Environmentally friendly wet-end paper reinforcement agents

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Abstract

Hot-water extraction of hardwoods within the biorefinery permits a higher rate of delignification during kraft pulping. Pulps from hot-water extracted woodchips can have the same kappa number produced at lower H-factors with the use of lesser amount of chemicals compared to conventional pulps from unextracted woodchips. Biorefinery kraft pulp offers a relatively higher sheet bulk compared to conventional kraft pulp which contributes to better opacity and absorption properties in paper. However, due to lower hemicelluloses content of the pulp, inter-fiber bonding is reduced and hence the strength-to-weight ratio of paper produced from biorefinery pulp needs to be improved to be competitive with conventional pulps. In the present study, we report the results of reinforcement of paper made from biorefinery kraft pulp with the two most widely used biopolymers; polylactic acid and cationic starch.

Introduction

The demand for alternative and sustainable sources of fuel, chemicals, and energy has increased geratly in recent years due to the high price of fossil resources, government policies to reduce dependence on foreign oil and to promote alternatives, and efforts to reduce greenhouse gas emissions. Significant efforts have been made to evaluate the use of renewable feedstocks including lignocellulosics for the production of fuels, solvents, chemicals, and plastics, and to develop biorefineries. A biorefinery based on hardwoods, such as northern hardwoods and plantation-grown willow biomass has been developed recently (Amidon et al. 2008). In this biorefinery, the first step is hot-water extraction (HWE) performed at temperatures up to 165 ºC and aimed at dissolving the relatively easily accessible hardwood hemicelluloses, mainly xylans, while avoiding further degradation of the resulting mixture of soluble monosaccharides and oligosaccharides. The two streams produced in HWE, hot-water extract and hot-water-extracted wood, are processed to produce a rich palette of products.

In the utilization of hot-water extract, research efforts have focused primarily on enabling the fermentation of monosaccharides resulting from hydrolysis of hot-water extract for the production of biofuels and bioplastics. Fermentation using the xylose-fermenting microbes has been suggested to produce ethanol. Hydrolyzed hot-water extracts may also be fermented to produce polyhydroxyalkanoates (PHA) or lactic acid and subsequently polylactic acid (PLA) Several value-added products from hot-water extract may be produced including, acetic acid, methanol, formic acid, furfural, and hydroxymethyl furfural; separated from the fermentable sugars by membrane separation of hot-water extract (Amidon et al. 2008).

In the utilization of extracted wood different products have been envisioned and produced, including pellets, reconstituted wood products, and pulps. In chemical pulp production an increase in delignification rate during kraft pulping has been observed (Amidon et al. 2008, Hasan et al. 2010). This is an important advantage of HWE, which leads to shorter reaction times and/or the use of fewer chemicals. The relative ease of kraft pulping may be attributed to several physico-chemical modifications of wood occurring during HWE including, an increase in porosity, an increase in content of free phenolic hydroxyl groups, a decrease in content of acetyl groups, and cleavage of lignin-carbohydrate bonds. In contrast to these positive effects, removal of hemicelluloses/xylans results in a biorefinery kraft pulp that is more difficult to refine and forms a weaker paper than kraft pulp from unextracted wood. To avoid this strength reduction in our recent study, we treated the surface of the biorefinery paper with PLA. The results have indicated that after reinforcement with 2% PLA based on OD fibers paper made from biorefinery (un)bleached sugar maple kraft pulp could be equivalent to or greater in strength than paper made from conventional (un)bleached sugar maple kraft pulp, while retaining its higher bulk. It has been proposed that the reinforcing effect of PLA depends on the chemical composition of fibers; PLA is more efficient in reinforcing biorefinery kraft pulps and unbleached pulps probably due to a higher attraction between relatively hydrophobic PLA and hemicellulose-depleted and lignin-containing fibers (Hasan et al. 2010). In addition, this conclusion implied that if PLA were successfully combined with an agent for stabilization in water dispersion it PLA might increase paper strength as an additive in the wet-end of the papermachine. This would avoid an additional operation, the more complicated and costly surface treatment tested in the reported study. Our first attempt in solubilizing PLA in the thin stock we used a common paper dry strength agent, cationic starch. Starch was selected as an environmentally friendly and

biorenewable polymer in line of efforts to reduce use of petrochemical-derived polymers in general in the paper industry. In this paper, we report the results of paper reinforcement obtained using two types of cationic starch (amylopectin-based starch; starch A and starch B) of different nitrogen content (starch B was of higher nitrogen content) to stabilize PLA in pulp stock. For comparative purposes, starch A and B were also used without PLA addition to measure the reinforcement effect of starch on paper made from biorefinery sugar maple kraft pulp. Based on the previously observed potential of PLA to improve wet tensile strength, we also expected and tested for an increase in wet tensile strength of paper reinforced with a cationic starch-PLA blend relative to paper reinforced with cationic starch only.

Materials and Methods

Sugar maple (*Acer saccharum*) wood obtained from the SUNY-ESF Lafayette Road Experimental Station in Syracuse, NY. Wood was chipped on a Carthage chipper and screening was performed using a Williams Classifier with 3/8 ", 5/8 ", and 7/8 " accepts. Screened chips were stored at ~8 °C.

HWE: Woodchips were extracted using aqueous media (160 °C; time to temperature 45 minutes) for two hours at water-to-wood ratio of 4 to 1 in an MK digester (500 g OD wood, oven-dry basis). The yield of extracted wood chips was 77% of OD wood.

Kraft pulping: Unextracted and hot-water-extracted extracted woodchips were pulped in an MK digester with 500 g OD wood at 165°C (time to temperature 60 minutes). The active alkali charge was maintained at 16% on OD wood, sulfidity was 25%, and the ratio of cooking liquor to wood was 4 to 1. Time at the cooking temperature was varied to produce pulps of different kappa numbers. The kappa number of the resulting pulps (conventional pulp, CP from unextracted woodchips and biorefinery pulp, BP from hot-water-extracted woood chips) was determined in accordance with the TAPPI method T236 om-06: Kappa number of pulp.

For refining and PLA reinforcement experiments two pulps were selected: unbleached pulps of similar high kappa number (CP, kappa number 45.5; BP, kappa number 42.5).

Refining/freeness: Freeness of the selected pulps was measured following the TAPPI freeness method: T227 om-4: Freeness of pulp (Canadian standard method), after refining the pulps in a PFI mill at 5,000 revolutions according to T248 sp-08: Laboratory beating of pulp (PFI mill method).

PLA treatment: PLA used in this study was poly(dl-lactic acid) with a molecular weight MW~20,000-30,000 (Polysciences, Inc.: Cat. #16585) dissolved in acetone.

Starch application: Sta-lok 156 (SA) and Sta-lok 190 (SB) with nitrogen content of 0.3% and 0.43% respectively, that were used in this study were obtained from Tate and Lyle inc's Sta-lok line of products.

Starch was first slurried by mixing dry powder with water and cooked at 0.3% solids at 95-97^{0}C temperature for an hour under constant stirring. It formed a clear aqueous starch paste ready to be applied in stock. Starch-only reinforced paper test sheets from BP were made with 1% starch based on OD fibers.

PLA-Starch mix: Since PLA is not soluble in water, PLA in acetone was mixed with the aqueous starch paste and together they formed a clear stable solution.

The starch or the PLA-starch mix was added in pulp slurry as needed, under constant agitation. The total amount of PLA and starch in pulp slurry ranged from 0.6% to 1.4% based on the OD fibers and different ratios of PLA-to-starch amounts were used. Handsheets from that furnish were made immediately.

Test sheet preparation and properties: Paper test sheets were made using the TAPPI method: T 205 sp-06: Forming handsheets for physical tests of pulp. The grammage, thickness, and density were determined for the handsheets with or without additives according to T220 sp-06: Physical testing of pulp handsheets. A tensile test was performed following T220 sp-06: (using constant rate of elongation apparatus used for Tensile breaking properties of paper and paperboard as in T 494 om-06). The wet tensile strength was measured by immersing the paper in water for 15 seconds and conducting tensile test as described above. For tear strength the T 414 om-04: Internal tearing resistance of paper (Elmendorf-type method) method was used.

Microscopy: The SEM images of the control and PLA sprayed sheets were observed on a JEOL 5800 scanning electron microscope at a magnification of 2500X. The specimens were sputter coated with 15 nm of Au-Pd prior to observation.

Results and Discussion

Selected properties of paper test sheets made from conventional sugar maple kraft pulp (CP) and biorefinery sugar maple kraft pulp (BP) of similar kappa number are presented in Table I.

The table clearly indicates that paper made from BP is bulkier (17% higher bulk of BP compared to CP paper) and able to retain more original dry strength upon wetting (wet tensile strength ~6% of dry tensile strength for BP *vs*. 3.5% for CP). However, paper made from BP must be reinforced to compete in mechanical properties with paper made from CP (more than two times lower tensile strength and more than three times lower tear strength of BP compared to CP paper). Potential for reinforcement of BP paper test sheets by surface treatment with PLA at 2% based on OD fibers has been examined in our previous study (Hasan et al. 2010a). Promising results were obtained especially in the improvement of wet strength. The results of examination of the PLA role in paper reinforcement by SEM are shown in figures 1 and 2, which present SEM micrographs of BP paper and PLA-surface-treated BP paper (BP and BPPLA2, respectively).

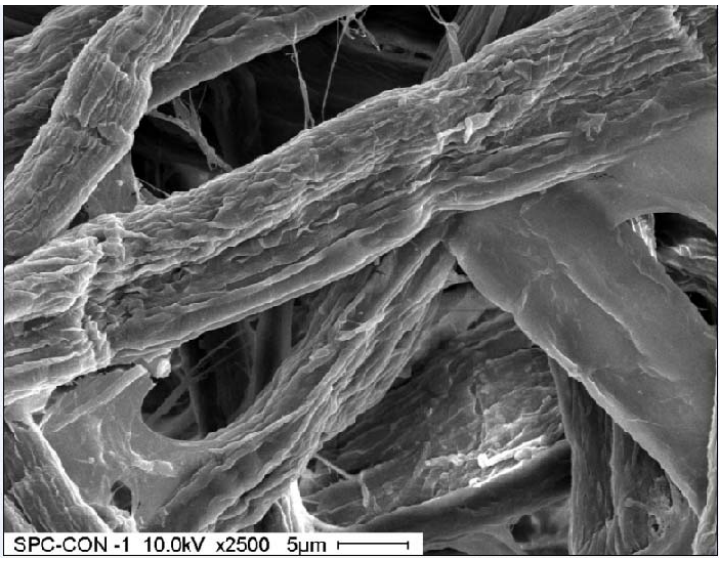

Figure 1: SEM micrograph of paper made from biorefinery pulp (BP)

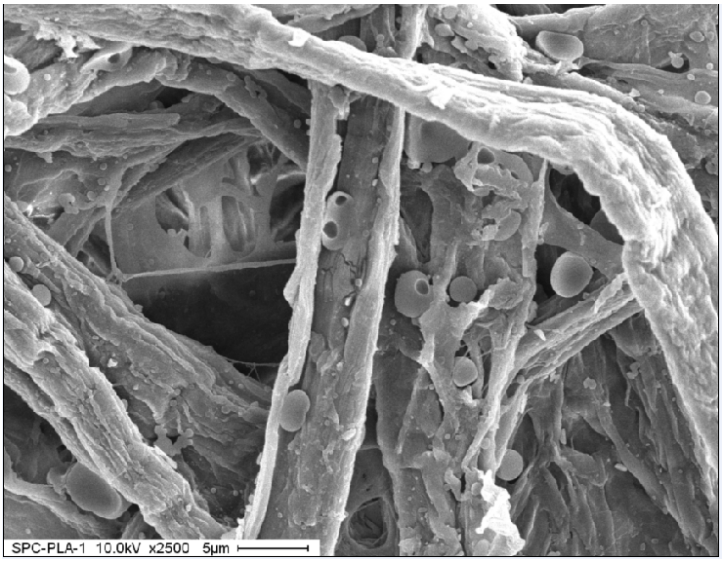

Figure 2: SEM micrograph of paper made from biorefinery pulp and treated in the surface with PLA (2% based on OD fibers) (BPPLA2)

PLA was observed dispersed in the fiber network and on the surface of fibers of BPPLA2 in form of globules. These results suggested that a more even distribution of PLA in the fiber network and/or better coating of fibers would probably contribute to a better reinforcing effect. In order for PLA to be added in wet-end as a way to obtain a more uniform distribution, PLA must be stabilized in the water suspension. In the subsequent experiments, two types of cationic starch, A and B were used to stabilize PLA in water dispersion. In these experiments, BP-based paper test sheets reinforced with a PLA-starch blend were proposed. Even though commonly used as a paper dry strength agent, being hydrophilic, regular cationic starch cannot improve wet strength of paper and may interfere with the resistance of paper to water. Blending cationic starch with hydrophobic PLA might be considered as a way to improve both wet and dry strength, as our preliminary results suggest (Hasan et al. 2010b). In the first series of PLA-starch blend experiments, the blend amount was maintained at 1% of OD fibers and two PLA-starch ratios of 0.5/0.5 and 0.9/0.1 were used. Four different BPPLASA(B) papers were made: BPPLA0.5SA0.5, BPPLA0.5SB0.5, BPPLA0.9SA0.1, and BPPLA0.9SB0.1. The results of these

experiments are shown in Table I. For comparative purposes, BP paper was reinforced using starch only (starch A and B added at 1% based on OD fibers (BPSA1 and BPSB1, respectively). The results of these reinforcement trials are also presented in Table I.

Table I: Selected properties of paper made from conventional pulp and biorefinery pulp before and after reinforcement with different agents

Paper	Reinforcement method			Bulk cm^3/g	Mechanical property			
	Surface	Wet-end						
	PLA % OD fiber	PLA % OD fiber	Starch % OD fiber		TI Nm/g	Stretch %	WTI Nm/g	Tear_I $mN/g/m^2$
CP	-	-	-	1.44	37.7	0.8	1.29	7.84
BP	-	-	-	1.74	17.0	0.8	1.00	2.50
BPPLA2	2	-	-	1.75	34.8	0.9	2.81	5.55
BPSA1	-	-	1	1.64	33.0	1.8	1.27	4.60
BPSB1	-	-	1	1.62	38.0	1.6	1.21	5.50
BPPLA0.5SA0.5	-	0.5	0.5	1.64	27.8	1.3	1.00	3.40
BPPLA0.5SB0.5	-	0.5	0.5	1.65	32.5	2.6	1.8	7.00
BPPLA0.9SA0.1	-	0.9	0.1	1.67	28.0	1.3	1.00	3.90
BPPLA0.9SB0.1	-	0.9	0.1	1.76	31.7	2.2	1.2	5.70

Paper test sheets made from biorefinery kraft pulp and reinforced with PLA in paper surface treatment (BPPLA2) or wet-end starch (BPSA1, BPSB1) were of similar tensile strength comparable to tensile strength of test paper made from conventional kraft pulp (BPSB1≈CP>BPPLA2>BPSA1). Starch B (1% of OD fiber) resulted in the highest increase in tensile strength of paper made from biorefinery kraft pulp; BPSB1 paper reached the tensile strength of CP paper. PLA (2% of OD fiber) and starch A were less effective than starch B, but they were able to increase the strength of BP paper to ~90% of tensile strength of CP. Overall, bulk of reinforced BP paper was higher than bulk of CP paper; hence, bulkier reinforced BP paper exhibited a comparable strength as CP paper indicating potential for a greater strength-to-weight ratio of paper made from biorefinery kraft pulp. In the case of PLA surface

reinforcement, the paper had more than two times higher wet tensile strength than CP paper (WTI of 2.81 Nm/g for BPPLA2, which is 8% of dry strength retained compared to WTI of 1.29 Nm/g for CP, which is 3.4% of dry strength retained). BPPLA2 showed also a superior wet strength compared to both starch-containing BP papers (BPSA1, BPSB1). Reinforcement improved tear strength of BP significantly, especially in the case of BPPLA2 and BPSB1. However, tear strength of CP paper was still superior (tear strength of CP paper was ~30% higher than tear strength of both BPPLA2 and BPSB1 papers of comparable tear strength).

Three of the four paper test sheets prepared with the PLA-starch blends had a lower strength than BP paper reinforced with PLA surface treatment (BPPLA2) or with starch A and B in the wet-end (BPSA1, BPSB1) (Table I). Specifically, the PLA-starch A blend applied in the wet-end in the amount of 1% of OD fibers, resulted in paper of inferior strength properties compared to BP paper treated with the same amount of starch A only (strength of both BPPLA0.5SA0.5 and BPPLA0.9SA0.1 lower than strength of BPSA1). This negative effect of the replacement of a certain amount of starch A with PLA may be caused by low retention of PLA with starch of low nitrogen content, i.e. low cationic charge. The results of paper reinforcement with the PLA-starch B blend were somewhat better, especially when the PLA-starch B ratio of 0.5/0.5 was used. Actually, tear strength and wet tensile strength of BPPLA0.5SB0.5 were higher than tear strength and wet tensile strength of BPSB1 (increase in tear strength for ~27% and in wet tensile strength for ~48%). Tensile strength of BPPLA0.5SB0.5 was lower than tensile strength of BPSB1 (decrease in tensile strength for ~15%). These results indicated that further improvement in strength properties of BP paper may be achieved by adjusting the ratio of PLA-to-starch in the PLA-starch B blend.

In the subsequent series of experiments, the starch amount was maintained constant at the level of 0.5% based on OD fibers while the amount of PLA was changed from 0.1% and 0.9% based on OD fibers. The total amount of PLA-starch blend was 0.6%, 0.7%, 1%, and 1.4% based on OD fiber with the PLA-starch ratios of 0.1/0.5, 0.2/0.5, 0.5/0.5, and 0.9/0.5, respectively (BPPLA0.1SB0.5, BPPLA0.2SB0.5, BPPLA0.5SB0.5, and BPPLA0.9SB0.5 paper test sheets were prepared, respectively). The graphs presented in Figures 3-6 illustrate the effect of the increasing amount of PLA in blends of PLA-starch applied in the wet-end with the constant amount of starch at 0.5% based on OD fibers on the bulk, tensile index, tear index, wet tensile index of these paper test sheets, respectively. For comparative purposes, the corresponding results obtained for CP, BP, and BPSB1 paper test sheets are also included in these diagrams.

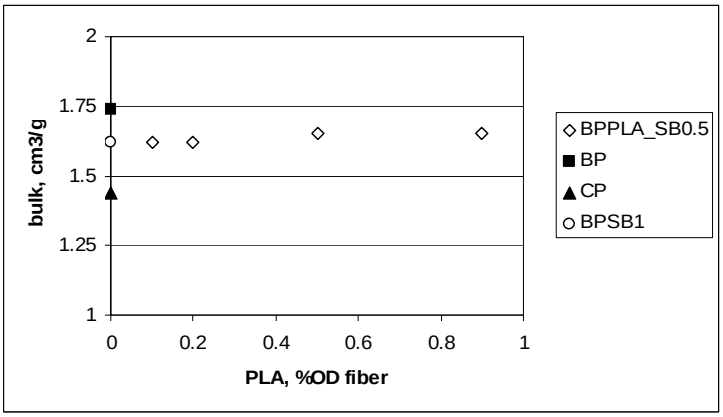

Figure 3: Effect of increasing amount of PLA in the PLA-starch B blend at the constant amount of starch B at 0.5% based on OD fiber on the bulk of biorefinery pulp (BPPLA_SB0.5)

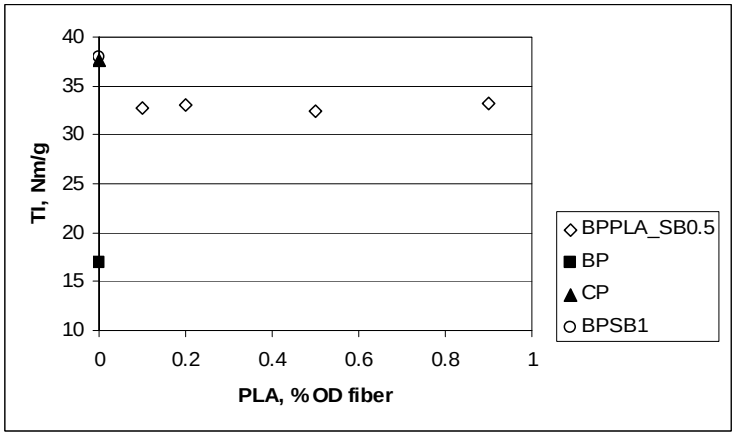

Figure 4: Effect of increasing amount of PLA in the PLA-starch B blend at the constant amount of starch B at 0.5% based on OD fiber on the tensile index of biorefinery pulp (BPPLA_SB0.5)

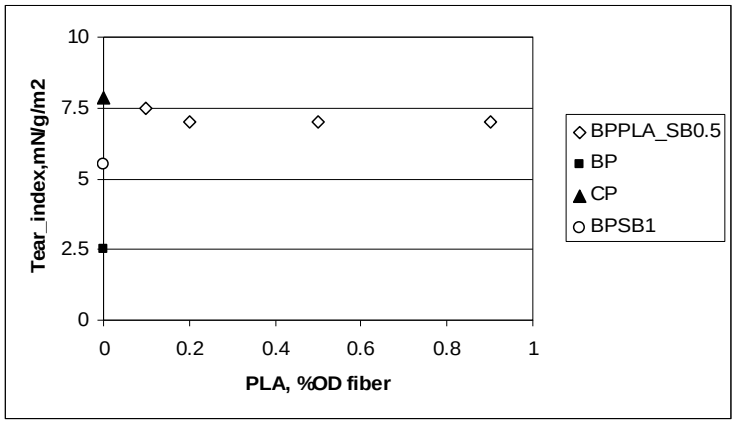

Figure 5: Effect of increasing amount of PLA in the PLA-starch B blend at the constant amount of starch B at 0.5% based on OD fiber on the tear index of biorefinery pulp (BPPLA_SB0.5)

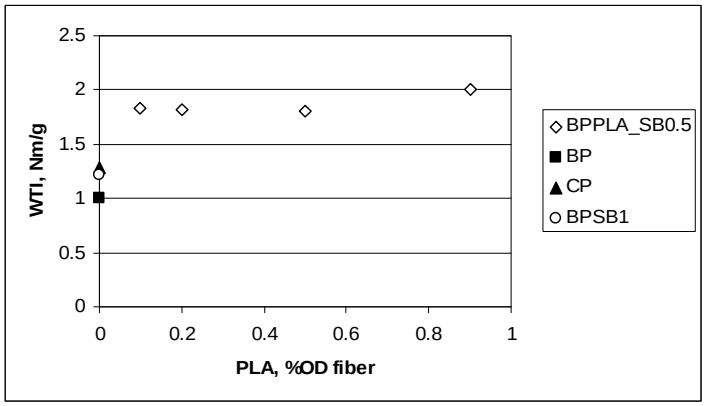

Figure 6: Effect of increasing amount of PLA in the PLA-starch B blend at the constant amount of starch B at 0.5% based on OD fiber on the wet tensile index of biorefinery pulp (BPPLA_SB0.5)

The graphs presented in Figures 3-6 clearly indicate that the amount of retained PLA was approximately the same and independent of the actual amount of PLA used since the bulk, tensile strength, tear strength, and wet tensile strength of BP paper test sheets reinforced with the PLA-starch (0.5% based on OD fiber) blends was approximately the same. Specifically, the wet-to-dry tensile strength ratio remained the same for all paper test sheets investigated in this series

of experiments (5.5-6% of the original dry strength retained upon wetting). Therefore, the following discussion is related to the properties of BP paper reinforced with the PLA-starch B blend at the total amount of 0.6% based on OD fibers with the ratio of PLA-to-starch of 0.1/0.5 (BPPLA0.1SB0.5). It can be seen that even though somewhat lower in bulk than BP paper (~6% higher bulk of BP paper), bulk of the BPPLA0.1SB0.5 paper test sheets was higher than the bulk of CP paper (~13% lower bulk of CP paper compared to that of BPPLA0.1SB0.5) and very similar to the bulk of BPSB1 paper (Figure 3). Tensile strength of the BPPLA0.1SB0.5 paper test sheets was almost two times higher than tensile strength of BP paper and only ~14% less than tensile strength of both CP and BPSB1 papers (Figure 4). It should be noted that at 0.1% PLA level, the total amount of PLA-starch blend (0.6% based on OD fiber) was 40% less than the amount of starch (1%) added in the wet-end for the reinforcement of BP paper (BPPLA0.1SB0.5), respectively. For the reduction in mass of reinforcing agent of 40%, loss in tensile strength was only ~12%. At the same time, tear strength and wet tensile strength were increased by more than 35% and 50%, respectively compared to biorefinery pulps without any additives(Figures 5 and 6, respectively).

Conclusion

Experiments were performed to evaluate the possibility of using PLA in the wet end to reinforce paper made from biorefinery kraft pulp. Results showed that the reinforcement of sheets is achievable by adding the PLA-cationic starch blend in the wet end. In addition, these experiments demonstrated that five parts of the cationic starch applied as a dry strength agent may be successfully replaced with one part of PLA with minimal loss of tensile strength and improvement in tear and wet tensile strength.

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