

Novel blend of biorenewable wet-end paper agents

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ABSTRACT: Recent studies have shown potential for a designed biorefinery product, polylactic acid (PLA), to increase the strength-to-weight ratio of paper produced from conventional kraft pulp and kraft pulp made from hot-water extracted hardwoods (biorefinery pulp). These results indicated that, after surface-treatment with 2 % PLA (per oven-dry [o.d.] fiber basis), paper made from sugar maple biorefinery pulp could be equivalent to or even greater in strength than paper made from sugar maple conventional kraft pulp, while retaining its higher bulk.

In the current study, we present the results of reinforcement of the pulps with PLA applied in the wet-end in combination with a known environmentally friendly dry strength agent, cationic starch. The preliminary results obtained with amylopectin-based starch of relatively high nitrogen content (starch B) were encouraging since strength, including wet strength and stretch, of paper reinforced with a blend of 0.5% starch B and 0.5% PLA was higher than strength of paper reinforced with 1% starch B. Moreover, based on the compatible strengths of paper reinforced with 0.6 % PLA-starch B blend (1/5) and of paper reinforced with 1% starch B, we hypothesize that there is a synergistic effect of PLA and starch B on tensile strength of paper.

The hypothesis was tested using pulps of different lignin content (Norway spruce thermomechanical pulp [TMP], hardwood unbleached kraft pulp, and softwood bleached kraft pulp). Tensile strength increased for papers made from these pulps. The effect was pronounced in the case of lignin-rich pulps, where tensile strength in the presence of 0.6% PLA-starch blend (1/5) exceeded that in the presence of 1% starch B. This result is in accordance with a higher attraction of lignin-rich fibers to hydrophobic PLA and indicates a promising approach in increasing strength-to-weight ratio of paper made from relatively hydrophobic pulps like TMP or unbleached kraft pulp. Accordingly, paper made from unbleached hardwood kraft pulp with 0.6% PLA-starch B blend (1/5) exhibited an improved resistance to water penetration.

Application: Polylactic acid as an envisioned biorefinery product may be used on site in an integrated biorefinery/pulp and paper mill to increase the strength of paper made from high-lignin content biorefinery or conventional pulps, such as TMP or unbleached kraft pulp.

The demand for alternative and sustainable sources of fuel, chemicals, and energy has increased tremendously 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 lignocelluloses, for the production of fuels, solvents, chemicals, and plastics, and to develop biorefineries. A scheme for biorefineries based on lignocellulosic hardwoods, such as northern hardwoods and plantation-grown willow biomass, has been developed recently [1]. In the design of this type of biorefinery, the first step is hot-water extraction (HWE) performed at temperatures up to 165°C and aimed at dissolving relatively easily accessible hardwood hemicelluloses, mainly xylans, while avoiding further degradation of the resulting mixture of 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 monosac-

charides resulting from hydrolysis of hot-water extract for the production of biofuels and bioplastics. Fermentation using xylose-fermenting microbes has been suggested to produce ethanol or butanol. Hydrolyzed hot-water extracts may also be fermented to produce polyhydroxyalkanoates (PHA) or lactic acid and subsequently polylactic acid (PLA). Several value-added products may be produced, including acetic acid, methanol, formic acid, furfural, and hydroxymethyl furfural, which are recovered from the hot-water extract by membrane separation [1].

In the utilization of extracted wood, different products have been envisioned and produced, including pellets, reconstituted wood products, and chemical pulps, called biorefinery kraft pulps. In pulp production, an increase in the delignification rate during kraft pulping of hardwoods has been observed [1-3]. This is an important advantage of HWE, which leads to shorter reaction times and 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 and in the content of free phenolic hydroxyl groups and a decrease in the content of acetyl groups, as well as cleavage of lignin-carbohydrate

bonds [1-5]. In contrast to these positive effects, removal of hemicelluloses/xylans results in biorefinery kraft pulp that is more difficult to refine and forms a weaker paper than kraft pulp from unextracted wood, i.e., conventional kraft pulp [3].

In our recent study, to avoid this adverse effect, the surface of the paper has been treated with PLA. This polymer was selected as a biorenewable biodegradable polymer, which had improved the strength of paper made from bleached chemothermomechanical and kraft pulps of different lignin content in previous research work by Hou et al. [6]. The results have demonstrated that after surface treatment with 2% PLA based on oven-dry (o.d.) fibers, paper made from biorefinery (un)bleached sugar maple kraft pulp could be equivalent to or even 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 might be more efficient in reinforcing biorefinery kraft pulps and unbleached pulps due to a higher attraction between relatively hydrophobic PLA and hemicellulose-depleted and lignin-containing fibers, respectively [3]. On the other hand, this conclusion implies that if successfully combined with an agent for stabilization in water dispersion, PLA may increase paper strength when added in the wet-end of papermaking to avoid the need of an additional surface treatment in the process. In our first attempt in this direction, we used a paper dry strength agent, cationic starch, which is a common stabilizing agent for water-insoluble polymers; for example, sizing agents [7]. Starch was also selected as an environmentally friendly and biorenewable polymer in line with efforts to reduce the use of petrochemical-derived polymers in general and in the paper industry. Promising results regarding the reinforcement potential of PLA were obtained [8].

In the present paper, we report the results of paper reinforcement obtained using two types of cationic starch (amylpectin-based starch; starch A, 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 used separately to measure the reinforcement effect of starch on paper made from biorefinery sugar maple kraft pulp. The previously noticed dependence of the reinforcement effect of PLA on the chemical composition of pulp was examined using softwood thermomechanical pulp (commercial TMP), hardwood unbleached kraft pulp (commercial linerboard pulp; HWLB), and bleached softwood kraft pulp (commercial BSKP). Since relatively hydrophobic PLA may be expected to improve paper resistance to water penetration, the potential sizing effect of PLA was evaluated using the HWLB pulp.

MATERIALS AND METHODS

Sugar maple (*Acer saccharum*) wood was obtained from the SUNY-ESF Lafayette Road Experimental Station in Syracuse, NY, USA. The wood was chipped on a Carthage chipper and

screening was performed using a Williams Classifier with 3/8 in., 5/8 in., and 7/8 in. accepts. Screened chips were stored at ~ 8°C.

Hot-water extraction

Woodchips were extracted using aqueous media (160°C; time to temperature 45 min) for 2 h at water-to-wood ratio of 4 to 1 in an MK digester (500 g o.d. wood, oven-dry basis). The yield of extracted wood chips was 77% of o.d. wood.

Kraft pulping

Unextracted and hot-water-extracted woodchips were pulped in an MK digester with 500 g o.d. wood at 165°C (time to temperature 60 min). The active alkali charge was maintained at 16% on o.d. wood, sulfidity was 25%, and the ratio of cooking liquor to wood was 4 to 1. The 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 wood chips) was determined in accordance with the TAPPI method T236 om-06 "Kappa number of pulp."

To examine the PLA reinforcement potential, 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 5000 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~20000-30000 (Polysciences [Warrington, PA, USA]; Cat. #16585) dissolved in a minimal amount of acetone at the PLA-to-acetone mass ratio of 1:1.

Starch application

The 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 the Tate & Lyle (Decatur, IL, USA) Sta-lok line of products.

Starch was first slurried by mixing dry powder with water and cooked at 0.3% solids at 95°C-97°C for half an hour under constant stirring. This formed a clear aqueous starch paste ready to be applied to the stock. In starch-only reinforced paper, test sheets from BP were made with 1% starch based on o.d. fibers.

PLA-starch blend

Since PLA is not soluble in water, PLA dissolved in a minimal amount of 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 into the pulp slurry under constant agitation. The total amount of PLA and starch in the pulp slurry ranged from 0.6% to 1.4% based on the o.d. fibers, and different ratios of PLA-to-starch amounts were used. Paper test sheets were made from the furnish immediately after preparation.

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 TAPPI method 220 sp-06 "Physical testing of pulp handsheets." A tensile test was performed following TAPPI T 220 sp-06 (using a constant rate of elongation apparatus as in TAPPI method T 494 om-06 "Tensile breaking properties of paper and paper-board"). The wet tensile strength was measured by immersing the paper in water for 15 s and conducting tensile test as described previously. For tear strength, TAPPI method T 414 om-04 "Internal tearing resistance of paper (Elmendorf-type method)" was used.

Microscopy

Images of the control and PLA sprayed sheets were observed on a JEOL (Tokyo, Japan) 5800 scanning electron microscope (SEM) at a magnification of 2500X. The specimens were sputter coated with 15 nm of Au-Pd prior to observation.

A second series of experiments on the reinforcement of paper with 0.6% PLA-starch B blend (1/5) was performed using Norway spruce (*Picea abies*), 2nd stage TMP, HWLB, and BSKP following the same procedures for handsheet preparation and testing as in the first series of experiments. For

HWLB, the sizing effects of the reinforcing agents (PLA-starch B or starch B only) were tested following T432 cm-09 "Water absorbency of bibulous papers," using 1.0 ml of water. Starch-only reinforced paper test sheets were made with 0.5% and 1% starch B. Control tests sheets were made from pure pulps.

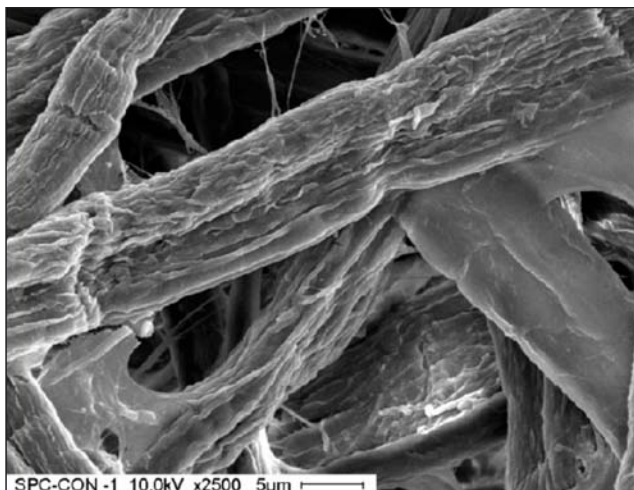
RESULTS AND DISCUSSION

Selected properties of paper test sheets made from conventional sugar maple kraft pulp (CP) and biorefinery sugar maple kraft pulp (BP) of similar kappa numbers are presented in **Table I**. It can be seen 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). The reinforcement of BP paper test sheets has been examined in our previous study by surface treatment with PLA at 2% based on o.d. fibers [3]. Promising results, especially noticeable in improvement of wet strength, were obtained in this series of experiments. The results of examination of the PLA role in paper reinforcement are shown in **Figs. 1-2**, which present SEM micrographs of BP paper and PLA-surface-treated BP paper (BP and BPPLA2, respectively).

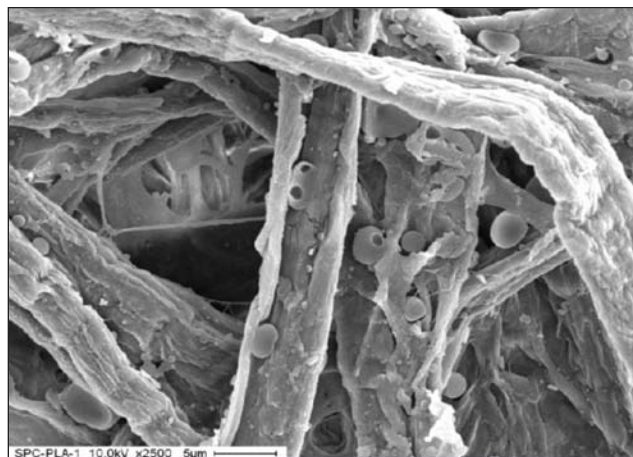
In the SEM micrograph presented in Figure 2, PLA may be noticed as dispersed in the fiber network and on the surface of fibers of BPPLA2 in the form of globules. These results implied that a more even distribution of PLA in the fiber network and/or better coating of fibers would probably contribute to a better reinforcing effect. For wet-end use in order to

Paper	Reinforcement Method			Bulk cm ³ /g	Mechanical Property			
	Surface	Wet-End			TI Nm/g	Stretch %	WTI Nm/g	Tear_I mN/g/m ²
	PLA % o.d. fiber	PLA % o.d. fiber	Starch % o.d. fiber					
CP	-	-	-	1.4	37.7	0.8	1.3	7.8
BP	-	-	-	1.7	17.0	0.8	1.0	2.5
BPPLA2	2.0	-	-	1.8	34.8	0.9	2.8	5.6
BPSA1	-	-	1.0	1.6	33.0	1.8	1.3	4.6
BPSB1	-	-	1.0	1.6	38.0	1.6	1.2	5.5
BPPLA0.5SA0.5	-	0.5	0.5	1.6	27.8	1.3	1.0	3.4
BPPLA0.5SB0.5	-	0.5	0.5	1.7	32.5	2.6	1.8	7.0
BPPLA0.9SA0.1	-	0.9	0.1	1.7	28.0	1.3	1.0	3.9
BPPLA0.9SB0.1	-	0.9	0.1	1.8	31.7	2.2	1.2	5.7

Table I. Selected properties of paper made from conventional pulp (CP) and biorefinery pulp (BP) before and after reinforcement with different agents.



1. Scanning electron microscope (SEM) micrograph of paper made from BP.



2. SEM micrograph of paper made from BP and treated on the surface with poly(lactic acid) (PLA) (2% based on o.d. fibers) (BPPLA2).

achieve a more even distribution, water-insoluble PLA must be stabilized in a water suspension. In the subsequent experiments, two types of cationic starch, A and B, were used to stabilize PLA in water. In these experiments, BP-based paper test sheets reinforced with the PLA-starch blend were made. Even though it is used as a paper dry strength agent, hydrophilic starch is not expected to improve the wet strength of paper. Blending with hydrophobic PLA may be considered a way to alleviate some of the water resistance problems as implied in our preliminary study [8].

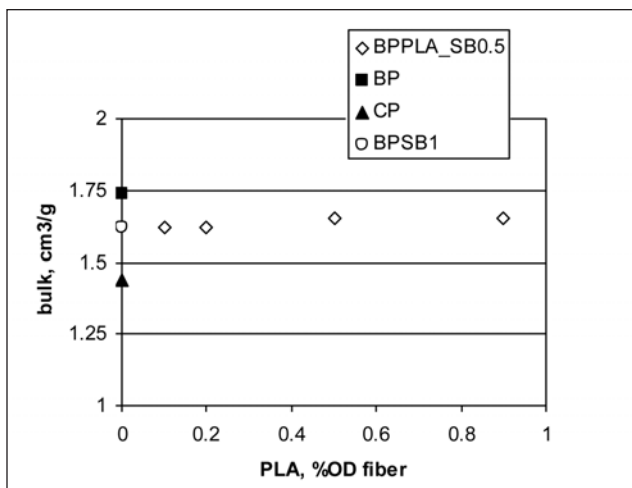
In the first series of PLA-starch blend experiments, the blend amount was maintained at 1% of o.d. fibers, and two PLA-starch ratios of 0.5/0.5 and 0.9/0.1 were used. Four different BPPLASA(B) papers were made: BPPLA0.5SA0.5, BPPLA0.5SB0.5, BPPLA0.9SA0.1, and BPPLA0.9SB0.1. Table I shows the results of these experiments. For comparative purposes, BP paper was reinforced using starch only (starch A and B added at 1% based on o.d. fibers (BPSA1 and BPSB1, respectively). The results of these reinforcement trials are also presented in Table I.

Paper test sheets made from biorefinery kraft pulp and reinforced with PLA in a paper surface treatment (BPPLA2) or wet-end starch (BPSA1, BPSB1) were of similar tensile strength and in some cases comparable to tensile strength of test paper made from conventional kraft pulp (BPSB1=CP>BPPLA2>BPSA1). Starch B (1% of o.d. 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. These results demonstrate that the tensile strength of paper made from biorefinery pulp may compete with the strength of paper made from conventional kraft pulp with cationic starch added at conventional levels used in paper industry [7].

Even though PLA (2% of o.d. fiber) and starch A were less effective than starch B, they were able to increase the strength of BP paper to ~90% of tensile strength of CP. Over-

all, the bulk of reinforced BP paper was higher than the bulk of CP paper; hence, bulkier reinforced BP paper exhibited a comparable strength as CP paper. 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 also showed 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). It seems that refining causes more damage of less swollen hemicellulose-depleted fibers from biorefinery pulps than of fibers from conventional pulps. The consequent reduction in tear strength cannot be completely recovered with starch B at 1% addition, in spite of significant improvement in interfiber bonding as shown by the increase in tensile strength from all additions in comparison with control BP.

Three of the four paper test sheets prepared with the PLA-starch blends had a lower strength than BP paper reinforced in 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 o.d. 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 are 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

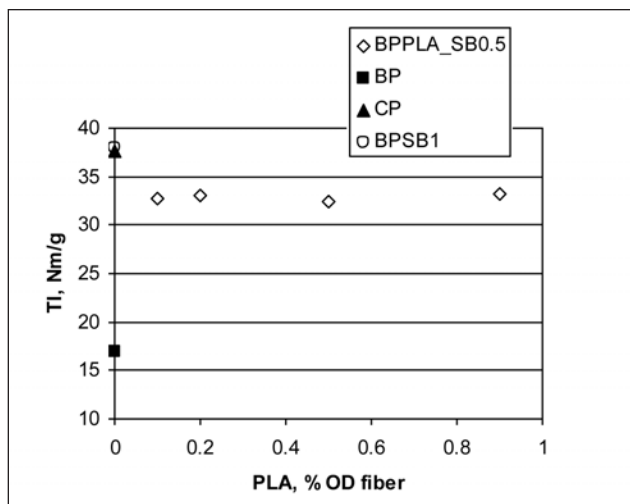


3. Effect of increasing amount of PLA in the PLA-starch B blend with a constant amount of starch B at 0.5% (based on o.d. fiber) on the bulk of the BP (BPPLA_SB0.5).

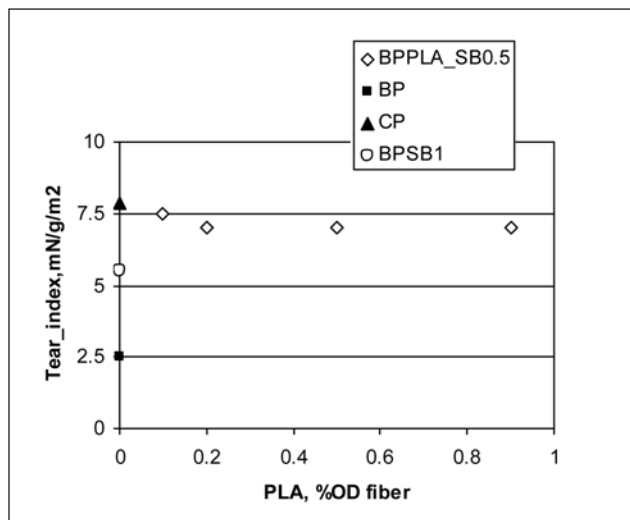
BPPLA0.5SB0.5 were higher than tear strength and wet tensile strength of BPSB1 (an increase in tear strength of ~21% and in wet tensile strength of ~33%). Tensile strength of BPPLA0.5SB0.5 was lower than tensile strength of BPSB1 (a decrease in tensile strength of ~15%). These results indicated that 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 a subsequent series of experiments, the starch amount was maintained constant at the level of 0.5% based on o.d. fibers while the amount of PLA was changed from 0.1% to 0.9% based on o.d. fibers. The total amount of PLA-starch blend was 0.6%, 0.7%, 1%, and 1.4% based on o.d. fibers, with the PLA-starch ratios of 1/5, 2/5, 5/5, and 9/5, 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 an increasing amount of PLA in blends of PLA-starch applied in the wet-end with a constant amount of starch, at 0.5% based on o.d. fibers, on the bulk, tensile index, tear index, and 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.

The graphs presented in **Figs. 3-6** indicate that the amount of retained PLA was approximately the same and might have been independent of the actual amount of PLA used, because the bulk, tensile strength, tear strength, and wet tensile strength of BP paper test sheets reinforced with the PLA-starch (0.5% based on o.d. 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

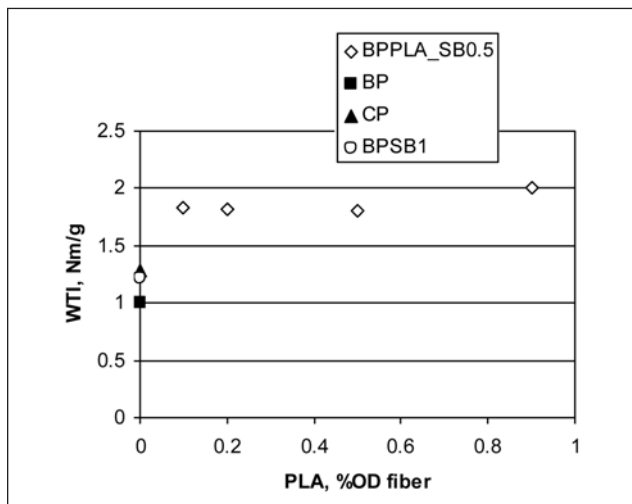


4. Effect of increasing amount of PLA in the PLA-starch B blend with a constant amount of starch B at 0.5% (based on o.d. fiber) on the tensile index of BP (BPPLA_SB0.5).

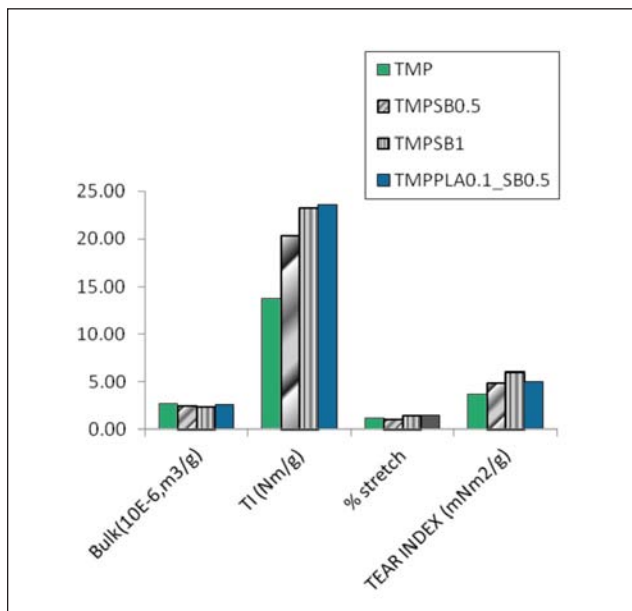


5. Effect of increasing amount of PLA in the PLA-starch B blend with a constant amount of starch B at 0.5% (based on o.d. fiber) on the tear index of BP (BPPLA_SB0.5).

0.6% based on o.d. fibers with the ratio of PLA-to-starch of 1/5 (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 (Fig. 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 (Fig. 4). It should be noted that at 0.1% PLA level, the total amount of PLA-starch blend (0.6% based on o.d. fiber) was 40% less than the amount of starch (1%) added in the wet-end for the reinforcement of BP paper (BPPLA0.1SB0.5 vs. BPSB1). For the reduction in mass of the reinforcing agent of 40%, loss in tensile strength was only



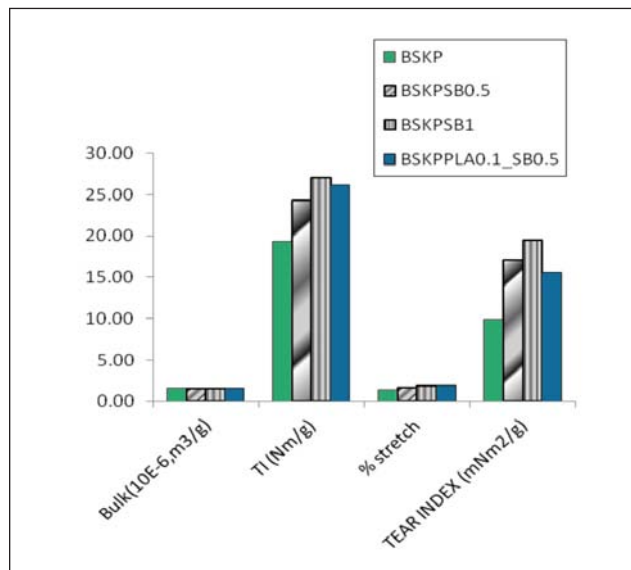
6. Effect of increasing amount of PLA in the PLA-starch B blend with a constant amount of starch B at 0.5% (based on o.d. fiber) on the wet tensile index of BP (BPPLA_SB0.5).



7. Properties of paper test sheets made from TMP: TMP with 0.5% and 1% starch B (TMPSB0.5, TMPSB1), and TMP with 0.6% PLA-starch B blend (1/5) (TMPPLA0.1_SB0.5).

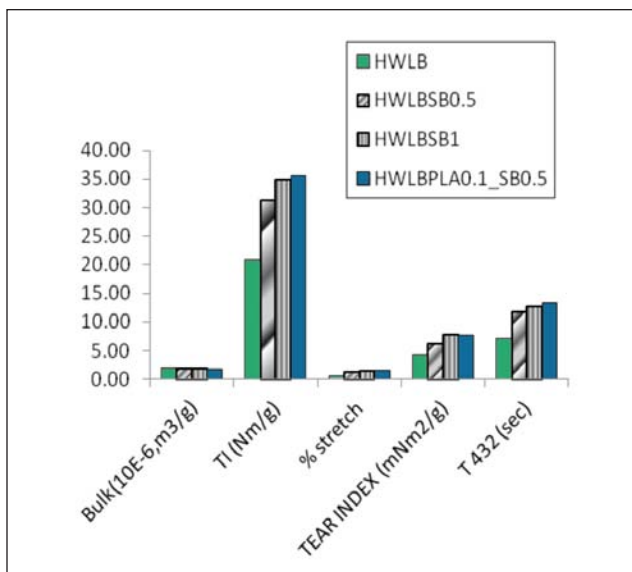
~12%. At the same time, tear strength and wet tensile strength were increased by more than 35% and more than 50%, respectively (Fig. 5 and Fig. 6, respectively).

The reinforcement experiments with conventional and biorefinery sugar maple unbleached kraft pulps showed that strength of paper may be increased with the PLA-starch blends and furthermore that there may be a synergistic effect of PLA and starch in improving strength of paper. To examine the potential synergy, PLA-starch B reinforcement experiments were conducted using two softwood pulps of different lignin content: a lignin-rich TMP and a lignin-free BSKP. This selection of pulps was made by taking into ac-



8. Properties of paper test sheets made from BSKP: BSKP with 0.5% and 1% starch B (BSKPSB0.5, BSKPSB1), and BSKP with 0.6% PLA-starch B blend (1/5) (BSKPPLA0.1_SB0.5).

count a previously observed positive correlation between hydrophobicity of pulp and the PLA reinforcement effect (3). In addition to paper test sheets that were made from pulps in the presence of 0.6% PLA-starch B blend (1/5) (TMPPLA0.1_SB0.5 and BSKPPLA0.1_SB0.5), for comparative purposes, control paper test sheets were made from pulp only (TMP and BSKP). To compare the reinforcement effect of PLA-starch B blend with the reinforcement effect of starch, two series of paper test sheets were also made from pulp with 0.5% and 1% starch B, respectively (TMPSB0.5, TMPSB1, BSKPSB0.5, and BSKPSB1). The results of these experiments for TMP and BSKP are presented in **Fig. 7** and **Fig. 8**, respectively. As expected, the addition of starch B caused an increase in tensile and tear strength of paper made from both pulps, whereas it did not influence the paper bulk. These results are consistent with an increase in strength-to-weight ratio of paper in the presence of starch. A higher reinforcement effect of 0.6% PLA-starch B blend (1/5) compared to 0.5% starch was confirmed for both pulps considering the tensile strength. Furthermore, in the case of TMP, tensile strength of 0.6% PLA-starch (1/5) reinforced paper test sheets was higher than that of paper test sheets reinforced with 1% starch. Tear strength, however, showed different results for the two pulps with tear strength increasing in the following order: for TMP, TMP<TMPSB0.5<TMPPLA0.1_SB0.5<TMPSB1; and for BSKP, BSKP<<BSKPPLA0.1_SB0.5<BSKPSB0.5<BSKPSB1. These results are comparable to the effect of surface treatment of PLA on bleached and unbleached conventional and biorefinery hardwood kraft pulps and show a much better reinforcement result of PLA on lignin-rich hemicellulose-depleted unbleached biorefinery kraft pulp, with an increase in tensile strength and a modest or even negative effect on tear strength [3].



9. Properties of paper test sheets made from HWLB: HWLB with 0.5% and 1% starch B (HWLBSB0.5, HWLBSB1), and HWLB with 0.6% PLA-starch B blend (1/5) (HWLBPLA0.1_SB0.5).

Tensile strength of BSKP-based paper tests sheets increased in the following order: BSKP<BSKPSB0.5<BSKPLA0.1_SB0.5<BSKPSB1. Tensile strength of TMP-based paper tests sheets increased in the following order: TMP<TMPSB0.5<TMPSB1<TMPPLA0.1_SB0.5. These results showed that PLA and starch exhibit a synergistic effect on tensile strength of paper, which is more obvious in the case of

lignin-rich pulp, i.e., more so in TMP than in the case of lignin-free BSKP. A greater increase in tensile strength of TMP in the presence of PLA may be explained by greater attraction between the more hydrophobic lignin-rich fibers of TMP and PLA than between the more hydrophilic lignin-free fibers of BSKP and PLA.

The results of the experiments performed on lignin-rich unbleached hardwood kraft pup (commercial linerboard HWLB) are presented in **Fig. 9**.

These results offer an additional evidence of benefits of using PLA in combination with starch B as the tensile strength of HWLB reached maximum with 0.6% PLA-starch B (1:5) and it increased in the following order: HWLB<HWLBSB0.5<HWLBSB1<HWLBPLA0.1_SB0.5. Tear strength of HWLBPLA0.1_SB0.5 was compatible with that of HWLBSB1. The resistance to water penetration of paper made from HWLB increased in the same order to a certain extent as expected due to the hydrophobic nature of PLA. This effect, however, was only modest.

CONCLUSION

The experiments were performed to evaluate the possibility of using PLA as a renewable polymer and a designed biorefinery product in the wet end of the papermaking process. These experiments showed that by using a PLA-cationic starch blend, paper tensile strength would increase. In addition, these experiments demonstrated a synergistic effect of PLA and cationic starch on the tensile strength of paper, especially paper made from lignin-rich pulps, such as TMP and

ABOUT THE AUTHORS

We chose this topic to explore ways of increasing the strength of paper made from a biorefinery and also for conventional pulps by using a chemical, which can be produced in an integrated biorefinery/pulp and paper mill. This research is an extension of earlier research performed to improve the strength of paper by surface treatment with PLA. In the present experiments, PLA was applied in the wet-end of papermaking.

The most difficult aspect of this research was that PLA is not soluble in water. For PLA stabilization in pulp slurry, we used a blend of PLA with starch.

We were most surprised by how the PLA-cationic starch blend (1/5) added at the amount of 0.6% based on o.d. fibers can improve the strength of paper made from high-lignin-content pulps (TMP, unbleached kraft pulp) more so than pure cationic starch added at the amount of 1% based on o.d. fibers.

From this research, mills can see how they might



Gong



Hasan



Bujanovic



Amidon

benefit from PLA as an envisioned biorefinery product that is used on site to improve paper strength. The next step in our research is to adjust the amount and ratio of PLA/cationic starch to maximize the strength of paper.

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ADDITIVES

unbleached kraft pulp. This result verifies an attraction of lignin-rich fibers to hydrophobic PLA and indicates a promising approach for increasing strength-to-weight ratio of paper made from high-lignin-content fibers. **TJ**

ACKNOWLEDGEMENTS

We are pleased to acknowledge, with thanks, the valuable help we received from Tate & Lyle, Decatur, IL, (Jeremy Zimmerman) with starch donation. We also would like to thank Dr. Robert B. Hanna, N.C. Brown Ultrastructure Center, SUNY-ESF, Syracuse, NY, USA, for performing SEM of paper test sheets.

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