Chemical Industry & Chemical Engineering Quarterly

Available on line at
Association of the Chemical Engineers of Serbia *AChE*
www.ache.org.rs/CICEQ

Chem. Ind. Chem. Eng. Q. 21 (1) 107–112 (2015) CI&CEQ

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SCIENTIFIC PAPER

UDC 676.2.014:547.992

DOI 10.2298/CICEQ131205012S

IMPROVEMENT OF LINERBOARD COMPRESSIVE STRENGTH BY HOT-PRESSING AND ADDITION OF RECOVERED LIGNIN FROM SPENT PULPING LIQUOR

Article Highlights

- The use of acid precipitated lignin can constitute an economic benefit
- Lignin use in cardboard manufacturing increases the compressive strength by 20%
- Addition of lignin recovered at the mill will reduce the linerboard basis weight by 10%

Abstract

This paper evaluates the effect of addition of precipitated lignin, from spent pulping black liquor, to a wet single-ply linerboard handsheet followed by hot-pressing at different temperatures, on the improvement of its compressive strength. Linerboard handsheets for testing the effect of lignin addition were prepared so that the lignin-modified sheets would have the same basis weights as the control handsheets. Both the commercial and the black liquor lignin were added as a powder to wet handsheets after couching from the handsheet mold. The experiments and testing of the physical and strength properties of dried handsheets were conducted according to TAPPI test methods. The results revealed that the addition of the recovered lignin (at pH of 2) to the wet handsheet followed by hot-pressing at 150 °C increased the compressive strength of linerboard handsheets by 10 to 20% above that for handsheets made without the addition of lignin. The same results were achieved using purchased lignin. However, with a 16% addition to linerboard, purchased lignin would be too expensive. These results indicate that inclusion of kraft lignin in linerboard sheets could be proved as an attractive option to reduce linerboard basis weight.

Keywords: lignin, compressive strength, linerboard, black liquor, kraft pulp.

Lignin, the most abundant aromatic biopolymer in the eco-system, is an amorphous hydrophobic polymer and is fundamentally random in its phenolic polymer structure [1,2]. It is estimated that lignin forms 30% of the earth's non-fossil organic carbon [3].

Lignin has several applications, which includes its use with formaldehyde as an adhesive resin [4], as an antioxidant stabilizer in polymer formulations and emulsions [5,6] and as a flame retardant additive [7]. Although it is utilized in a wide range of products, only 1 to 2% of the kraft lignin, which is produced as a by-product from the paper and pulp industries, is commercially used [8]. Generally, lignin can be recovered from black liquor either by ultrafiltration or precipitation. However, acid precipitation is currently the most common method employed for lignin recovery from spent pulping liquor [9,10].

In the papermaking industry, there is a need to improve the containerboard qualities because of its wide use in the packaging market. Linerboard is usually a two-layer sheet with the bottom layer giving strength and the top one providing appearance. The properties of the linerboard depend on the furnish

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Paper received: 5 December, 2013
Paper revised: 30 April, 2014
Paper accepted: 7 May, 2014

(type of fiber chemical additives and fiber treatment), which commonly ranges from 100% virgin softwood kraft fiber to 100% recycled fiber. A primary determinant of the performance of containerboard is the compressive strength as measured by short-span compressive (STFI) tests. In particular, the cross--direction (CD) compressive strength is critical not only because of the weaker direction but due to the fact that stacking load of corrugated boxes takes place in vertical direction which is the CD direction of the board. Various studies have been conducted on the cardboard qualities, where the findings of these studies reported that cardboard is a very sensitive material and can lose rigidity depending on environmental conditions [11,12].

According to the literature, several methods have been used to increase the stiffness and compressive strength of manufactured linerboard and corrugating medium. Anderson and Back [13] proposed a method of heat treatment of corrugated board that involved blowing hot air at 190 °C through stacks of board. The process improved the wet compression strength by a factor of 2 to 3 and gave a wet stiffness of 25 to 30% of the dry value. The original system design was for an enclosed chamber, where stacks of board could be heat-treated and then cooled with a cycle time of 100 min. Such a system would not be practical for a large production facility [13,14]. However, the press drying has been found to be a powerful way to improve compressive strength and creep resistance under high RH [14].

Morgan [15] conducted a series of tests with different methods for increasing the compressive strength of linerboard. The treatments were as follows: addition of CTMP for part of the furnish, addition of Kymene or PVA, additional pressing, and heat treatment of the dry sheet at 140 °C for 40 min. These treatments were tried singly or in combination, with testing at both 50 and 95% RH. All of the treatments were found to increase the short-span compression strength, with the addition of CTMP having the greatest effect, particularly in combination with the heat treatment [15].

Hot pressing technique is widely tested and commercially used for producing high strength linerboards. It is well-known that hot pressing improves compressive strength since at high temperature and moisture content lignin melts and acts as fiber bonding materials. However, there are few reports on the vital role of lignin as a natural adhesive and its addition influence on containerboard's compressive strength and other mechanical properties [16].

In this context, the main objective of this study was to investigate the use of acid-precipitated lignin from black liquor as a natural adhesive, which was added as dry powder for the first time to wet linerboard sheet followed by hot-pressing at laboratory scale, to improve the compression strength of linerboard.

EXPERIMENTAL

Materials

The samples used in the present study were Virgin unbleached softwood kraft (USK) pulp, kappa number 100, from Inland Container, USA, and black liquor (provided by Lignotech AB, Sweden) were provided by a nearby cardboard and paper making company.

The pH and consistency of the kraft pulp stock were 5.2 and 0.43%, respectively. The softwood unbleached kraft pulp stock was refined in a Valley Beater to a freeness of 420 ml (CSF).

The black liquor was characterized in terms of pH and total dissolved solids (TDS). The pH of 12.43 was determined using a digital pH-meter. The black liquor TDS of 5.8% was estimated according to TAPPI standard test method T-650 pm-84.

Two types of commercial lignin were used in the study: A water-soluble sulfonated kraft lignin (Polyfon O FB14, lignosulfonic acid, sodium salt) and an unsulfonated Kraft lignin (INDULIN AT, heterogeous guaiacylpropane polyether), where both of them were purchased from MeadWestvaco.

Methods

Lignin recovery from black liquor

Two liters of black liquor were treated with 4 N H_2SO_4 to obtain different pH values of either 8 or 2. Acid-precipitated lignin was centrifuged at 3000 rpm for 15 min, filtered, washed thoroughly with distilled water to remove impurities, and then followed by freeze-drying at −25 °C for 45 min to remove the acidified water.

Handsheet preparation

Standard 159 mm diameter single-layer control handsheets were manually prepared, without additives addition (similarly to TAPPI T205 procedure) using a handsheet former (Model SCA Type, Fibretec Instruments, India), at a basis weight (grammage) of 238 to 245 g/m^2. This results in good rigidity of commercial containerboard and satisfies other requirements such as the degree of z-strength of the containerboard. Sheets for testing the effect of lignin addition were prepared at grammage ranging from approximately 153 to 205 g/m^2. After the addition of this lignin, the lignin-modified sheets have approximately the same basis weights as the control handsheets (238 to 245 g/m^2).

Both the commercial and acid-precipitated lignin were added as a powder, using stainless steel fine mesh powdered lignin shaker, to the wet handsheets (80 to 90% moisture content) after couching from the handsheet mold and before any pressing step. The resulting sheets were then consecutively pressed in two stages for 5 and 2 min at 3.45 bar at room temperature, during which the lignin powder is subject to two forces. The first one is the perpendicular pressing force which causes the lignin to penetrate through the handsheet structure leading to the redeposition of lignin onto cellulose fibers of the handsheet, while the other force causes the lignin to diffuse via radial flow towards its outer edges causing homogeneous distribution of lignin onto the entire surface of the handsheet. Despite the fact that the pressing step in two stages for 5 and 2 min at 3.45 bar at room temperature is a TAPPI T205 requirement for handsheet preparation for physical test of pulp, this requirement was left out in some preparations. This is to investigate the effects of hot-pressing of handsheets (with an added lignin at higher moisture content (80 to 88%) on the handhseets strength properties.

The 159 mm diameter sheets were then hot--pressed for 10 min at 120, 150 or 200 °C in a computer-controlled heated press (at press load of 3.45 bar) with homogeneous drying in radial direction of the sheet. Prior to physical properties testing, the hot-pressed handsheets were conditioned under conventional conditions (23 °C and 50% RH) for more than 24 h, and consequently its final moisture was expected to be less than 1%. Thirty-five handsheets of each treatment were made and the best thirty handsheets were selected and tested.

Mechanical testing and statistical analysis

The 159 mm diameter dried handsheet were cut into five 6“×15 mm consecutively adjacent strips using a cutter. The strength and other physical properties of strips were measured by clamping the strip between two grips and applying a load until the strip breaks using tensile instrument (model UEC-1005B, India) and short span compression tester (model UEC-1027, India) according to TAPPI T826, TAPPI T494 and TAPPI T414. Sixty four strips were tested for each of tensile and short span compression tests at each testing condition (temperature, % of added lignin, etc). However, the results were statistically presented using ANOVA by means of a table showing the average value of the property (with the least significant difference at the 0.05 level of probability) for each temperature, for each added amount of lignin, and for each added lignin type and treatment. The least significant differences at the 0.05 level of probability were rejected according to the null hypothesis (*i.e.*, unlikely to have occurred by chance alone).

Differential scanning calorimeter (DSC) analysis

Glass transition temperature (T_g) of both commercial lignins and acid-precipitated lignin were determined using a Netzsch 200 F3 Maia DSC. Prior DSC characterization, the lignin samples were dried at 60 °C under vacuum for 12 h. Samples of about 5-10 mg were weighed in the DSC aluminum pan, sealed by lid, and run at a heating rate of 10 °C/min under nitrogen atmosphere up to 160 °C to eliminate any stored thermal history within the lignin's glassy state. Subsequently, the sample was heated to 200 °C at a rate of 20 °C/min to measure the T_g of the lignin sample.

RESULTS AND DISCUSSION

The compression strength of linerboard mainly depends on fiber-fiber bond strength for low and medium densities linerboard. Therefore, it is reasonable to expect that the addition of lignin, which acts primarily on improving fiber-fiber bond strength, would be effective in increasing compression strength in low and medium densities boards.

Glass transition temperature

Lignin undergoes thermal softening which affects the thermomechanical properties of the handsheets. Glass transition temperatures are between 90 and 180 °C according to the literature [17,18]. This T_g was associated to hydrogen bonds between hydroxyl groups and to the lignin aromatic nature [19]. In the present work, significant changes were not observed between T_g value of commercial lignin and lignin obtained at lower and higher values pH as shown in Table 1.

Table 1. Glass transition temperature (T_g) values of all different lignin types used in this study

Lignin type	T_g / °C
Sulfonated kraft lignin (POLYFON O FB14)	112.7
Unsulfonated kraft lignin (INDULIN AT)	115.3
Acid-precipitated lignin at pH 2	106.2
Acid-precipitated lignin at pH 8	108.6

Effect of lignin addition and hot-pressing temperature

Handsheets prepared through wet pressing as per TAPPI 205 standard procedure, where the moisture content of handsheet after standard pressing is less than 80%, without and with 15.7% weight sulfonated lignin (POLYFON), were hot-pressed at 3.45 bar for 10 min and at three temperatures (120, 150 and 200 °C).

The pressing temperature values were higher than all types of lignin's T_g values listed in Table 1. As shown in Table 2, the strength results are given as compressive strength and tensile strength, divided by basis weight so as to eliminate the effect of the varying basis weights of the tested handsheets.

The compression strength index was found to increase by about 5% at 120 °C and 22% when pressed at 150 °C. This indicates that the incorporation of lignin overcomes the fiber matrix discontinuity. Moreover, when lignin is added to the handsheet, it can act as plasticizer or stiffener while filling the pores space of fibers. Hence, it is expected to increase the fiber stiffness as a consequence of pore closure during hot-pressing and drying.

However, increasing the pressing temperature to 200 °C had only caused a 17% increase in the compression strength index, which did not result in any additional gain in comparison with the results at 150 °C. This is perhaps due to the degradation of the lignin-hemicelluloses matrix caused by the cleavage of the covalent bonds between hemicelluloses fiber and lignin at high pressing temperatures (*i.e.*, 200 °C). Moreover, the thermoplastic behavior of lignin might be restricted by the secondary intermolecular bonding with the fiber. Therefore, at high pressing temperatures the secondary intermolecular interactions are affected and this adversely influences the lignin plasticization behavior.

On the other hand, the added lignin decreased the tensile index by about 10%, because there was a small amount of fiber in the lignin-added sheets made at the same total basis weight. Hence, lignin bears load under compressive loading but not under tensile loading.

Effect of hot-pressing of adding commercial lignin at high initial moisture content

Additional handsheet tests were done by adding lignin to the wet handsheet, which prepared without the standard pressing as prescribed by TAPPI 205 procedure. In this case, the moisture content of the sheet with the added lignin was much higher (80 to 88%) prior to the hot-pressing at 3.45 bar and 150 °C for 10 min. Both the soluble lignin (POLYFON) and the insoluble lignin (INDULIN) were used in order to explore the effect of lignin sorption mechanism on the handsheet properties regardless if the adsorbed lignin on the fiber surface or imbibed into pores. The results are shown in Table 3, where the sheet density and compression strength of the control are lower than in the previous tests because of the absence of the standard handsheet pressing. However, the addition of nearly 20% weight lignin increased the compressive strength index significantly by about 47% for the water-soluble lignin and 72% for the insoluble lignin.

Effect of adding precipitated black liquor lignin at high moisture content

Another source of lignin, which was precipitated directly from black liquor, was also tried as an additive to the handsheets. The handsheets (with moisture content of 80 to 88%) in this case did not have the two-stage standard pressing and were only hot-pressed for 10 min at 3.45 bar and 150 °C after the lignin addition. As shown in Table 4, the increase in lignin addition increases the compression strength. For instance, at 16% addition, the compression strength increased around 20%. The effect was the same as that achieved with commercial lignin products. As in the previous tests with added lignin, there was a reduc-

Table 2. Effect of commercial lignin addition and hot pressing temperature on handsheet strength properties; hot-pressed at 3.45 bar for 10 min (moisture content < 80%); L.S.D is the least significant difference at the 0.05 level of probability

Hot pressing temperature, °C	Average lignin added, %	Basis weight g/m^2	Density g/cm^3	Average short span compression index[a], N m/g	Average tensile index[a], N m/g
120	0	243	733	37.2	67.3
150	0	238	656	38.4	71.2
200	0	245	595	36.5	69.6
120	15.7	238	710	39.1	60.3
150	15.7	239	660	47.0	64.9
200	15.7	244	562	42.7	58.9
$L.S.D_{0.05}$	-	-	-	1.09	1.42

[a]Each value is an average of sixty samples

Table 3. Effect of addition of different commercial lignin on handsheet strength properties; hot-pressed at 3.45 bar for 10 min at 150 °C (moisture content < 80%); L.S.D is the least significant difference at the 0.05 level of probability

Sample	Average lignin added %	Initial moisture content[a], %	Basis weight g/m^2	Density, g/cm^3	Average short span compression index[b], N m/g
Control	0	87.9	240	484	28.8
Soluble lignin	18.8	81.0	200	478	42.4
Insoluble lignin	19.7	84.2	191	455	49.6
$L.S.D_{0.05}$	-	-	-	-	1.09

[a]Initial moisture content prior to two stages for 5 min and 2 min at 3.45 bar at room temperature; [b]each value is an average of sixty samples

Table 4. Effect of addition of different pH acid-precipitated lignin on handsheet strength properties; hot-pressed at 3.45 bar for 10 min at 150 °C (moisture content < 80%); L.S.D is the least significant difference at the 0.05 level of probability

Sample	Average lignin added, %	Basis weight g/m^2	Density g/cm^3	Average short span compression index[a], N m/g	Average tensile index[a], N m/g
Control	0	239	607	37.4	73.4
Black liquor lignin pH 2	10	239	550	40.8	59.7
Black liquor lignin pH 2	15.7	240	572	45.0	58.8
Black liquor lignin pH 8	15.6	239	560	42.7	61.6
$L.S.D_{0.05}$	-	-	-	1.09	1.42

[a]Each value is an average of sixty samples

tion in tensile strength due to the lower amount of fibers in the handsheets with added lignin at the same total basis weight.

Interestingly, it is noticed that the overall densities of the control and lignin-modified sheets decrease as the hot pressing temperature increases, and specifically as the compressive stress was released. This springback of handsheet causes substantial and sudden overall handsheet density loss as described in the previous research [20-22]. The Handsheet springback is temperature-dependent based on visco-elasticity theories, where the relaxation time and relaxation behavior strongly depend on temperature levels. For instance, at high temperature, the relaxation time has a rather a small value, and consequently the rapid relaxation behaviour causes a strong springback effect that leads to sudden overall sheet density loss within milliseconds [22]. In the case of lignin-modified sheets, the increase of temperature more than the T_g of lignin will activate the effect of visco-elasticity and this will lead to higher relaxation effect and subsequently lowers the density of the lignin-modified sheets.

As reported in the literature, some color changes of the acid-precipitated lignin at different pH values can be observed due to occasional association of macromolecules (chromophoric functional groups including carbonyl groups, carboxylic acids, phenolic hydroxyl groups, etc.) [23]. In the present work, the presence of impurities in the raw material, mainly hemicelluloses and silicates might lead to darker color of lignin at a relatively higher pH value (8) [19,24]. Hence, the presence of these impurities has influenced the mechanical qualities of the handsheets. This is clearly shown in Table 4, when comparing the compression strength and the tensile strength of the handsheets two pH values (2 and 8) of both black liquor lignin. The presence of hemicelluloses and silicates at black liquor lignin pH value of 8 has increased the tensile strength and decreased the compression strength.

CONCLUSIONS

In this present sutdy, the aim was to evaluate the effect of the addition of lignin as a dry powder to a wet linerboard handsheet followed by hot pressing for the enhancement of its compression strength. The results of the present research show that the addition of the recovered lignin from the black liquor to the wet handsheet (approximately 80% initial moisture content) followed by hot-pressing at 150 °C was generally more effective in improving the compression strength of linerboard handsheets.

One of the significant findings of this study was that when lignin had an effect on the compression strength at 16% addition, the compression strength increased 20%. However, the basis weight reduction of the linerboard is recommended to be investigated in future work.

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NAUČNI RAD

POBOLJŠANJE KOMPRESIVNE JAČINE RAVNOG KARTONA PRESOVANJEM NA TOPLO I DODATKOM LIGNINA IZDVOJENOG IZ CRNOG LUGA

U ovom radu je ispitan uticaj dodavanja lignina istaloženog iz crnog luga iz proizvodnje papira vlažnom ravnom kartonu koji je zatim presovan na različitim temperaturama na njegovu čvrstoću pri pritisku. Kartoni na kojima se testira efekat dodavanja lignina su pripremljeni tako da listovi modifikovani ligninom imaju iste osnovne težine, kao i kontrolni listovi. I komercijalni i lignin dobijen iz crnog luga se dodaju u obliku praha na vlažne listove posle formiranja lista u kalupu. Eksperimenti i testiranja fizičkih osobina i otpornost prema kidanju na suvim listovima izvršeno je u skladu sa TAPPI test metodama. Rezultati su pokazali da dodavanje lignina dobijenog iz crnog luga (pri pH 2) na vlažni list koji je posle presovan na toplo na 150 °C povećava kod listova čvrstoću pri pritisku za 10 do 20% u odnosu na listove kojima nije dodavan lignin. Isti rezultati su postignuti korišćenjem komercijalnog lignina. Međutim, dodatak 16% komercijalnog lignina bilo bi preskupo. Ovi rezultati ukazuju da je korišćenje kraft lignina jedna atraktivna opcija kojom se smanjuje osnovna težina kartona.

Ključne reči: lignin, čvrstoća pri pritisku, lineri, crni lug, Kraft pulpa.