# Improvement of Pulp Handsheet Strength Properties by Polylactic Acids

Q.X. Hou[1], X.S. Chai[2], R. Yang[2] and A.J. Ragauskas[2]
[1]Tianjin Key Lab. of Pulp & Paper, Tianjin University of Science & Technology, Tianjin 300222, China
[2]Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, GA 30332, USA

## ABSTRACT

Polylactic acids polymer (PLA) was applied as an additive to improve the strength properties of handsheets prepared from three unbleached southern pine kraft pulps with different kappa number and an aspen bleached chemithermomechanical pulp (BCTMP). The results showed that PLA could greatly improve the tensile and burst strength of the pulp handsheets. Heat pressing effect was also important to enhance the strength properties. For unbleached kraft pulps, it was found that an appropriate amount of residual lignin in pulps had a positive effect on the handsheets strength improvement when adding PLA. The thickness of the handsheet did not change the PLA strengthening effect. In general, PLA effect on tear strength improvement could be neglected. However, it had a significant effect on the improvement of tear strength for the aspen BCTMP handsheets not containing sufficient amount of fines.

**Key words**: Polylactic acids (PLA), Heat pressing, Unbleached kraft pulp, Bleached chemithermomechanical pulp (BCTMP), Handsheet

## INTRODUCTION

Polylactic acid polymers (PLA) are biodegradable polymers produced from a renewable resource – sugar [1]. The process includes: extracting the sugar from biomass materials, using the sugar to ferment lactic acid, separating and purifying the lactic acid, forming the lactide dimer from the lactic acid, and polymerizing the lactide dimer to PLA. Attribute to the versatility and anticipated price/performance of the newly generated PLA, it will enable to displace a significant volume of fossil fuel-based polymers, which can significantly reduce the impact on environment.

Currently, due to its higher cost, the focus on PLA as a packaging material is limited to high value film, rigid thermoformed food and beverage containers, coated papers and other products [2-5]. With the environment concern, development of "green" packaging will be a trend in the packaging industry and "green" packaging materials will play more and more important role nowadays [6]. Among those "green" packaging materials, cellulose fiber from wood pulping process is regarded as one of dominant materials that are widely used in packaging industry. However, one of the major disadvantages for the cellulose fibers as packaging material is due to its poor strength properties when compared with plastics, which greatly limits cellulose fiber utilization. Besides strength properties, cellulose based packaging materials also have a poor gas- and moisture-resistance, which is particularly important to the applications in food industry. Many polymers, such as polycarboxylic acids and polyvinyl alcohol, have been reported to be used as bonding additives for improving the paper or paperboard wet and dry strength in paper industry, which was achieved by the increase of bonding strength between fiber to fiber and fiber to polymers [7]. Clearly, with the presence of a compatible polymer additive, the strength properties of the cellulose-based product can be greatly improved, which is beneficial to utilization of cellulose material in not only packaging but also other areas. As a biodegradable polymer, PLA is very attractive additive in such an aspect.

In this study, the effect of PLA on pulp handsheet strength properties was investigated combining with other parameters such as heat pressing temperature, time, and pulp type.

# EXPERIMENTAL

## Materials

*Pulps*

As shown in Table 1, three unbleached laboratory kraft southern pine pulps (KP) and a commercial aspen bleached chemithermomechanical pulp (BCTMP) were used in this study. These kraft pulps were made with different kappa number. They were 24.1, 58.3, and 84.3. Their corresponding values of Canadian Standard Freeness (CSF) were 755ml, 760ml, and 765ml. The brightness and CSF of the Aspen BCTMP were 83.3% ISO and 255ml, respectively. All tests conducted were based on the TAPPI test standards [8].

*Chemicals*

Poly (DL-Lactide) with a molecular weight of 75,000-120,000 was purchased from Aldrich-Sigma, Inc. PLA solution was prepared by dissolving 10 grams of polymer in 500 ml chloroform and the solution was stored at 0°C.

*Handsheet*

Handsheets were prepared according to Tappi Standard Method T220sp-01 and T262 sp-02 [8]. The handsheets from BCTMP were made with and without white water to evaluate the effect of BCTMP fines on sheet strength properties. All handsheets were air-dried in a moisture-control room for 24 hours before testing.

*Handsheet conditioning and heat pressing*

Handsheet conditioning: The handsheet was immersed in a proper amount of the PLA solution for 5 minutes, and then taken out and air-dried in a hood.

Heat pressing: The handsheet was pressed by heat pressing equipment. The heat pressing was carried out at 25, 60, 95, 130, 165, and 190 °C under 2296 kPa for 5 minutes.

*Physical strength testing*

Handsheets were tested for tensile, burst and tear strength according to Tappi Standard Method T494 om-96, T403 om-97, and T414 om-98 [8

**Table 1. The characteristics of the original pulps**

| Pulp type | Kappa number | CSF ml | Residual lignin,% | Brightness % ISO | Bulk $cm^3/g$ | Density $g/cm^3$ | Opacity % |
|---|---|---|---|---|---|---|---|
| KP | 24.1 | 755 | 3.61 | | | | |
| KP | 58.3 | 760 | 8.75 | | | | |
| KP | 84.3 | 765 | 12.64 | | | | |
| BCTMP | - | 255 | | 83.3 | 1.96 | 0.51 | 79.5 |

# RESULTS AND DISCUSSION

## Effects of PLA charge and heat pressing

The effects of PLA and heat pressing on pulp handsheet (kappa number 58.3) strength were investigated and the results are shown in Fig.1. From Fig.1a and 1b, regardless of heat pressing or not, the tensile and burst strengths of the handsheet can be significantly improved by the addition of PLA, The handsheet tensile strength increase represents the fiber bonding strength increase. Based on the Derek Page Equation [9], shear bond strength between fibers and the relative bonded area in a handsheet are two critical factors contributed to tensile strength of the handsheet. At most probability, the tensile and burst strength improvement obtained from the addition of PLA is from the increased bonds between fiber-polymer. Tear strength is mainly affected by fiber strength. Thus, the addition of PLA has evident effect on the tear strength as shown in Figure 1c.

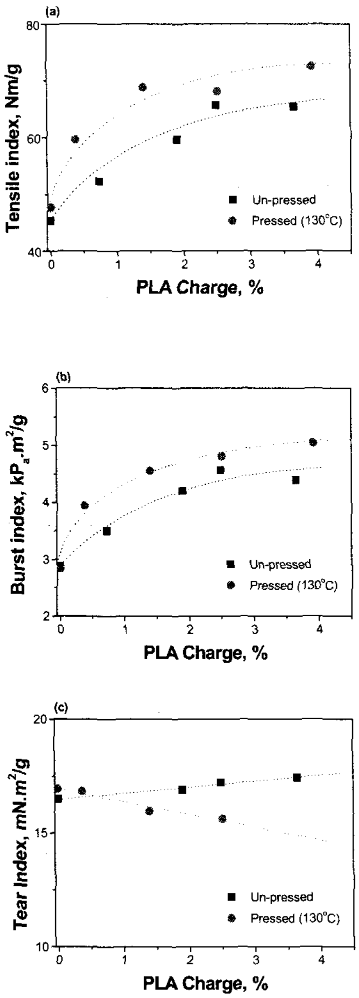


**Fig. 1. Heat press effect on the strength properties of the handsheet (2296 kPa for 5 minutes)**

The data in Fig.1 also showed the sheet tensile and burst strength improvement by heat pressing with the presence of PLA. As reported [10], fibers would create great larger bonding areas due to more flexible of cellulose fiber under heat and pressure. Accordingly, such a treatment should be mainly responsible for the fiber bonded area increase and therefore the fiber bonding strength increases. Similarly, heat pressing on tear strength of the handsheet can also be neglected as shown in Fig. 1c.

According to Fig. 1, about 50 % increase in both tensile and burst strength of the handsheet with 1% of PLA charge and with heat pressing can be achieved compared with that without heat pressing.

## Effects of heat pressing temperature, time and pressure

As discussed, the role of PLA in handsheet is to increase fiber bonding, which leads to the improvement in handsheets strength properties. It is known that the glass transition temperature is about 60 – 80 °C for PLA and less than 130 °C for lignin, and the softening temperature of hemicellulose in pulps is much lower than that of lignin [10]. Therefore, a higher heat pressing temperature above the glass transition point of PLA will greatly increase the softness and flexibility of the fiber and therefore increase the fiber bonding opportunities in the handsheets. As expected, the tensile strength of the handsheets increases with a higher heat pressing temperature applied as shown in Fig. 2a. At such high pressing temperatures, the softened hemicellulose and retained PLA in flexible fibers will easily spread or "flow" around under pressure. As a result, both bonding area and bonding strength will increase, leading to the sheet strength improvement. The higher the heat pressing temperature is, the larger the fiber bonding areas should be, and the more the sheet tensile strength improvement will obtain, which is represented by the experimental data in Figure 2a. With the limitation by the current heat press facility used, we were not able to conduct a testing by reaching a heat press temperature at above 200°C.

However, the effect of pressing time and pressure on sheet tensile strength did not vary linearly as shown in Figure 2(b, c). At a constant temperature of 130°C around lignin transition point, an optimal point for the tensile strength improvement in both cases were all observed which were 5 minutes and pressure of about 2296 kPa respectively. Both too long and over pressing would result in the reduction of sheet elongation or even crush. Therefore, appropriate pressing time and pressure are needed to obtain best strength improvement from heat pressing.

 

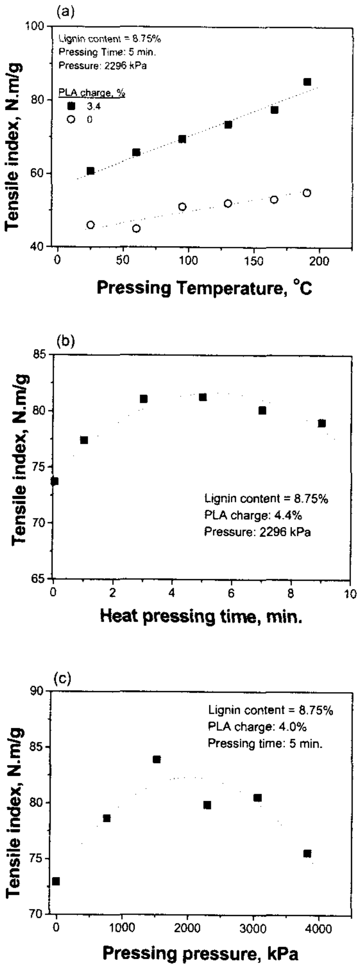


**Fig. 2. Effects of heat press conditions on the strength properties of the handsheets**

## Effect of pulp kappa number

For unbleached softwood kraft pulp, the residual lignin in pulp is the major source that contributes to the kappa number. Therefore, kappa number is an important parameter that indicates the degree of delignification in chemical pulping. With a higher amount of residual lignin remaining in pulps (a higher pulp kappa number), the strength and stiffness of an individual fiber are much higher. That will result in much less bonding areas and weaker bonding strength between fibers, and finally in worse tensile and burst strength of the paper sheet before heat pressing [11]. Among the three pulps in this study, the tensile and burst strength of the pulp (kappa number 24.1 and 3.61% lignin) should be the highest, and that of the pulp (kappa number 84.3 and 12.64% lignin) should be the lowest. But as shown in Fig. 3a, with the absence of PLA there is no significant difference in the tensile strength of the handsheets for the pulps with kappa number of 24.1 and 58.3, respectively. It can be explained that the bonding strength of the sheet could be further improved by heat pressing and the enhancing effect is dependent on the amount of hemicellulose and proper lignin content remaining in the pulp [10]. We can find that the pulp of medium kappa number (58.3) had the most improvement especially in the range of 0.5-2% PLA usage among the three pulps.

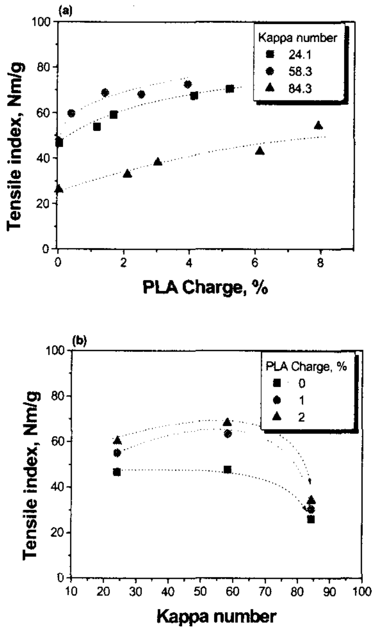


**Fig. 3. Effect of pulp kappa number (heat press temperature at 130°C)**

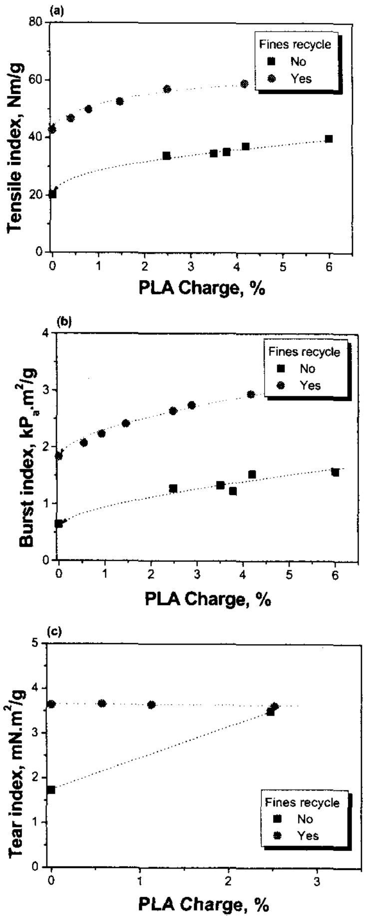


**Fig. 4. Strength comparison for the handsheets with/without fines recycling, and PLA effect (heat press temperature at 130°C and 2296 kPa for 5 minutes)**

## Effect of fines in BCTMP

Since the fiber length of mechanical pulps are much shorter than that of chemical pulps, there is a relative large amount of fines remaining in the white water during BCTMP handsheet making. As shown in Fig. 4, the fines play a very important role in the strength improvement if compared with the handsheets having a limited amount of fines.

It is interesting to note that PLA has an independent effect on both tensile and burst strength improvement regardless of recycling the fines or not during the handsheet making process (Fig. 4a and 4b). However, it seems that PLA could compensate a part of the tear strength loss caused by fines escaping during the handsheet making without white water recycling, as shown in Fig. 4c. From the figure, we can also find that the PLA effect on tear strength improvement is not significant for the BCTMP handsheet with fines recycling.

## Effect of handsheet thickness

The sheet thickness is a required parameter for some paper and paperboard grades. The effect of sheet thickness on strength improvement by applied PLA was also studied in this experiment. Four different thickness handsheet samples were made with the same kind of pulp of kappa number 58.3 by varying their basis weight in hanndsheet making. The results are presented in Figure 5.

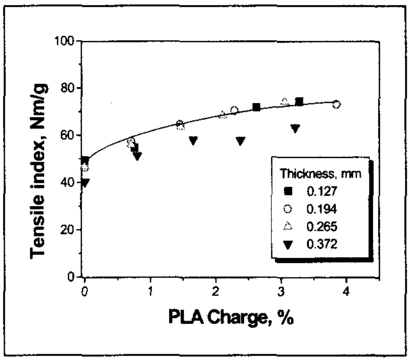


**Fig. 5. Effect of handsheet thickness (kappa number 58.3, heat press temperature at 130°C and 2296 kPa for 5 minutes)**

Clearly, with a thickness of handsheet below 0.265 mm, the handsheet strength difference in the presence of PLA can be neglected. For a handsheet with a larger thickness (0.372 mm), its tensile strength rise trend with added PLA is the same as that for lower sheet thickness. But the final sheet strength is consistently lower than that of lower thickness sheet, which is mainly caused by the sheet thickness difference. Therefore, the sheet thickness does not change the PLA strengthening effect.

## PLA/heat pressing effect on other properties

As known, pressing will reduce the sheet brightness and raise the density due to the decrease of the void fraction within the sheet. The same observation was obtained from the data in Table 1 for PLA application in Aspen BCTMP. One of the major properties for the sheet made from high yield pulp is its high bulk property. The data in Table 2 shows that the addition of PLA coupled with heat pressing can lead to some further increase for the density, which is probably caused by the increased bonding from applied PLA. As bulk is equal to the reciprocal of density, for those sheets requiring very high bulk or thickness, this will be a little trade-off for the application of PLA to achieve strength improvement.

**Table 2. PLA/heat press effect on other properties**

| Handsheet type | Density, $cm^3/g$ | Brightness, % ISO |
|---|---|---|
| Original | 0.48 | 83.3 |
| Heat Pressed | 0.58 | 80.8 |
| PLA* + Heat pressed | 0.63 | 80.4 |

*** PLA charge: 2.48 %**

## CONCLUSIONS

The strength properties of handsheets from unbleached kraft pulps and Aspen BCTMP with addition of PLA coupled with heat pressing have been investigated. It was found that 0.5-4% addition of PLA can greatly improve the tensile and burst strength of the handsheets. However, its effect on tear strength improvement is not significant. Heat pressing can increase the tensile and burst strength. It was also found that the optimal conditions for the strength improvement at the temperature of 130 °C and heat press pressure of about 2296 kPa for 5 minutes. For unbleached kraft pulps, an appropriate amount of residual lignin in pulps is great helpful on the strength improvement of the handsheets at the presence of PLA, and thickness of the handsheet does not change the PLA strengthening effect. For the Aspen BCTMP handsheets, fines play an important role in the strength properties and do not affect PLA enhancing effect. However, with the addition of PLA the tear strength loss due to an insufficient amount of fines maintained in the BCTMP handsheets can be partly compensated. Furthermore, the addition of PLA coupled with heat pressing can reduce the brightness and bulk of the final handsheets.

## LITERATURE CITED


1. Bogaert, Jean-Christophe; Coszach, Philippe, "Poly(lactic acids): a potential solution to plastic waste dilemma". *Macromolecular Symposia (2000)*, 153(Recent Advances in Ring Opening (Metathesis) Polymerization), 287-303.
2. Datta, R., Tsai, S., Bonsignore, P., Moon, S., and Frank, J., "Technological and economic potential of poly(lactic acid) and lactic acid derivatives." *FEMS Microbiology Reviews*, 16:221-231, 1995.
3. Verespej, Michael. "Winning Technologies: Polylactic Polymers." *Industry Week*, December 11, 2000.
4. Harper, Charles A., *Modern Plastics Handbook*, New York: McGraw-Hill, 2000.
5. Leaversuch, Robert, "Renewable PLA polymer gets 'green light' for packaging uses", *Plastics Technology*, (3):50-55, 2002.
6. Kelly, W; Gupta, A., "Polylactic Acid Is Versatile, Engineerable Material", *1997 Polymers, Laminations & Coatings Conference*, Toronto, Ontario, Canada, 145-148.
7. Page, D.H., A theory for the Tensile Strength of Paper, *Tappi*, 52(4), 674-681, 1969.
8. *2002-2003 TAPPI TEST METHODS*, TAPPI PRESS, Atlanta, Georgia, USA, 2002.
9. Gumagul, N., Ju, S., Page, D. H., "Fiber-fiber bond strength of once-dried pulps", *Journal of Pulp & Paper Science*, (3):88-91, 2001.
10. Richard A. Horn, "Bonding in Press-dried Sheets from High-yield Pulps", *TAPPI*, 62(7):77-80, 1979.
11. G. A. Smook, *Handbook for Pulp & Paper Technology*, 2nd edition, Angus Wilde Publications, 1992.