sodium hypophosphite (SPH) after which they were complexed to chitosan as part of an on-going general chemical strategy in our laboratories to improve their incorporation into old corrugated container (OCC) matrix and thus increase inter-fiber bonding. Approximately 2% SPI-EDTA-chitosan and hydrolyzed SPI-EDTA-chitosan additives by mass (OCC-based slurry) were thoroughly mixed before generating a sheet for physical testing. The tensile and burst indices of the SPI-EDTA-chitosan additive-treated OCC pulp sheet increased 46.3% and 61.85%, respectively, while the inter fiber bonding of SPI-EDTA-chitosan additive-treated OCC pulp sheet increased 74.86% compared to the control, albeit having a decreased tear strength and roughness, with significantly increased gloss. The additive-treated pulp sheet was characterized by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and ATR to provide evidence for product synthesis.

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1. Introduction

Soy protein isolate is a long chain biopolymer consisting of 18 different polar and nonpolar amino acids. Polar amino acids such as cysteine, arginine, lysine, histidine and others can act as effective chemical pivots to crosslink the protein and improve the mechanical, thermal, and physical properties, while reducing water sensitivity and hydrophilicity [1]. Earlier research reported that isolated soy proteins may be cross linked with aldehydes such as formaldehyde, glutaraldehyde (GA), glyoxal, and glyceraldehyde through *Maillard* reactions [2]. Isolated soy proteins cross linked with GA yield biopolymers with enhanced mechanical properties [3]. Chemical modification of pulp fibers within the pulp & paper market is currently a common practice for improving printing quality, surface gloss, surface sizing, and calendaring. In addition, mechanical property improvements tend to be regulated by relatively costly chemical additives such as cationic starch or polyacrylamides. The low cost, commercial availability, and chemical derivatization power of soy protein flour (>50% protein), not surprisingly, is extremely attractive for the development of novel functional soy protein derivatives for paper strength improvements. Typically, starch is used for printing and writing grade papers for surface sizing, i.e., for improving paper surface resistance to uneven penetration and flow of inks/liquid media and acceptable printability [4]. The reclaimed paper market has been mostly focused on attaining improved mechanical strength properties.

Within the reclaimed paper market, the utilization rate of waste old corrugated containers (OCC) (recycled containerboards) in 1963 was 21.1% in the US, while in 2001 it increased to 67% with a recovery rate of nearly 70% [5]. Recently, the American Forest & Paper Association (AF&PA) released a 2011 recovery rate for OCC with a new high of 91.2 percent. Therefore, research in this area is necessary to improve the strength of OCC because waste fibers are typically mechanically inferior to their virgin equivalents. Early work identified several chemical treatments that yielded improvements in the bonding strength of recycled sheets [6,7]. Further innovative studies have shown that fiber surface chemical

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derivatization can prevent strength losses [8,9]. The paper industry is currently using commercial dry strength agents such as cationic starch, polyacrylamide, and glyoxylate polyacrylamide to improve the strength of OCC, but the improvement is still very low relative to virgin pulp [10,11]. In addition, a number of these studies have been conducted with nonrenewable inorganic fillers and petroleum-based matrices for applications that include packaging, a high value sector of the pulp market. Increasing environmental concerns have led to new flexible barrier bio-based packaging materials and the potential uses of renewable resources to offset the use of the inorganic fillers and petroleum-based materials [12].

The present study focuses on the application of an isolated soy protein derivative for improving the mechanical properties of OCC. It will focus on the characterization of the soy protein derivatives and explore their applicability to OCC.

2. Experimental

2.1. Materials

Soy flour was provided by Archer Daniel Midland (ADM, Decatur, IL). The OCC pulp was furnished by Azko Nobel Pulp and Performance Chemicals, Marietta, GA. Commercial dry strength agents such as Glyoxylate-PAM and cationic starch were supplied by Azko Nobel Chemicals, Marietta, GA and Cargill Incorporated, Minneapolis, MN, respectively. Cross linking agents such as ethylenediaminetetraacetic acid (EDTA) and chitosan (Ch) were purchased from Sigma–Aldrich and used as received. Chemicals of reagent grade utilized were sodium hypophosphite, (SHP) CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2, *Alcalase* product No. 126741, and denatured alcohol and acetic acid from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water as the medium.

2.1. Extraction of the soy protein isolate

Soy flour was carefully added into acidified water so that solution pH was within the isoelectric range of the soy protein (pH 4.0–4.8) and that only the soluble fraction of the soy flour dissolved. The resulting mixture was centrifuged to separate the protein-rich precipitate from the supernatant to give a high quality concentrate soy protein [13].

2.2. Hydrolysis of the soy protein isolate

For hydrolysis of soy protein isolate, three different routes were followed: acid, alkali, and enzymatic treatments. Approximately 1 g of soy protein isolate was added into 50 ml of 1 N HCl or NaOH solution and heated at 70 °C for 3 h. The suspension was centrifuged at 5300 rpm for 15 min. to concentrate the hydrolyzed soy protein isolate and remove the excess aqueous acid or alkali. The resultant precipitate was rinsed and re-centrifuged until constant neutral pH [14]. The enzymatic hydrolysis was carried out with Alcalase as follows: soy protein isolate was dissolved in water at 50 °C for 10 min. When the protein solution temperature reached 50 °C, the Alcalase (2.4U/g) was added. The soy protein isolate and enzyme ratio was 1:0.002. pH of solution was maintained at 7 by adding 1 N NaOH during the first 15 min. of reaction, while at the end of reaction, pH was adjusted to 4.5 using 1 N HCl. The mixture was cooled, adjusted to pH 7.0, and heated at 95 °C for 15 min. to inactivate the enzyme. The enzymatic hydrolyzed soy protein isolate was centrifuged, rinsed, and re-centrifuged until constant neutral pH [15]. The mixture was freeze-dried and stored.

2.3. Chemical modifications of soy protein isolate (SPI) and hydrolyzed soy protein isolate

Into 15 mL of 1 N sodium hydroxide solution in a 50 ml Petri Dish, 5 g of EDTA and 1 g of SHP were dissolved. Soy protein isolate or hydrolyzed soy protein isolate (5 g) was added to the solution and manually mixed with a glass rod. The mixture was placed in an oven at 130 °C for 3 h. Reaction products were washed with water and filtered several times to remove unreacted materials. The product obtained was a modified soy protein isolate that was air dried at 50 °C in an oven overnight [16]. The proposed reaction scheme is shown in Fig. 1.

2.4. Polyelectrolyte complexation

Chitosan (Ch, 1 g) was dissolved into 50 ml of 1.5% acetic acid solution. Modified soy protein isolate (1 g) was dissolved with 50 ml water and added to a 50 ml chitosan solution in a 250 ml round bottom flask. The reaction mixture was stirred at 70 °C for 90 min [17]. The proposed reaction scheme is shown in Fig. 2.

2.5. Preparation of OCC pulp sheet

The sheet was prepared according to TAPPI Standard Method T 205 using a 600 ml pulp slurry (1.8 g oven dried OCC pulp) in a sheet molder machine. The pulp slurry was diluted with 10 L of DI water in a sheet molder to produce a uniform sheet. The sheet was conditioned and cured at 105 °C for 1.0 h [17].

3. Testing methods

3.1. Determination of carboxyl content

A known amount of soy protein isolate derivative was dissolved in 0.1 N NaOH and hydrolyzed for one hour. The excess amount of NaOH was determined by titration with 0.1 N HCl using phenolphthalein as an indicator [18] while the carboxyl content in milliequivalents (meq.) per 100 g was calculated as follows:

$$\text{Carboxyl Content } (meq) = \frac{(V_2 - V_1) \times N \times 10}{W} \quad (1)$$

N = Normality of HCl
V_2 = Volume of HCl without sample
V_1 = Volume of HCl with sample
W = Weight of Sample.

3.2. Gloss testing

The gloss of OCC pulp hand sheet was tested with a GLOSSMETER according to TAPPI T 480 test method.

3.3. Roughness testing

The roughness of OCC pulp hand sheet was tested with an L & W roughness tester according to TAPPI T 538 test method.

3.4. Tensile strength

The tensile of OCC pulp hand sheet strength was tested with an ALWETRON TH1 tester according to TAPPI T 220 test method.

3.5. Burst strength

The burst strength of OCC pulp hand sheet was tested with a MULLEN tester according to TAPPI T810 test method.

3.6. Tear strength

The tear strength of OCC pulp hand sheet was tested with an L & W tester according to ASTM D 689 test method.

3.7. Inter fiber bonding strength

The inter-fiber 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.

3.8. ATR analyses

IR Spectra of all modified soy flour samples were recorded on a Perkin Elmer ATR spectrophotometer [19].

3.9. Thermal gravimetric analyses (TGA)

The TGA used in this study was a TGA Q500 (TA Inc., New Castle, DE) under a nitrogen atmosphere. The temperature range and heating ramp were 30–600 °C and 5 °C/min, followed by isothermal heating at 600 °C [20].

3.10. Measurement of storage modulus

Dynamic mechanical analysis was performed using a DMA Model 2980 (TA Inc., New Castle, DE) 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 200 °C using a temperature ramp of 3 °C/min (20 μm amplitude, at 1 Hz) [21].

4. Results and discussion

4.1. Characterization of soy protein isolate derivatives

Soy protein isolate possesses a highly chemically rich surface covered with amine groups that allow for facile surface decoration using appropriate reactive species. The reaction pathways that were chosen for surface functionalization are shown in Figs. 1 and 2. The carboxyl content of the soy protein isolate increased from 210 meq./100 g in the control to 430 meq./100 g in the test sample as a result of surface functionalization.

4.1.1. ATR analysis

The ATR spectra of the soy protein isolate and soy protein isolate-EDTA are shown in Fig. 3. The spectrum of soy protein isolate shows a prominent peak at 1635 cm^{-1} which can be ascribed to the amide linkage of the soy protein isolate, although the carbonyl region does not clearly show a carbonyl stretch. However, when the soy protein isolate was reacted with EDTA, a peak appeared at approximately 1740 cm^{-1} that is attributable to the carbonyl group. The appearance of the peak provided compelling evidence that EDTA is cross linked to the soy protein isolate [18].

4.1.2. Thermal behavior

The thermogravimetric behavior of the soy protein isolate derivatives was evaluated over a 5 °C/minute heating ramp under nitrogen and shown in Fig. 4. The weight loss below and near 100 °C was attributed to water evaporation [20]. However, the weight loss above 100 °C was due to thermal decomposition of the soy protein isolate derivatives [22]. EDTA had a single sharp decomposition peak at 228.6 °C, whereas the soy protein isolate showed a single weight loss peak at 301.15 °C; however, all derivatives of soy protein isolate show a decrease in their respective maxima for degradation temperature and weight loss, and also significantly higher residual mass after heating to 600 °C. This may be explained by the fact that the soy protein isolate surface-modifying agents on the surface of the soy protein isolate have a lower decomposition temperature and are attached via relatively labile ester bonds that also have a lower temperature of degradation [18].

4.2. Application of soy protein isolate-EDTA-chitosan derivatives for OCC strength improvement

Mechanical resistance is one of the most important properties of generic paper substrates. These substrates need to display sufficient resistance in packaging, wrapping, or sealing. In general, such gross resistance can be attributed at the molecular level to a network of hydrogen bonds. Also, it depends on the quantity and area of the overall bonding sites. In recycling, fibers are irreversibly damaged, a fact which affects their final paper resistance properties. Fig. 5 shows the tensile index of OCC recycled pulp hand sheet that results after the addition of either virgin (non-recycled) pulp or dry strength agents.

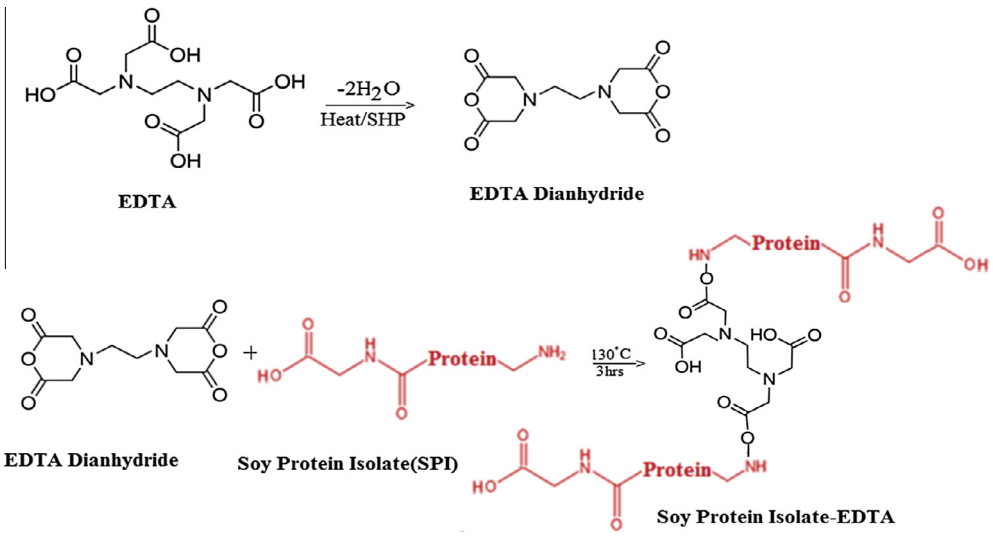

Fig. 1. Esterification reaction of soy protein isolate with EDTA.

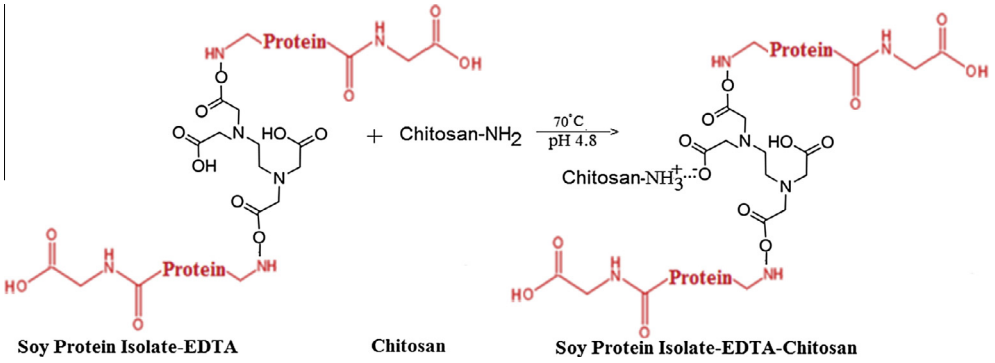

Fig. 2. Polyelectrolyte complexation of soy protein isolate-EDTA with chitosan.

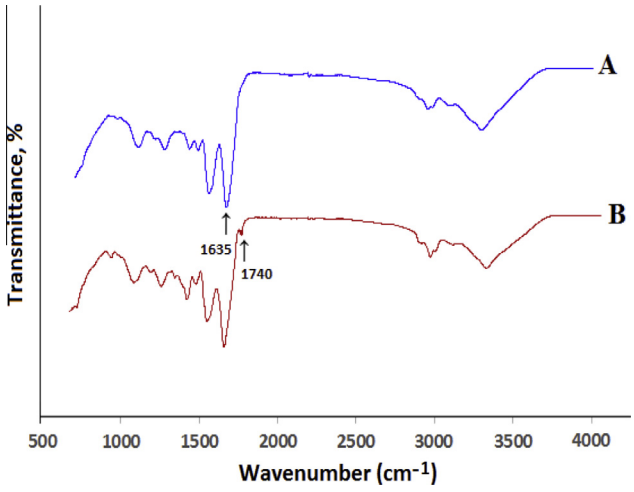

Fig. 3. Shown are ATR spectra of soy protein isolate (A) and soy protein isolate-EDTA (B). The 1740 cm^{-1} band can be attributed to the ester carbonyl stretch, whereas the 1635 cm^{-1} band is representative of the carbonyl groups in an amide bond of the soy protein isolate.

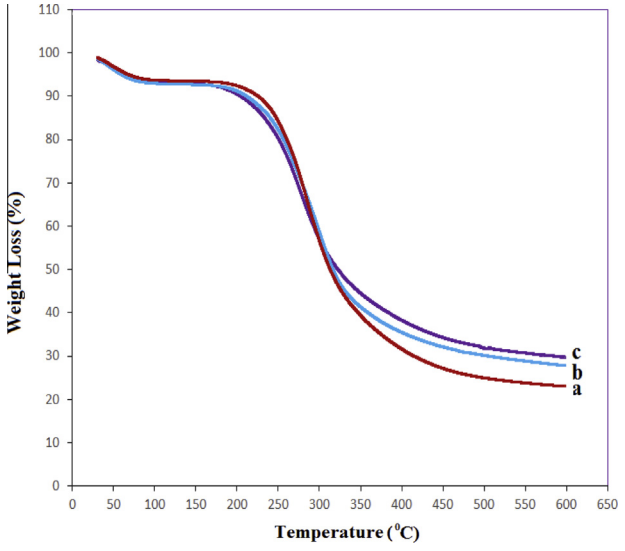

Fig. 4. Thermogravimetric analyses of soy protein isolate (a), soy protein isolate-EDTA (b), and soy protein isolate-EDTA-chitosan (c).

Virgin pulp has in theory a much higher mechanical resistance because the fibers have not been reclaimed. The control for these studies was the base OCC recycled pulp (CSF = 400, a measure of the adsorption of water, i.e., higher value, less adsorption). Earlier research reported that the range of tensile index (Nm/g) for OCC pulp sheet is 20–35 [23]. Defibrillated or non-defibrillated virgin softwood kraft pulp (revolutions = 5000, CSF = 530) was blended with OCC recycle pulp (50:50) to increase strength properties. In addition, 2% SPI derivatives (based on the mass of dried pulp) were mixed with a separate batch of OCC pulp slurry. The non-defibrillated virgin pulp sample demonstrated a decreased tensile index, but the defibrillated virgin pulp blend sample had a significantly increased tensile index compared to the control sample (Fig. 5). This may happen due to a significant decrease in the fiber size and an increase in the bonded area at the high revolutions (defibrillations). The SPI and hydrolyzed SPI did not affect the tensile index of the OCC pulp hand sheet (Fig. 5).

The tensile indices observed in Fig. 5 from the application of 2% SPI derivatives-treated OCC pulp are shown as follows where "(%)" is the percentage that the system is superior to the tensile index of the control (non-treated) sample: SPI-Ch (30.4), SPI-EDTA-Ch (46.3); acid hydrolyzed: SPI-Ch (29.2), SPI-EDTA-Ch (43.0); alkali hydrolyzed: SPI-Ch (27.5), SPI-EDTA-Ch (38.4), and enzymatic hydrolyzed: SPI-Ch (15.9), SPI-EDTA-Ch (27.2). The results were significantly higher than what has been found for commercial dry strength additives such as glyoxylate polyacrylamide, cationic starch, and soy flour. This may be because of the extremely high level of carboxylic acid and amine groups in soy protein isolate derivatives that give rise to stronger interactions with OCC pulp when the sheet is generated with soy protein isolate derivatives [24,25].

In contrast, the tensile indices of 2% SPI-EDTA-Ch, acid hydrolyzed SPI-EDTA-Ch and alkali hydrolyzed SPI-EDTA-Ch derivatives-treated OCC pulp samples were also better than defibrillated virgin pulp blends (Fig. 5). Similarly, the bursting strength %-age gains of the SPI derivatives-treated OCC pulp sample systems were "(%)" higher than the control: SPI-Ch (44.3), SPI-EDTA-Ch (61.8); acid hydrolyzed: SPI-Ch (60.7), SPI-EDTA-Ch (64.6); alkali hydrolyzed: SPI-Ch (40.8), SPI-EDTA-Ch (57.4), and enzymatic hydrolyzed: SPI-Ch (53.9), SPI-EDTA-Ch (65.5), while all the cases provided better results compared to the commercial dry strength additive (Fig. 6).

It is also observed from Fig. 7 that the tear strength of all soy protein isolate and soy protein isolate derivatives-treated OCC pulp samples were lower than the control sample, but higher than the glyoxylate polyacrylamide-treated sample.

The *t*-Test of paired samples (for the mean of the tensile index) was measured to confirm the significance of the improvements in tensile index of the additive treated pulp hand sheets. In each of the cases, an untreated sheet was compared to a sheet formed from the treated fibers. The *t* values for the OCC pulp sheet (control) and SPI-EDTA-Ch, acid hydrolyzed SPI-EDTA-Ch, alkali hydrolyzed SPI-EDTA-Ch, and enzymatic hydrolyzed SPI-EDTA-Ch-treated OCC

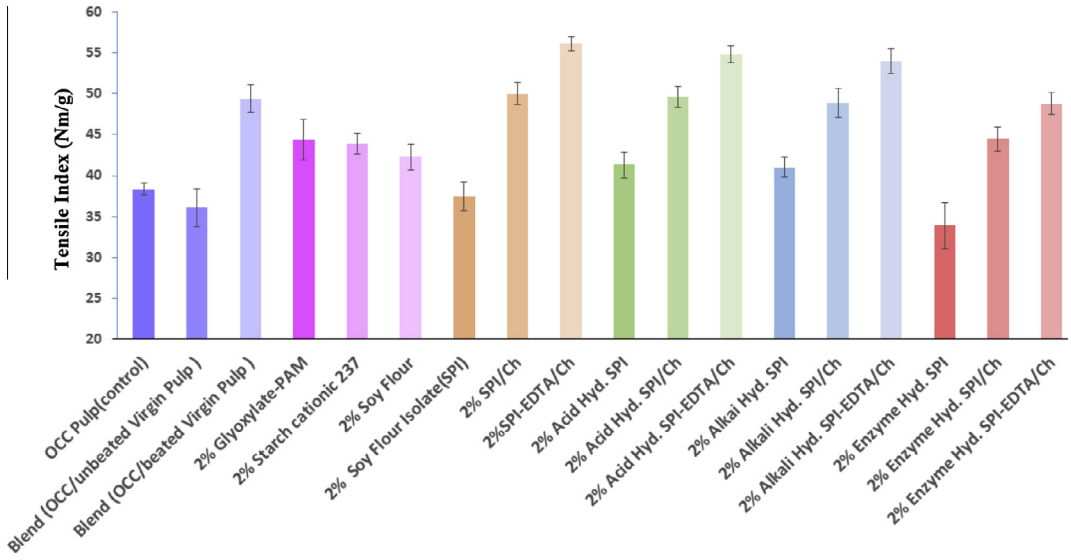

Fig. 5. Tensile strength of soy protein isolate derivative-treated OCC recycle pulp hand sheets.

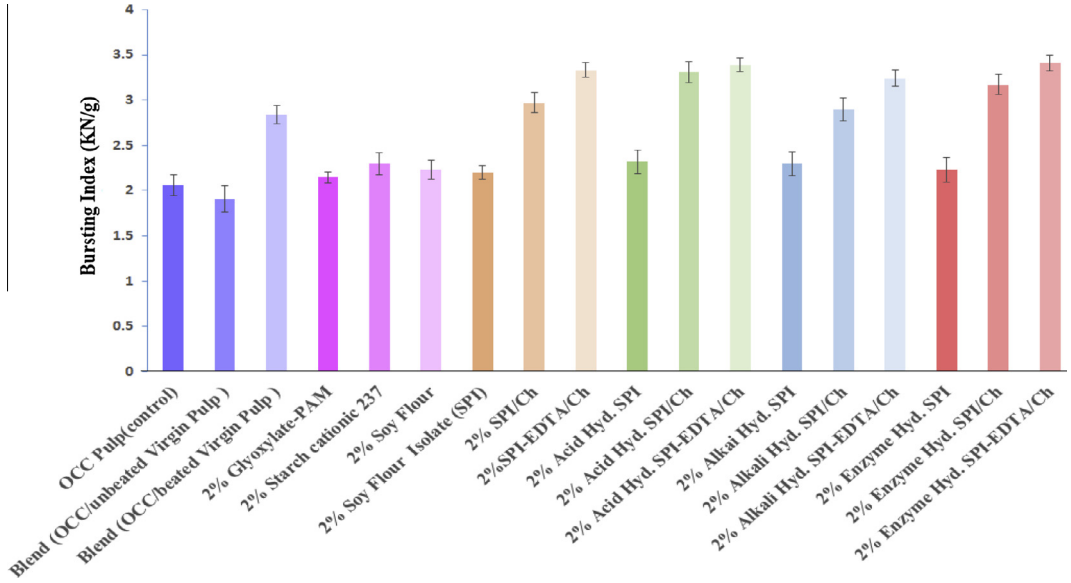

Fig. 6. Bursting strength of soy protein isolate derivative-treated OCC recycle pulp hand sheets.

pulp sheets were significantly negatively lower than the negative *t* table distribution value. The *p* value of OCC pulp sheet (control) and SPI-EDTA-Ch, acid hydrolyzed SPI-EDTA-Ch, alkali hydrolyzed SPI-EDTA-Ch, and enzymatic hydrolyzed SPI-EDTA-Ch-treated OCC pulp sheets were much lower than the α value 0.05 ($p < 0.05$). Therefore, there was significant difference in tensile indices between the control and soy protein isolate derivatives-treated pulp sheet samples. In addition, SPI-EDTA-Ch-treated pulp sheet had significantly increased gloss, but decreased roughness. This may happen due to increased density of SPI-EDTA-Ch-treated pulp sheet compared to control sample [26].

4.3. Bond formation with OCC recycle pulp

The basic groups ($-NH_2$) on every ring in soy protein isolate-EDTA-chitosan derivatives develop positive charges when they are in a sufficiently acidic medium and can form ionic or covalent bonds with negatively charged cellulosics in paper fibers during paper making [27]. In addition, the EDTA in soy protein isolate-EDTA-chitosan derivatives contains a number of free carboxyl groups (protonated in acidic medium) that can engage in hydrogen bonds with the fiber surface of pulp and increase the relative bonded area between fibers. The combined interactive effects attributable to the carboxylic acid and amine groups for increasing bonding between fibers during sheet formation also contributed to an increase in tensile strength [28].

The inter-fiber bonding strength of soy protein isolate-EDTA-chitosan additive-treated OCC pulp hand sheets increased approximately 74.86% compare to a control OCC pulp hand sheet. It is likely partially attributable to condensation reactions mediated by the high temperature (105 °C) that causes two carboxylic acid groups in EDTA to form an anhydride. Anhydrides can subsequently lead to other chemical reactions (e.g., esterification) with the enriched surface hydroxyl groups of OCC pulp and can contribute to inter-fiber bonding strength [29]. In addition, a 1.35% higher residual char value was observed in the soy protein

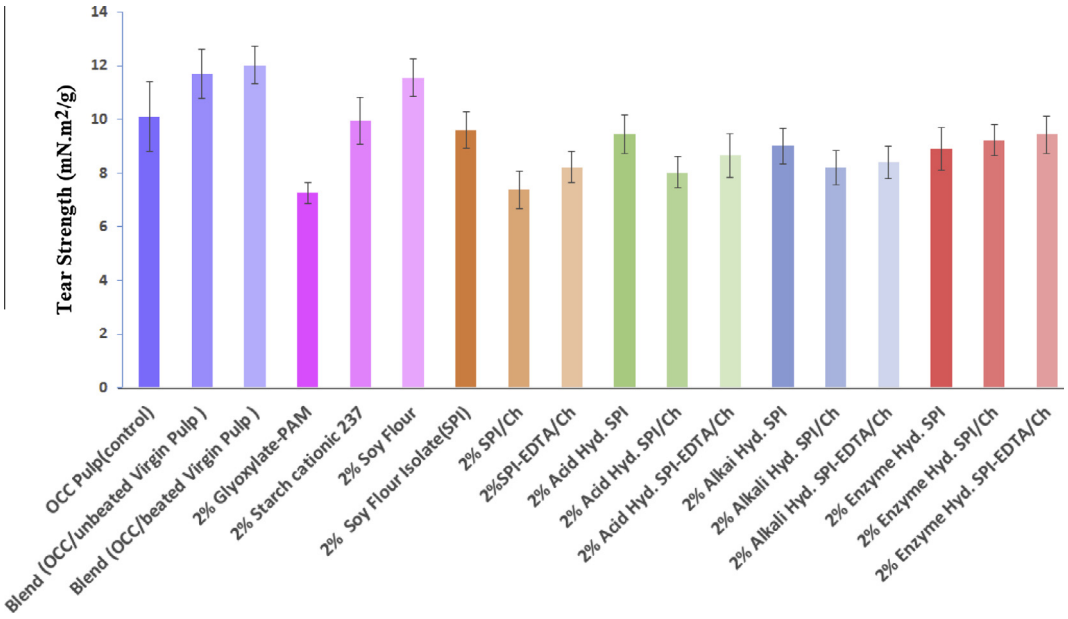

Fig. 7. Tear strength of soy protein isolate derivative-treated OCC recycle pulp hand sheets.

isolate-EDTA-chitosan-treated OCC pulp sheet compared to the control (OCC pulp sheet) after heating at 600 °C (Fig. 8). This higher residual char points to the likelihood that soy protein isolate-EDTA-chitosan is cross linked to the OCC pulp fibers.

The storage modulus and loss modulus both decrease with increased temperature as shown in Fig. 9. It was observed that the storage modulus of the soy protein isolate-EDTA-chitosan-treated OCC pulp sheet was 25–27.3% higher when the temperature range was between 35 and 197 °C. The higher storage modulus is likely a result from the additive treated OCC pulp sheet being more flexible due to cross linking with the soy protein isolate-EDTA-chitosan additive [16]. However, the loss modulus for the OCC pulp hand sheet over the same temperature range decreased approximately 10%, while for the soy flour isolate-EDTA-chitosan additive-treated OCC pulp sheet, it decreased roughly 14%.

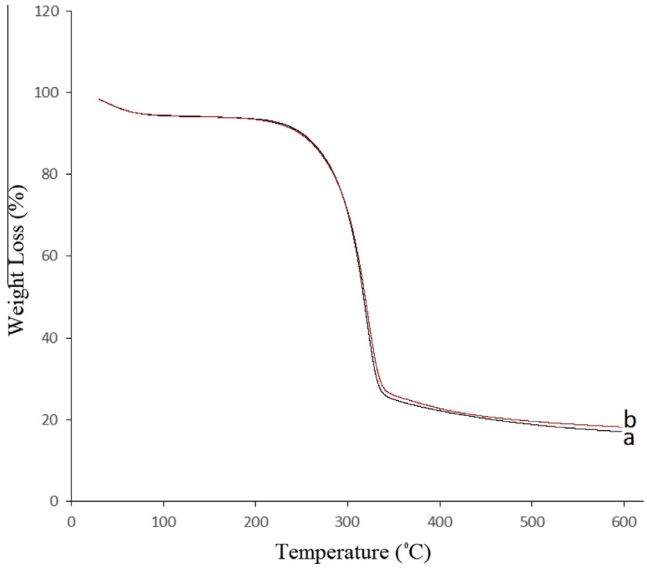

Fig. 8. Thermogravimetric analyses of OCC pulp sheet and soy protein isolate-EDTA-chitosan additive-treated OCC pulp sheets.

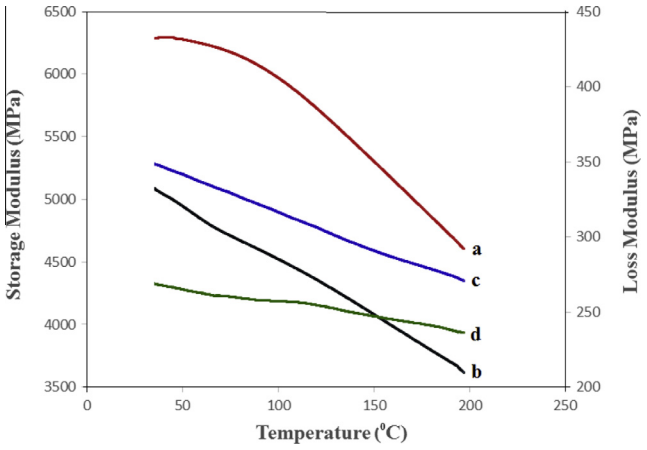

Fig. 9. DMA of a = Storage modulus of SF-EDTA-chitosan treated-OCC pulp hand sheet, b = Storage modulus of OCC pulp hand sheet, c = Loss modulus of SF-EDTA-chitosan treated-OCC pulp hand sheet, and d = Loss modulus of OCC pulp hand sheet.

5. Conclusions

Soy protein isolate (SPI) from soy flour and its hydrolysates from separate treatments of acid, alkali, and enzyme were studied for their effect on OCC pulp sheet dry strength. Soy protein and hydrolyzed soy protein isolates were modified with EDTA in the presence of sodium hypophosphite (SHP) to increase their ability to better bond recycled fibers during paper formation. It was found that the carboxyl group content of modified soy protein isolate significantly increased relative to the unmodified soy protein isolate, a driving hypothesis for the observed strength gains. The EDTA coupled soy protein isolate and hydrolyzed EDTA coupled soy protein isolate were later cross linked with chitosan (Ch). Approximately 2% of soy protein isolate-EDTA-chitosan and their derivatives (acid hydrolyzed SPI-EDTA-Ch, alkali hydrolyzed SPI-EDTA-Ch, and enzymatic hydrolyzed SPI-EDTA-Ch) were blended with OCC recycle pulp separately before making samples. The tensile and burst strengths increased 46.3%, 43.02%, 38.35%, and 27.2%, and 61.85%, 64.56%, 57.42%, and 65.5%, respectively, compared to

the control samples. These results were also significantly higher than what was typically found for commercial dry strength agents and blended OCC pulps. The *t*-test of paired samples (for the mean of tensile index) confirmed the significance of the improvements in tensile index of the additive treated pulp hand sheets. The inter-fiber bonding strength of a soy protein isolate-EDTA-chitosan additive-treated OCC pulp hand sheet increased approximately 74.86% relative to a control OCC pulp hand sheet. It displayed significantly increased gloss (100%), but decreased roughness (70%) and tear strength.

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References

[1] T.G. Dastidara, A.N. Netravali, Green Chem 15 (2013) 3243.
[2] K.S. Park, H.D. Base, J Am Oil Chem Soc 11 (2000) 879–883.
[3] S. Chabba, F.G. Matthews, A.N. Netravali, Green Chem 7 (2005) 576–581.
[4] M.T.M. Isabel, F.J.T. Paulo, F.L. Margarida, BioRes 6 (2011) 4259–4270.
[5] Anon. Mill Trade J. Recycling Markets, vol. 34, 1996. P. 3.
[6] J.E. Stone, A.M. Scallan, A.M. British Paper and Board Makers Assoc., 1966. p. 145.
[7] H.J. Klungness, F.D. Caufield, Tappi J 65 (1982) 94–97.
[8] E. Gruber, J. Weigert, Papier 52 (1998) 20–26.
[9] V.J. Laivins, M.A. Scallan, Pulp Paper Sci 22 (1996) 178.
[10] M. Nemati, N. Seyyedmohammadi, A. Samariha, J Basic Appl Sci Res 1 (2011) 2314–2318.
[11] R.C. Howard, C.J. Jowsay, Pulp Paper Sci 15 (1989) 225.
[12] D.L. Corre, J. Bras, A. Dufresne, Biomacromolecules 11 (2010) 1139–1153.
[13] US patents no. 4704289A. Acidified water. 10, 1984.
[14] L.R. Hill, Biochem Eng J 39 (2008) 221–229.
[15] Z.X. Kong, M.M. Guo, D. Cao, C.M. Zhang, Biores Technol 99 (2008) 8873–8879.
[16] A. Salam, J.J. Pawlak, A.R. Venditti, K. El-Tahlawy, Biomacromolecules 11 (2010) 1453–1459.
[17] A. Salam, L.A. Lucia, H. Jameel, ACS Sustainable Chem Eng 1 (2013) 1584–1592.
[18] A. Salam, J.J. Pawlak, A.R. Venditti, K. El-Tahlawy, Cellulose 18 (2011) 1033–1041.
[19] C. Demitri, R.D. Sole, F. Scalera, A. Sannino, G. Vasapollo, A. Maffezzoli, L. Ambrosio, L. Nicolais, J Appl Polym Sci 110 (2008) 2453–2460.
[20] P. Bernabé, C. Peniche, W. Argüelles-Monal, Polym Bull 55 (2005) 367–375.
[21] L.C. Walker, Thermochim Acta 367 (2001) 407–414.
[22] X. Liu, L. Yu, H. Liu, L. Chen, L. Li, Polym Degrad Stability 93 (2008) 260–262.
[23] M.E. Eugenio, R. Martin-Sampedro, E. Revilla, J.C. Villar, Forest Syst 21 (2012) 460–467.
[24] M. Mitikka-Eklund, M. Halttunen, M. Melander, K. Ruuttunen, T. Vuorinen, Yokohama (1999) 432–439.
[25] C. Fors, Department of pulp and paper chemistry and technology, Royal Institute of Technology, Stockholm, Sweden, 2000, p. 78.
[26] Z. Koran, Tappi J. 77 (1993) 167–170.
[27] M. Mucha, D. Miskiewicz, J Appl Polym Sci 77 (2000) 3210.
[28] E. Duker, T. Lindstrom, Nord Pulp Pap Res J 23 (2008) 57–64.
[29] D. Alonso, M. Gimeno, R. Olayo, H. Vazquez-Torres, J.D. Sepúlveda-Sánchez, K. Shirai, Carbohyd Polym 77 (2009) 536–543.