Characterization of Lignocellulosic–Poly(lactic acid) Reinforced Composites

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ABSTRACT: The effects of adding poly(lactic acid) (PLA) to the physical strength of paper test sheets prepared from three unbleached loblolly pine kraft pulps with different amounts of lignin and an aspen bleached chemothermomechanical pulp were studied. The physical strength studies demonstrated that relatively low levels of PLA addition (0.5–4.0%) could dramatically improve the tensile and burst strength properties as a function of the amount of PLA added. Hot pressing the test sheets was shown to be an important treatment for enhancing the strength properties. An analysis of untreated and PLA-treated hot-pressed test sheets by atomic force microscopy indicated that the addition of PLA markedly altered the surface properties of the sheets. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1346–1349, 2006

Key words: additives; atomic force microscopy (AFM); biopolymers; fibers; strength

INTRODUCTION

The need to develop new composites derived from renewable biomaterials that exhibit improved physical strength properties and can be readily integrated into natural life cycles while addressing environmental performance issues is a growing concern of societal importance.[1,2] The use of natural fibers instead of glass or aramid fibers to enhance the performance of biocomposites has seen increasing research and applications in a variety of fields, from medical and transportation materials to packaging.[3,4] For many applications, natural fibers provide reinforcement properties at lower cost, lower density, and reduced abrasion to processing equipment than can be achieved with synthetic fibers. In addition, biocomposites reinforced with natural fibers simplify disposal issues at the end of their product lifetimes. Of the many biopolymers and bioplastics that are available, poly(lactic acid) (PLA) is a relatively new addition.[5] As such, the performance of PLA reinforced with natural fibers has only recently begun to be investigated. Shiata et al.[6] examined the physical properties of PLA with untreated and esterified abaca fibers and reported that these materials did not improve the flexural strength of the composite. In contrast, Levit et al.[7] found that bleached kraft paper filled with PLA yielded enhanced dry tensile index values when employing a 30–40% charge of PLA. Under these conditions, they demonstrated a 50–100% increase in the dry physical strength properties for PLA-reinforced paper, whereas low charges of PLA did not appear to be beneficial with respect to paper strength properties. In addition, they demonstrated that laminates of unbleached kraft paper and PLA films yielded a product that exhibited a 25–240% increase in the dry tensile strength, which depended on the number of plies of PLA film employed.

These latter results are indicative of the potential for PLA to enhance the physical strength properties of paper. In this study, we examined the interactions between PLA and lignin-containing pulps, including bleached chemothermomechanical pulp (BCTMP) and unbleached kraft pulps. It was anticipated that these pulps would exhibit improved strength benefits from PLA as the surface lignin in these pulps interferes with fiber–fiber bonding. Chemothermomechanical pulp is prepared by the application of mechanical energy to wood to liberate fibers, and this process frequently exhibits pulp yields greater than 90%. These fibers contain all three major wood biopolymers: lignin, hemicellulose, and cellulose. Kraft pulps are prepared by the cooking of wood in the presence of sodium hydroxide and sodium sulfide. This process liberates fibers by chemically degrading lignin. According to the pulping conditions employed, kraft pulps with

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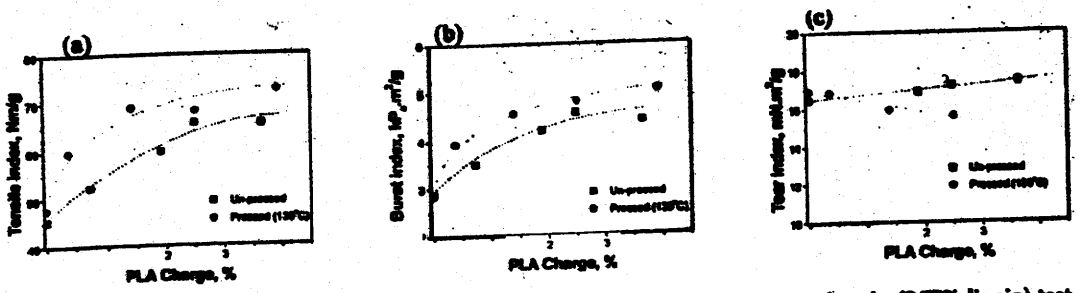

Figure 1 Evaluation of the strength properties for control and PLA-impregnated pine kraft pulp (8.75% lignin) test sheets.

various amounts of lignin can be prepared, and in this investigation, the kraft pulps contained 3.61–12.64% lignin. The effects of treating lignin-containing pulp fibers with PLA were assessed from the perspective of the surface chemistry and physical properties.

EXPERIMENTAL

Materials

Three unbleached laboratory-prepared kraft pulps were produced from loblolly pine wood according to standard procedures for batch digesters.[8] These kraft pulps were made with 3.61, 8.75, or 12.64% residual lignin (i.e., kappa number of 24.1, 58.3, or 84.3, respectively). A commercial aspen BCTMP, bleached with alkaline peroxide, was also used in this study. The brightness and Canadian standard freeness of the aspen BCTMP were 83.3% ISO and 255 mL, respectively. DL-Polylactide with a molecular weight of 75,000–120,000 was purchased from Aldrich–Sigma, Inc. (St. Louis, MO).

Test sheet preparation and testing

Paper test sheets were prepared according to Tappi Standard Methods T220 sp-01 and T262 sp-02.[9] The test sheets from BCTMP were made through the recycling of white water to retain pulp fines in the sheets. The PLA-treated paper sheets were prepared by the immersion of sheets into a 0–10 wt % PLA chloroform solution. These sheets were air-dried overnight in the absence of light. All test sheets were air-dried in a moisture-control room for 24 h before testing. Paper test sheets, with and without PLA, were pressed (2.30 $\times 10^3$ kPa) for 5 min at 25, 60, 95, 130, 165, and 190°C. The test sheets were analyzed for the tensile, burst, and tear strength according to Tappi Standard Methods T494 om-96, T403 om-97, and T414 om-98.[9]

Atomic force microscopy (AFM) analysis

AFM analysis of paper test sheets was performed at atmospheric pressure and room temperature in the tapping mode over a 5-μm-square area with a silicon nitride tip and a resolution of 512 pixels × 512 pixels on a Digital Instruments 3100 scanning probe microscope. The samples were held in place by double-sided tape. The test sheets were evaluated by the imaging of three positions on eight fibers for each treatment. Height, amplitude, and phase images were collected for each, and the root-mean-square (RMS) roughness for the height of each was determined.

RESULTS AND DISCUSSION

The results summarized in Figure 1(a,b) for kraft test sheets with 8.75% lignin, impregnated with 0.5–4%

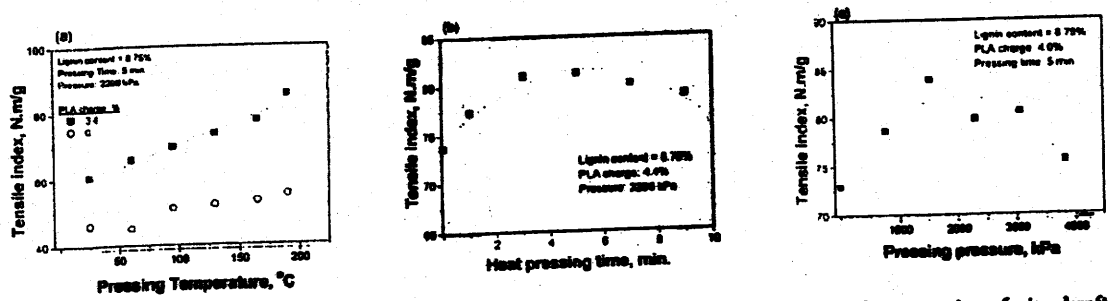

Figure 2 Characterization of the press temperature, pressure, and press time on the strength properties of pine kraft pulp (8.75% lignin) test sheets with various levels of PLA.

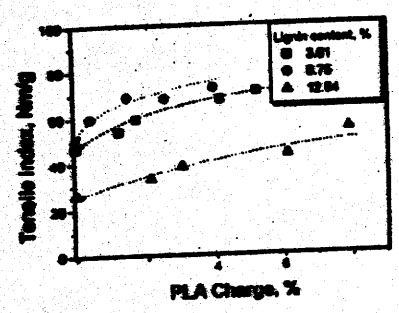

Figure 3 Analysis of PLA addition to pine kraft pulp test sheets prepared with different levels of residual lignin at a press temperature of 130°C and a press pressure of 2.30 × 10^3 kPa for 5 min.

PLA, indicate improvements of 20–35% depending on the charge of PLA.

The burst index values also benefited from the addition of PLA, increasing by 40–70% with increasing amounts of PLA. Hot pressing the test sheets with a press temperature of 130°C for 5 min enhanced the tensile/burst index values for the PLA-treated sheets. In comparison, the tear index values exhibited no changes with the PLA treatment, whereas the hot-pressed PLA sheets exhibited a slight decrease in the tear index performance. Typically, the tensile sheet strength represents an increase in the fiber bonding strength. The Page equation[10] explains how at a constant fiber strength and fiber length the two critical components contributing to the tensile strength are the shear bond strength and the relative bonded area. In this study, the same pulp was used in both cases; hence, the fiber length was constant. In addition, the tear strength results [Fig. 1(c)] suggest that the fiber strength was not affected. Thus, the observed increase in the tensile strength associated with PLA addition was most likely due to better bonding between the load-bearing elements in the sheet.

The effects of the hot-pressing conditions (temperature, time pressure) on the PLA-treated test sheets are summarized in Figure 2. The tensile index data demonstrate that the effects of hot pressing kraft test sheets are primarily due to the addition of PLA and not simply due to the hot pressing of the lignocellulosic fibers. The data presented in Figure 2(b,c) suggest that the improvements in the tensile index for the PLA-treated sheets came about at even short press times and pressures when a press temperature of 130°C was employed.

The beneficial effects of PLA addition to the tensile index properties of kraft pulps with various lignin contents are summarized in Figure 3 and are consistent with the prior observations, but these results extend PLA benefits to lignin-rich paper. Furthermore, these data demonstrates that the beneficial strength properties observed when low levels of PLA are added to paper sheets can be achieved with kraft pulps of different lignin contents. Indeed, the strength benefits appear to be dominated by the amounts of PLA added to the test sheets and not the intrinsic lignin content of the pulp.

The effects of PLA impregnation on the properties of high-lignin BCTMP pulps are summarized in Figure 4. These results indicate that the addition of PLA to BCTMP test sheets produced a 40–60% increase in the tensile and burst index depending on the amount of PLA added to the sheets. As before, the addition of PLA to BCTMP sheets was shown not to influence the tear properties.

To further explore the effects of the PLA treatment on the test sheets, a series of control and PLA-treated and pressed test sheets were submitted for AFM analysis. As summarized in Figures 5 and 6, amplitude and phase AFM images of the control pine kraft (8.75% lignin) and BCTMP sheets yielded data similar to those of literature reports.[11,12] The kraft and BCTMP sheets impregnated with PLA yielded phase and amplitude AFM images dramatically different from those for the control sheets.

The results of this analysis suggest that the addition of PLA, followed by hot pressing, alters the surface of test sheets by removing many of the structural features usually observed by AFM for kraft and mechanical pulps. Indeed, the RMS roughness values calculated from the height AFM data were 45.1 for the kraft

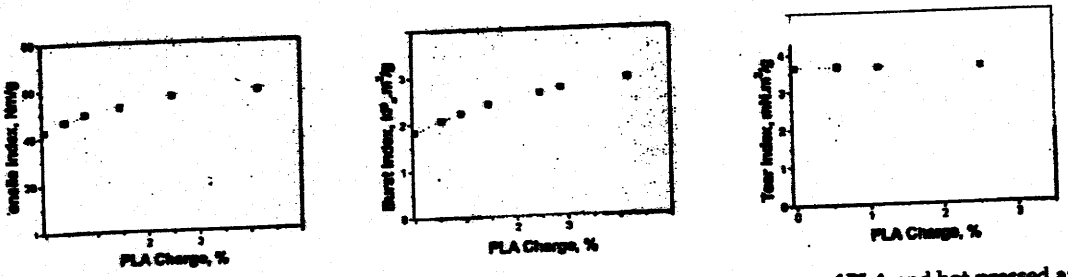

Figure 4 Strength comparisons for aspen BCTMP test sheets treated with various amounts of PLA and hot-pressed at 130°C and 2.30 × 10^3 kPa for 5 min.

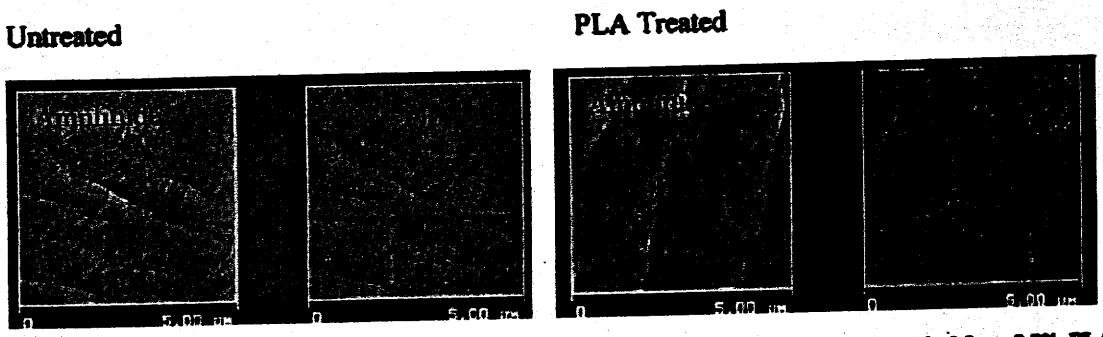

Figure 5 Amplitude and phase AFM analysis of 8.75% lignin pine kraft test sheets treated with 0.0 or 2.5% PLA and hot-pressed (press Conditions: 130°C, 2.30 × 10^3 kPa, and 5 min).

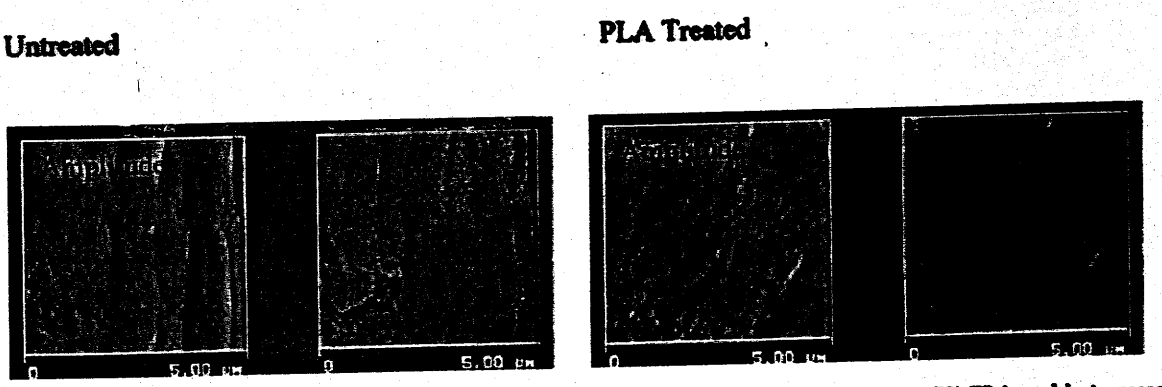

Figure 6 Amplitude and phase AFM analysis of aspen BCTMP test sheets treated with 0.0 or 2.5% PLA and hot-pressed (press conditions: 130°C, 2.30 × 10^3 kPa, and 5 min).

control sheet and 40.9 for the PLA-treated kraft sheet. Analogously, the control BCTMP sheets had an RMS roughness value of 42.2 versus 38.4 for the PLA-treated BCTMP sheet.

CONCLUSIONS

This study demonstrates that low levels of PLA can provide enhanced strength benefits for lignin-containing kraft and BCTMP sheets. Specifically, the addition of 0.5–4% PLA can greatly improve the tensile and burst strength of the test sheets. However, the effect of PLA on the sheet tear strength properties is not significantly altered. Hot pressing increases the benefits of PLA with respect to the tensile and burst strength properties. Our studies suggest that the optimal pressing conditions for the strength improvement occur at 130°C with a press pressure of about 2.30 × 10^3 kPa for 5 min. The AFM studies clearly indicate that the polymer is distributed across the surface of the test sheets and improves surface smoothness. Additional studies are ongoing to identify the fundamental sheet properties that contribute to the improved strength properties when low levels of PLA are added to paper.

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References

1. Mohanty, A. K.; Misra, M.; Drzal, L. T. J Polym Environ 2002, 10, 19.
2. Riedel, U.; Nickel, J. Materialwiss Werkst 2001, 32, 493.
3. Julson, J. L.; Subbarao, G.; Stokke, D. D.; Gieselman, H. H.; Muthukumarappan, K. J Appl Polym Sci 2004, 93, 2484.
4. Li, Y.; Mai, Y.-W.; Ye, L. Compos Sci Technol 2000, 60, 2037.
5. (a) Vink, E. T. H.; Rabago, R.; Glassner, D. A.; Springs, B.; O'Connor, R. P.; Kolstad, J.; Gruber, P. R. Macromol Biosci 2004, 4, 551; (b) Ouchi, T.; Ohya, Y. J Polym Sci Part A: Polym Chem 2004, 42, 453.
6. Shibata, M.; Ozawa, K.; Teramoto, N.; Yosomiya, R.; Takeishi, H. Macromol Mater Eng 2003, 288, 35.
7. Levit, M. R.; Farrell, R. E.; Gross, R. A.; McCarthy, S. P. Tappi Polymers, Laminations and Coatings Conference Proceedings, Boston, MA, Sept 1996; Vol. 2, p 545.
8. Froass, P. M.; Ragauskas, A. J.; Jiang, J. Ind Eng Chem Res 1998, 37, 3388.
9. 2002–2003 Tappi Test Methods; Tappi: Atlanta, GA, 2002.
10. Gurnagul, N.; Ju, S.; Page, D. H. J Pulp Paper Sci 2001, 27, 88.
11. Duchesne, I.; Daniel, G. Nordic Pulp Paper Res J 1999, 14, 129.
12. Koljonen, K.; Osterberg, M.; Johansson, L.-S.; Stenius, P. Colloids Surf A 2003, 228, 143.