

# The Study on Urea-Lignin Copolymer Adhesive from Kraft Black Liquor for Plywood Manufacturing\*<sup>1</sup>

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## Kraft Pulp 廢液을 利用한 合板用 尿素 Lignin 接着劑 研究\*<sup>1</sup>

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### 요 약

接着劑 製造를 위하여 펄프廢液중의 리그닌을 利用하는 研究가 1930年頃부터 進行되어 아황산 펄프廢液중의 Lignosulfonate 의 경우는 페놀樹脂나 尿素樹脂에 增量시키거나 反應시키는 研究인데 비하여 kraft 리그닌을 利用하는 경우는 페놀樹脂의 報文이 主流를 이루고 있으나 尿素系 共縮合樹脂는 아직 發表된 바 없으며 또한 아직까지 리그닌을 利用한 商業的인 接着劑가 製造되어 活用되지 못하고 있는 實情이다.

따라서 本 研究는 合板製造의 原價節減, 廢液利用의 環境保存觀點에서 Kraft Pulp 廢液중의 리그닌을 Urea-Formaldehyde 와 共縮合反應시켜 靛存 尿素樹脂보다 良好한 接着強度를 지닌 요소-리그닌接着劑의 製造하고자 實施하였으며, Urea-Lignin 接着劑의 塗布量은 一般的으로 合板에 塗布되는 尿素樹脂의 量(320 g/cm<sup>2</sup>)과 同一하고 壓搾壓力은 均一하게 12kg/cm<sup>2</sup>으로 하여 熱壓條件(溫度, 時間)의 影響을 아울러 糾明하였다. Urea-Formaldehyde 와 Kraft lignin 의 混合比는 重量比(N.V.C)로 7:3으로 合成樹脂를 만들어 合板製造를 通하여 究明을 結果 다음과 같은 結論을 얻었다.

1. 本 實驗의 結果 尿素樹脂의 約 30%가 kraft lignin 으로 代替할 수 있음을 보여준 바, Pulping 工程의 副產物로 얻어진 廢液은 合板製造時 接着劑의 代替源으로 有效하다.
2. 經濟的觀點에서 合板製造를 위한 最適熱壓條件은 160℃에서 3分으로 壓搾하는 것이 適切하였다. (常態) : 16.49kg/cm<sup>2</sup>, 耐水 : 18.56kg/cm<sup>2</sup>, 耐溫水 : 12.53kg/cm<sup>2</sup>)
3. 요소-리그닌 接着劑로 製造된 合板의 剪斷引長強度는 良好한 接着力을 나타냈으며, 耐水接着力(30℃에서 3時間 沈積後 試驗)은 常態接着力과 別차이가 없거나 더 높은 引長強度力을 보여준 바, 耐水合板用 接着劑로 상당한 展望을 나타냈다.

### 1. Introduction

Chemicals, synthetic resins, binders, adhesives, and coatings manufactured from petrochemicals and natural gas derivatives are becoming more and

more important.

Petroleum-based synthetic binders, phenolic and urea-formaldehyde resins, are largely used to produce wood-based panels such as plywood, particleboard, fiberboard, and waferboard.

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The plywood and particleboard industries are confronted with soaring production costs, in which adhesive cost constitutes about 30% for plywood and about 50% for particle board (Ramos, 1980).<sup>13)</sup> Adhesives are very expensive because they are currently synthesized from petrochemicals.

Furthermore, during the 1970s, the energy crisis and the gloomy forecast of depleted fossil fuel resources by early in the 21st century made the researchers in industry, academia, and government concentrate their effort in investigating the utilization of biomass as an alternative energy resources. One such effort is the utilization of spent black liquor which is produced as a by-product in the pulping process.

Each year, tremendous amount of black liquor, about 9,300,000 ton worldwide and about 200,000 ton in Korea, is produced in the pulp and paper industries. It has been burned to recover pulping chemicals and to be used as fuel, or dumped into waterways resulting in water-pollution. (Cho, 1987).<sup>18)</sup>

Kraft black liquor is an exceedingly complex mixture of spent inorganic chemicals, wood extractives, carbohydrates, degradation compound (principally saccharinic acid), and lignin in the form of kraft lignin or alkali lignin. (Mere-wether, 1962).<sup>11)</sup>

Lignin could be extracted from black liquor by acids such as carbon dioxide ( $\text{CO}_2$  gas) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ). (Browning, 3 1967).<sup>3)</sup> Therefore, the spent black liquor is one of the important sources of lignin, and has great potential for the replacement of expensive petroleum-based materials.

Kraft lignin can be used as dispersing, fuel, and stabilizing agents as adhesives in rubber, resins, and plastics. Condensation of lignin with formaldehyde and cross-linking with phenols may yield thermosetting polymers useful as adhesive for wood-based panels. However, commercial utilization of lignin is limited because its physical and chemical characteristics have great variation

and are not completely known yet. (Sjöström, 1981).<sup>15)</sup>

Recently, spent black liquor has received extensive attention as an ingredient for cheaper adhesives because concentrated waste black liquor has adhesion properties, which is partially due to the sticky gums. (Allan, 1979).<sup>1)</sup>

Utilization of lignin as an adhesive for wood-based panels has been continuously increased in the world. However, it has been limited to the cases of the phenol-formaldehyde and urea-formaldehyde resins with spent sulphite liquor and phenol-formaldehyde resins with the kraft black liquor.

The objectives of this study are to investigate the possibility of utilizing the lignin extracted from spent kraft black liquor as the Urea-Lignin Copolymer Adhesive for plywood, the properties of the adhesive, and the plywood manufacturing conditions such as hot-pressing temperature and time.

## 2. Materials and Methods

### 2.1 Materials

#### 2.1.1 Spent Kraft Black Liquor

Spent Kraft Black Liquor used in this experiment was obtained from Dong Hae Pulp Co., Ltd.

Initially, the solid content of spent black liquor was about 15 to 23%. The liquor was concentrated in Multiple Effect Vaporators to solid contents about from 50 to 70% in order to achieve proper burning of the organic substance in the recovery furnace.<sup>14)</sup>

The physical properties of spent black liquor are shown in Table 1.

The physical properties of each solution were measured by the following methods.<sup>10)</sup>

- Specific Gravity (KS M3707): Pycnometer
- pH (KS M3712): Glass Electrode pH Meter

Table 1. Properties of concentrated spent black liquor.

	Sp. Gr (at 25°C)	PH (at 20°C)	Viscosity (at 25°C, cp)	N.V.C. (%)	Ash content (%)
Black Liquor	1.13	12	260	61	32

- Viscosity (KS M3708): Brookfield Synchro-Letric Viscometer
- Nonvolatile content (KS M3709): About 1.5g of black liquor was dried in a drying oven at 105°C for 3 hours, and the following formula was used to calculate the content;

$$N = D/S \times 100 (\%)$$

where, N: Nonvolatile Content of the sample, %

D: the weight of the sample after drying, g

S: the weight of the sample before drying, g

- Ash content (American Can Company Method Analytical Procedure 5.51).<sup>9)</sup>

The procedure includes firing at 800°C for 20 minutes. The ash content was calculated according to the following equation;

$$A = C/B \times 100 (\%)$$

where, A: the content of the sample, %

B: the weight of the sample before firing, g

C: the weight of the ash residue, g

### 2.1.2 Preparation of veneer

Veneers used to manufacture three-ply plywood in this study were Kapur rotary-cut veneers taken from the Dae Sung Wood Industry Company.

Characteristics of veneers are shown in Table 2.

### 2.1.3 Adhesive

The adhesives were prepared in the laboratory. The raw materials for adhesives were Urea, Formaldehyde (37%), Spent kraft black liquor,

Table 2. Characteristics of Veneer.

Specific Gravity	: 0.7
Species	: Kapur (Dryobalanops spp)
Size (mm)	: 250 x 250
Thickness(mm) core	: 2.5
face and back	: 1.15
Moisture Contents(%)	: 10-12

NaOH, Oxalic acid, and Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>).

As an extender, wheat flour was added to the resin. The amount was 20% of the total weight of the resin.

Ammonium Chloride (NH<sub>4</sub>Cl) was used to accelerate the hardening of the resin.

The amount was 0.5% of the total weight of the resin.

## 2.2 Experimental Procedure

### 2.2.1 Preparation of Kraft Lignin

The lignin can be recovered from the black liquor by acid precipitation using the chemicals such as sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and Carbon dioxide (CO<sub>2</sub> gas) from the black liquor, although any others may be used.<sup>19)</sup>

The lignin differs from the other constituents of the black liquor. Lignin is not water-soluble, hence, acidification offers a means of separating the lignin from the other constituents. Acidification of black liquor precipitates only the lignin, while the other constituents remain in solution.<sup>11)</sup>

In this experiment, the spent black liquor was gradually acidified to pH 8 by adding concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) while stirring at high speed (about 3,000rpm), and then Kraft Lignin was precipitated by heating for two hours. The

agglomerated lignin substance was cooled, filtered and washed with water in order to obtain the lignin material in the original liquor. The masses that may be removed are unreacted soluble wood sugars and their derivatives.<sup>1)</sup>

The ash content of the solids was 10% which was determined by American Can Company Method Analytical procedure 5.51. When the kraft lignin is recovered from the spent black liquor in dry condition, it generally is in the form of an amorphous brown powder.

Kraft lignin is the term for a polydisperse, branched phenolic macromolecular composite derived from native lignin in the kraft pulping process and isolated by precipitation with acid from the black liquor. It has a variety of functional groups, high thermal stability, and high heat value. It is highly reactive in various reactions involving the hydroxyls or the phenolic structure.<sup>5)</sup>

### 2.2.2 Adhesive Manufacture

#### 2.2.2.1 Urea-Formaldehyde (U-F) Resin

Preparation of urea-formaldehyde resin (control) is illustrated in Table 3.

The results were listed in Table 7.

#### 2.2.2.2 Preparation of Urea-Lignin-Copolymer Adhesive

In this experiment, modified Urea-Lignin Copolymer Adhesive was manufactured from the Kraft Lignin as illustrated in Table 4. First, Urea

Table 3. Molar ratio and catalyst for manufacturing Urea-Formaldehyde Resin.

Material	Urea (U)	Formaldehyde (F) (37%)	Catalyst
Molar Ratio	1	1.8	10% NaOH 10% Oxalic acid

and Formaldehyde was mixed, then the mixture was reacted at 60°C for 20 minutes. A weight ratio of the Kraft Lignin to Urea-Formaldehyde solution was 7:3 in the ratio of nonvolatile content (N.V.C.). In second stage, the Kraft Lignin was added slowly to the manufactured urea-formaldehyde solution while the mixture was stirred about 2,500 rpm until the Kraft Lignin resolved completely. In third stage, 10% NaOH solution was added until pH of the solution reached 8.5, and it was reacted at 75-80°C for 70-minutes. In fourth stage, pH of the solution was decreased to 5.5-6.0 by adding 10% Oxalic acid, and the solution was reacted at 85-90°C for 50 minutes. In fifth stage, pH of the solution was again increased to 8-8.5 by adding 10% NaOH solution, and the temperature was elevated to 90-95°C, and then reacted for 60 minutes. Finally, the solution was cooled quickly to room temperature in following cool water.

The physical properties of the adhesive manufactured are listed in Table 7.

Table 4. Experimental method of manufacturing Urea-Lignin-Copolymer Adhesive.

State	pH	Chemicals	Temperature(°C)	Time (Min)
1			60	20
2			60	
3	pH 8.5	an aqueous solution of 10% NaOH	75-80	70
4	pH 5.5-6	an aqueous solution of 10% Oxalic acid	85-90	50
5	pH8-8.5	an aqueous solution of 10% NaOH	90-95	60
6	Cooling quickly	Flowing cool water	below 60	

### 2.2.3 Plywood manufacture

The moisture content (M.C) of veneer was adjusted to 5-6% in a drying oven.

The resin was applied to the veneer in the form of solution with a hand brush at the rate of 320g/m<sup>2</sup>.

The veneer were assembled to three-ply plywood and hot-pressed.

In manufacturing the plywood, the pressing temperature and time were varied from 120°C to 180°C and 1 to 8 minutes, respectively, with the fixed pressure of 12kg/cm<sup>2</sup>.

Due to the limitation of the size of Hot Press used, 25 x 25cm plywood was manufactured at one time.

### 2.3 Testing

The mechanical and physical testing was in accordance with the Korean Industrial Standard.

Once the plywood panels were manufactured, they were stored in the laboratory for several days so that they reached E.M.C, with the surrounding air. After conditioning, each panel was cut into 15 shear specimens. In this experiments, KS M3720 method was used to access the strength properties of the adhesives by shear testing of the specimens. Each 15 specimen set cut from one panel was equally divided into three groups, each of which were subjected to the following strength test;

- 1) Dry bond strength test
- 2) Wet bond strength test after soaking in water for 3 hours at 30°C and for 10 minutes at 20°C.
- 3) Wet bond strength test after soaking in water for 3 hours at 60°C.

Each test was repeated 15 times which was considered to be enough to obtain the strength value representing each property.

The failure types of shear specimens were visually observed.

Strength properties were compared between

the plywood specimen glued with the U-F resin and Urea-Lignin Copolymer Adhesive manufactured in the laboratory.

According to the KS standard, Normal Test corresponds to type III plywood, Hot and Cold Water Tests correspond to type II plywood (Interior type). These had a limited level of bond strength of 7.5kg/cm<sup>2</sup> after each test.

To evaluate the level of significance of the results, the data were analyzed by the ANOVA-TABLE and DUNCAN'S MULTIPLE-RANGE Test.

## 3. Results and Discussion

### 3.1 Specific gravities of plywood

It is reported that average specific gravity of plywood increased slightly with the adhesive spread and press processing on veneer in plywood manufacturing. (Lee, 1984)<sup>16)</sup> Shown in Table 5, the specific gravity of plywood manufactured was slightly higher than that of the kapur veneer (Mean 0.7).

Table 5. Specific gravities and moisture contents of plywood manufactured from each adhesive.

	Urea-Lignin Copolymer Adhesive	Urea-Formaldehyde Resin (control)
Sp. Gr(Mean)	0.77(0.02) <sup>a</sup>	0.76(0.01)
M.C(Mean,%)	8(0.38)	9(0.31)

a; Numbers in parentheses indicate standard deviation

### 3.2 Moisture contents of plywood

Moisture contents (M.C) of plywood was between 8 and 9%. The results showed that the adhesives used were very stable to variation in moisture contents of plywood. Their Moisture Contents (M.C) met the KS requirement (less

than 13%).

### 3.3 Bond quality of the plywood

Bonding strength of plywood was evaluated in terms of dry shear strength, wet shear strength and wood failure.

Generally, bonding strength varies depending on the pressing temperature, time, and pressure. In this study, the pressure was fixed. Therefore, the variation of bonding strength affected by the

pressing temperature and time was studied.

The results obtained are presented in Table 6.

#### 3.3.1 Dry bond strengths

According to the K.S. Standard, Normal Test of dry bond strength corresponds to type III plywood which must preserve the bonding quality with variations of normal dryness.

As being illustrated in Table 6, dry bond strength manufactured with these experimental

Table 6. Influence of pressing conditions of Urea-Lignin-Copolymer adhesive on bond quality.

Press Temperature(°C)	Press Time (Min)	Shear strengths (Kg/cm <sup>2</sup> )		
		Dry	After 3hr at 30°C	After 3hr at 60°C
120	6	13.75(1.00) <sup>a</sup>	13.31(0.63)	10.68(3.27)
	7	14.06(0.56)	13.94(3.29)	10.84(0.48)
	8	16.25(1.17)	16.02(1.63)	10.84(0.48)
130	5	14.32(0.47)	14.53(1.21)	10.37(0.65)
	5.5	14.48(0.47)	15.21(1.27)	11.37(1.03)
	6	16.34(1.07)	15.94(1.75)	12.30(1.43)
140	3.5	13.20(0.84)	13.56(1.91)	10.29(1.59)
	4	13.92(2.37)	14.54(1.11)	11.04(2.29)
	4.5	15.97(1.81)	15.53(1.39)	13.39(2.35)
150	2.5	13.92(0.91)	13.01(0.92)	10.01(0.98)
	3	15.10(1.97)	14.42(1.10)	10.13(0.90)
	3.5	15.33(0.88)	14.57(1.81)	11.25(1.09)
160	2	14.58(1.03)	13.69(2.48)	9.68(1.92)
	2.5	14.66(0.98)	15.75(1.72)	11.32(1.04)
	3	16.49(0.72)	18.56(1.48)	12.53(1.06)
170	1.5	14.11(0.42)	13.62(0.83)	10.22(0.33)
	2	15.55(0.81)	16.98(1.20)	11.68(0.83)
	2.5	17.21(1.57)	17.42(1.61)	13.72(1.47)
180	1.5	14.59(0.18)	14.28(0.70)	10.46(0.71)
	2	16.30(0.07)	17.47(1.51)	12.16(0.70)
	2.5	17.35(1.51)	18.22(2.51)	15.05(2.93)
Control (U-F Resin)				
120	1.5	13.19(0.70) <sup>a</sup>	12.43(1.45)	8.90(0.48)

\*a: Mean (Standard deviation)

conditions met the KS requirement (above  $7.5\text{kg}/\text{cm}^2$ ). But dry shear strength of the pressing conditions of hotpressed with a low temperature and short time (4.5 minutes at  $120^\circ\text{C}$ , 4 minutes at  $130^\circ\text{C}$ , 2.5 minutes at  $140^\circ\text{C}$ , 1 minute and 1.5 minutes at  $150^\circ\text{C}$ , 1 minutes at  $160^\circ\text{C}$ ) appeared lower than that of the control (U-F Resin).

### 3.3.2 Wet bond strengths

According to the KS Standard, the Hot and Cold Water Test corresponds to the type II plywood (Interior type) which must maintain the bonding quality with exposure to the air, normal moisture, and water.

As being shown in this experiment, plywood could not be manufactured with the pressing conditions such as 4.5 minutes at  $120^\circ\text{C}$ , 4 minutes at  $130^\circ\text{C}$ , 2.5 minutes at  $140^\circ\text{C}$ , 1 minutes at  $150^\circ\text{C}$ , and 1 minutes at  $160^\circ\text{C}$ , because the bonding strength did not meet the KS requirement (above  $7.5\text{kg}/\text{cm}^2$ ).

In other conditions (Table 6), the shear strengths increased significantly and the wet shear strength (After 3hr, at  $30^\circ\text{C}$ ) presented was similar to the dry shear strength, or higher than that.

The dry and wet shear strength test of plywood manufactured with Urea-Lignin Copolymer Adhesive was better than those of the control (U-F resin). The results were presented in Table 6 and Figure 1.

### 3.3.3 Effect of pressing conditions

As illustrated in Figure 1, the pressing conditions were considered to be an important factor in Urea-Lignin Copolymer Adhesive for manufacturing plywood. The effect of pressing conditions such as hotpressing temperature and time were investigated on Urea-Lignin Copolymer Adhesives.

The range of the pressing temperature and time were  $120^\circ\text{C}$ - $180^\circ\text{C}$  and 1-8 minutes, respectively, at the fixed pressure of  $12\text{kg}/\text{cm}^2$  and the fixed glue spread level of  $320\text{g}/\text{cm}^2$ .

The results indicated that the pressing conditions are highly related to the bonding quality of the Urea-Lignin Copolymer Adhesive (Table 6, Fig. 1).

In the hot pressing stage the high-molecular-weight lignin copolymerises with the Urea-Lignin-Formaldehyde Adhesive forming an infinite polymer (Forss K.G. 1980).<sup>6)</sup>

Pressing time is the very important factor in manufacturing plywood. Thus, to determine the best curing time for Urea-Lignin Copolymer Adhesive, plywood specimens were manufactured with various pressing time and their strength were compared.

As shown in Table 6 and Figure 1, the shear strength properties directly proportional to the pressing time. The increase on strength was remarkable with the increase of pressing time within 6-8 minutes at low temperature and 2-3 minutes at high temperature.

The relation of the shear strength properties and the pressing conditions (hot-pressing time and temperature) was illustrated in Fig. 2. The results in Fig. 2. shows that bond quality presented high in the long time at low temperature and in the short time at high temperature.

The results in Table 6 and Fig. 1 shows that the higher pressing temperature produces, the higher bonding quality with the same pressing time. This is probably partly because of the incomplete cross-linking and condensation polymerization the low pressing temperature.

As illustrated in Fig. 1 and Fig. 2, higher pressing temperature and longer pressing time result in better bond qualities within the range of those conditions employed in this experiment.

Even though the adhesives and species used in tests were different, comparing the results with the other literatures (reference numbers) may give the relative index for the quality of the Urea-Lignin Copolymer Adhesive manufactured in this experiment. When comparing the results, the Urea-Lignin Copolymer Adhesive was similar to the others (4, 7, 13) in dry shear strength.

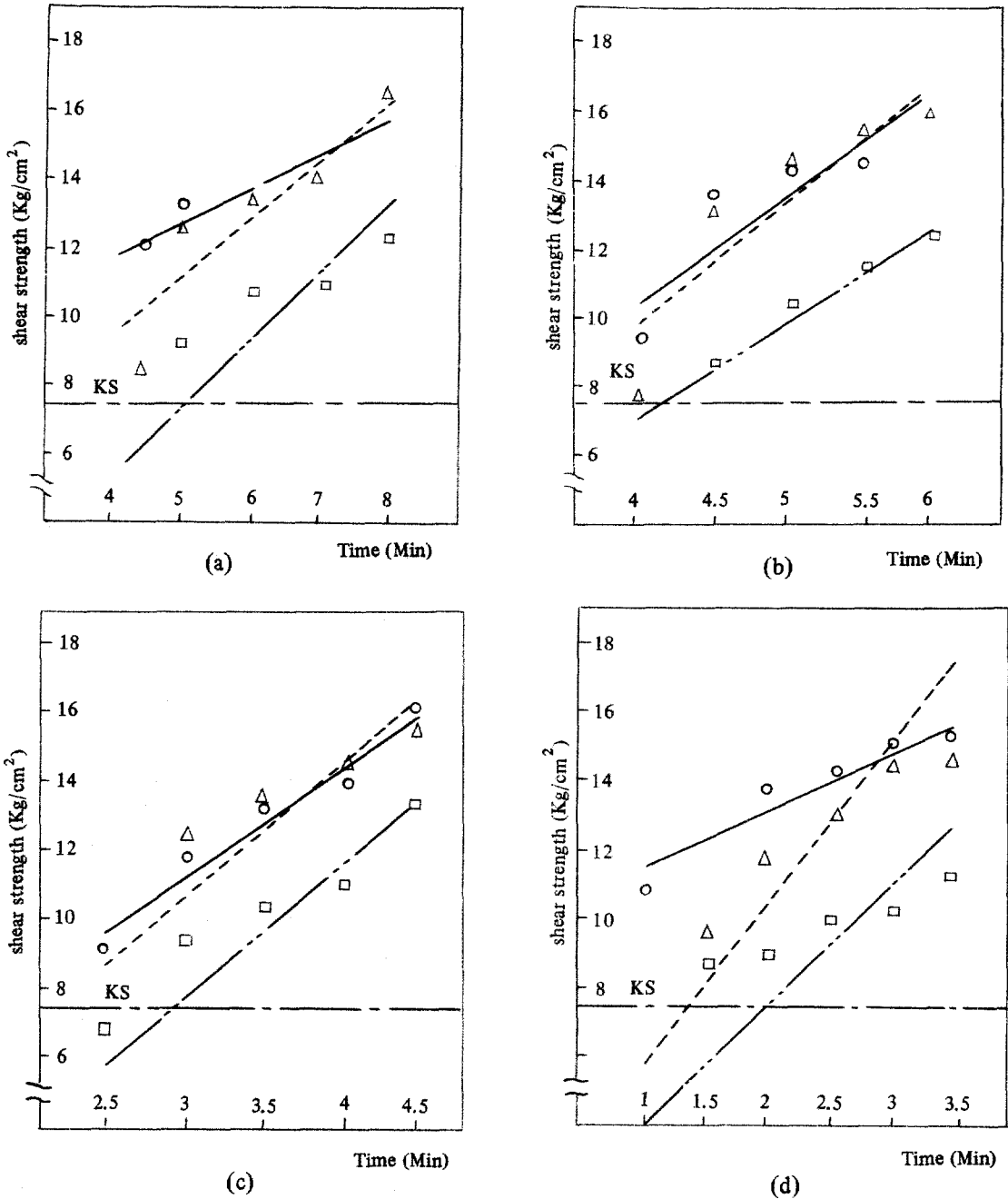


Fig. 1. Influence of the hot pressing time on bond quality; pressing temperature

- (a) 120°C      (b) 130°C      (c) 140°C      (d) 150°C      (e) 160°C  
 (f) 170°C      (g) 180°C      KS: 7.5Kg/cm<sup>2</sup>

Legend

- Dry bond strength
- - - Wet shear strength (After 3 hr, at 30°C)
- - - Wet shear strength (After 3 hr, at 60°C)
- average of dry bond strength
- △ average of wet (at 30°C) shear strength
- average of wet (at 60°C) shear strength



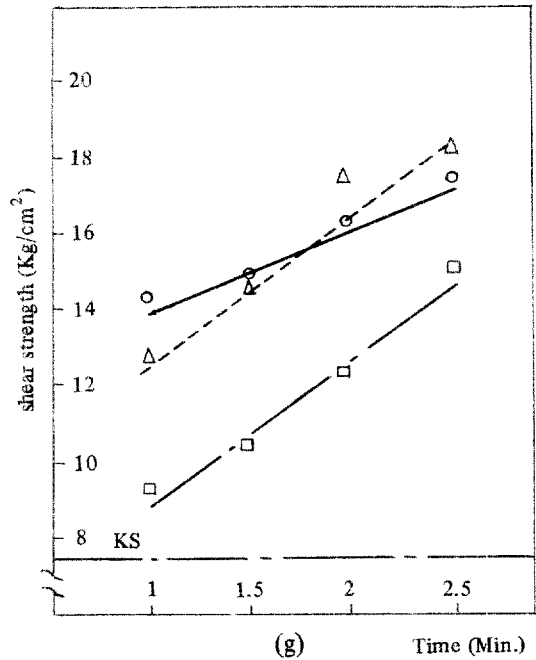
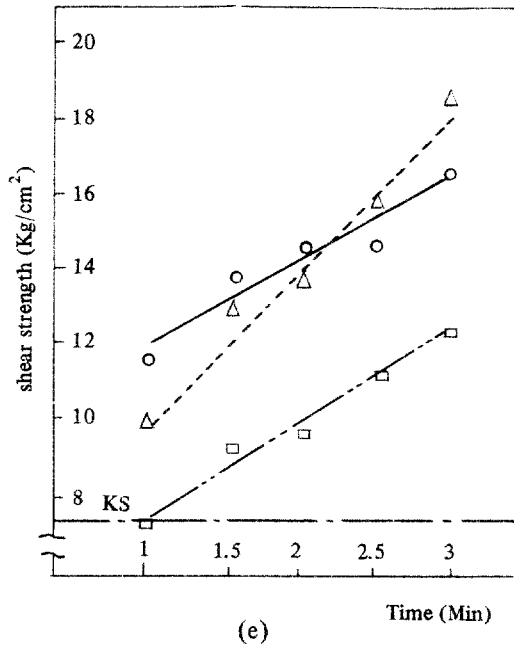
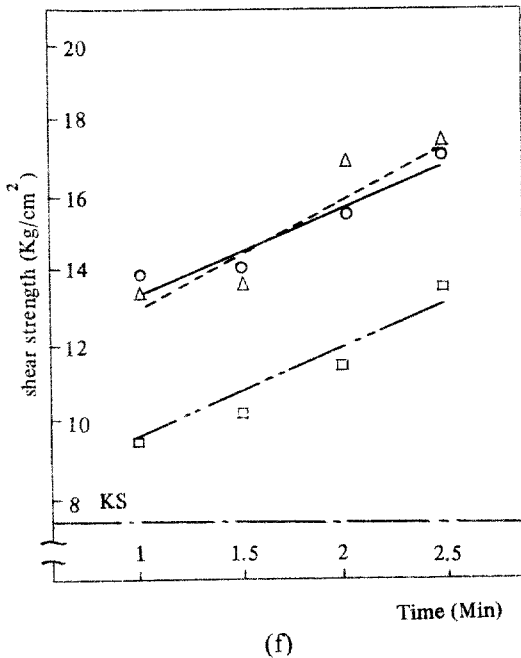


Fig. 1. Continued (e-g)



### 3.4 Properties of adhesive

The properties of each adhesive manufactured in this experiment are shown in Table 7.

The result showed that the specific gravity of the Urea-Lignin Copolymer Adhesive was higher than that of the U-F Resin, and the viscosity was lower than the control (U-F Resin), as being shown in Table 7.

The reason is considered that lignin has a higher specific gravity (1.255) than the U-F resin. And Schwer reported that the viscosity was low.<sup>2)</sup>

In the wood product industries, the plywood and particleboard industries are the major consumers of adhesive. The manufactures of plywood and particleboard are mainly using Phenol-Formaldehyde resins and Urea-Formaldehyde type.

The major advantage of a Phenol-Formaldehyde adhesive is the weatherproof nature of the glue-line, and the chemical stability of the cured adhesive. However, the high cost is a disadvantage.

The advantage of Urea-Formaldehyde resins lie in their short pressing time and comparatively low cost. Their disadvantages are poor water-proofness and the emission of formaldehyde.

But the Urea-Lignin Copolymer Adhesive exhibited that the wet shear strength test (After 3hr, at 30°C) of plywood did not appear to be a great difference from the dry shear strengths, or better than those. [Table 6 and Fig 1]

Therefore, the poor water-proofness of U-F Resins could be complemented. But the water-proofness of this adhesive must be further studied.

Table 7. The physical properties of each adhesive.

Adhesive Ingredients	Sp. Gr (at 25°C)	pH (at 25°C)	Viscosity (at 25°C, cp)	N.V.C. (%)
U-F Resin <sup>a</sup>	1.19	7.5	510	51
U-L-F Resin <sup>b</sup>	1.21	9	400	51

a; U-F Resin; Urea-Formaldehyde Resin

b; U-L-F Resin; Urea-Lignin-Formaldehyde Copolymer Resin

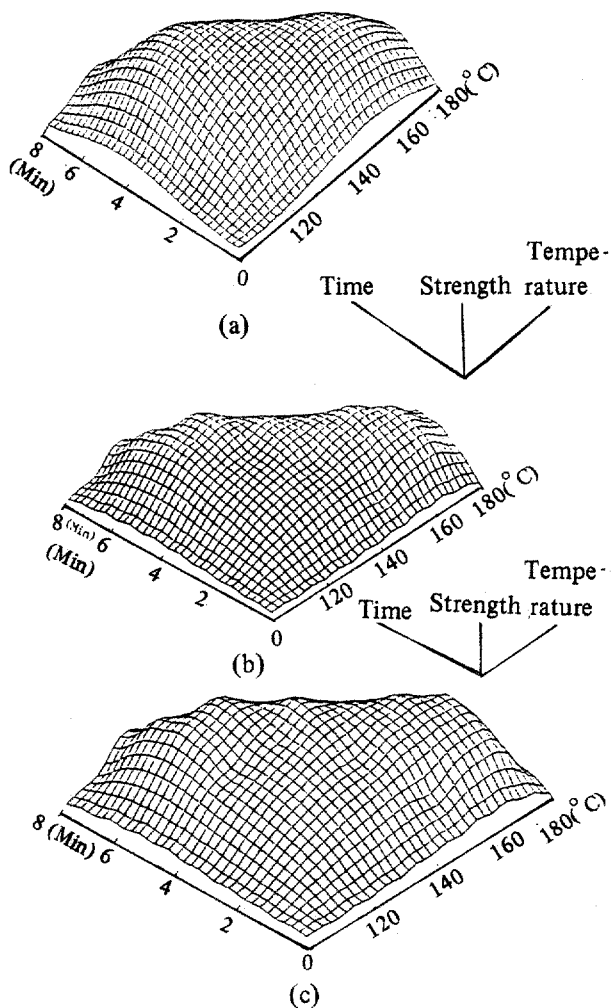


Fig. 2. (a-c) The relation of the shear strength properties and the pressing conditions (hot-pressing time and temperature)

(a) Dry shear strength

(b) Wet shear strength (at 30°C)

(c) Wet shear strength (at 60°C)

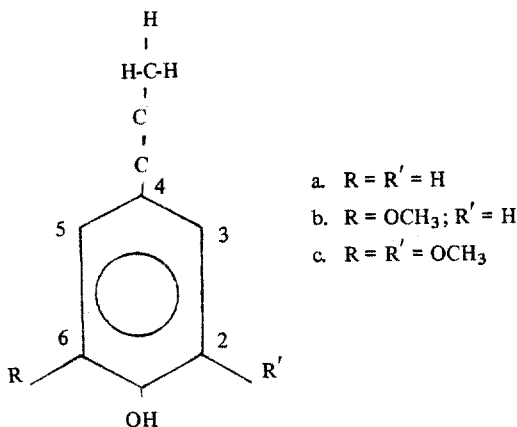
Angle of tilt: 28°C

Ramos et al. (1) reported that was decreased due to the reduction of U-F resin.

Formaldehyde left in glue line is considered as the major factor of formaldehyde release. However, in Urea-Lignin Copolymer Adhesive, formaldehyde reacts with lignin, which results in less formaldehyde left and less release of it.

The disadvantage of the Urea-Lignin Copolymer Adhesive is its manufacturing process which require higher pressing temperature and longer pressing time than those of Urea-Formaldehyde Resin.

Further investigations are needed to find economic and optimum pressing temperatures and



- a. R = R' = H
- b. R = OCH<sub>3</sub>; R' = H
- c. R = R' = OCH<sub>3</sub>

Fig. 3.

times. The details of physical and chemical properties of Urea-Lignin Copolymer Adhesive and its economic feasibility should also be studied in the future.

There has been many researches on cross-linking reactions between Kraft Lignin and chemicals such as epoxies, isocyanates, ethyleneamines,

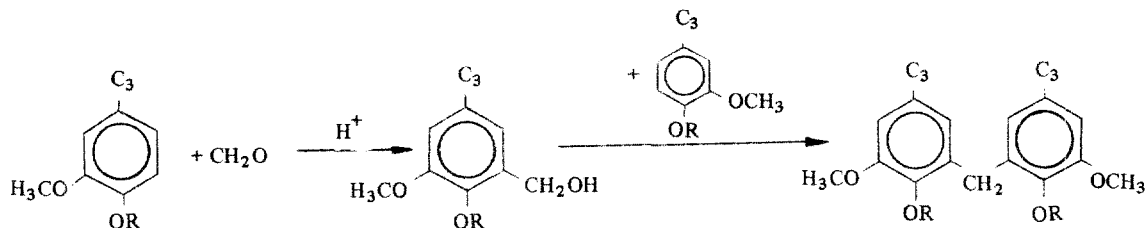


Fig. 4. Cross-linking of lignin by formaldehyde.

and phenol-formaldehydes.<sup>6)</sup>

Lignin is built up largely of methoxylated p-hydroxyl phenyl propane stones with varying degree of oxidation of their side chains, as shown in Figure 4 (Marton et al, 1966).<sup>13)</sup>

The 2- and 6-positions of the phenolic nuclei were theoretically reactive with alkaline formaldehyde. Experimental results of Marton et al showed that about half of the nuclei in lignin were unsubstituted and reacted. (Ramos, 1980)<sup>13)</sup>

results in cross links of methylene bridge.

In Urea-Formaldehyde solution, there exist formaldehyde, monomethylol urea, and dimethylol urea. Therefore, when Kraft Lignin is added to this solution, methylene and ether bridge can be produced between lignin and the chemicals in urea solution. (Fig. 4)

But further research must be needed to investigate the cross-linking of lignin in detail.

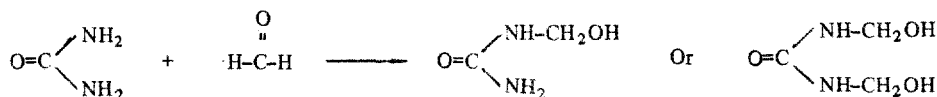


Fig. 5. Addition reaction of urea-formaldehyde.<sup>17)</sup>

Lignin obtained from the kraft pulping processes contains both aliphatic and aromatic hydroxyl groups, which are potential sites of modification and reaction.<sup>8)</sup>

Terje Enkvist (1962) reported that the dimethylation of lignin by pressure heating would be more reactive and thus more useful for condensation with formaldehyde than the original lignin.<sup>4)</sup>

Lignin is polymers of phenylpropane unit which is similar to the unit of phenolic resin. Thus, lignin is likely to react and form cross-links with formaldehyde. Cross-links in lignin can be resulted from either by condensation or by radical coupling reaction as shown in Fig. 3.<sup>12)</sup>

Addition reaction between Kraft Lignin and formaldehyde produces methylol lignin, and condensation between lignin and methylol lignin

#### 4. Conclusions

For the past several decades, spent black liquor has been studied for utilization as an adhesive for wood-based panels. But it has been limited to the case of the P-F Resins and U-F Resins made from spent sulfite liquor (SSL), and Phenol-Formaldehyde Resin made from spent kraft black liquor.

The purpose of this study was to investigate the possibility of utilizing the spent kraft black liquor as a Urea-Lignin-Formaldehyde Copolymer Adhesive for manufacturing plywood, and to investigate the properties of the adhesive and the plywood manufacturing conditions such as hot-pressing temperature and time.

The kraft lignin extracted from kraft black liquor, a waste material obtained as a by-product

of chemical pulp processing, was manufactured into an adhesive for manufacturing plywood in the laboratory. The weight ratio of Kraft lignin to Urea-Formaldehyde was 7 to 3 in oven-dry weight.

The results are summarized as follows;

1. In the results of this experiment, about 30% of the U-F Resin could be substituted with the kraft lignin, on a weight-by-weight basis, and it is an effective source of adhesive.
2. In the view of economics, the optimal hot-pressing condition for manufacturing plywood may be a pressing time of 3 minutes with a pressing temperature of 160°C (Dry strength; 16.49kg/cm<sup>2</sup>., After 3hr, at 30°C; 18.56kg/cm<sup>2</sup>., After 3hr, at 60°C; 12.53kg/cm<sup>2</sup>).
3. The shear strength of plywood manufactured from the Urea Lignin Copolymer Adhesive showed good bonding qualities and the wet shear strength (After 3hr, at 30°C) did not show a significant difference from the dry shear strength. Therefore, this Adhesive exhibited considerable promise as an adhesive for manufacturing semi-water-proof plywood.

### Literature Cited

1. Allan G.G. 1979. Process for the partial substitution of ammonium liginosulfonate for phenol in phenolic-aldehyde resin adhesives. U.S. Patent No. 4, 127, 544.
2. Brauns F.E. 1960. The chemistry of lignin. p. 173-187, 551-576.
3. Browning B.L. 1967. Methods of wood chemistry. p. 717-823.
4. Enkivist Terje., Kohannes Turunen., and Theore Sashorn. 1962. The demethylation and degradation of lignin of spent liquors by heating with alkaline reagents. 45(2): 128-135.
5. Falkehang S.I. 1975. Lignin in materials. Appl. Polym. Sym. 28. 247-257.
6. Forss K.G., and Fuhrmann A. 1979. Finnish plywood, particleboard, and fiberboard made a lignin-base adhesive. For. Prod. J. 29(7): 39-43.
7. Gardner Douglas J., and Terry Sellers Jr. 1986. Formulation of a lignin-based plywood adhesive from steam-exploded mixed hardwood lignin. For. Prod. J. 36(5): 61-67.
8. Herrick F.W. 1983. Water-soluble sulfited lignin-phenolic formaldehyde complex. U.S. Patent No. 3,095,392.
9. Hollis J.W., and Sch enherr M.W. 1981. Lignin-containing resin adhesive U.S. Patent No. 4,303,562.
10. K.S.M. 3707,3708,3709,3720. 1982. Korean Industrial Standard.
11. Merewether J.W.T. 1962. The precipitation of lignin from eucalyptus kraft black liquors. Tappi. 45(12) 159-163.
12. Pizzi A. 1983. Wood adhesive. Chemistry and Technology. p. 247-288Z.
13. Ramos J.R., Olano C.D., Chan F.D., and San Pearo M.P. 1980. Kraft black liquor as adhesive for plywood. NSDB Tech. J., April-June. 42-49.
14. Sarkanen K.V., and Ludwig. 1971. Lignins. p. 670-859.
15. Sjöström. 1981. Wood Chemistry, Fundamentals and Applications. p. 68-207.
16. 李華珩. 1984. 家具 및 특수용도를 위한 PB와 Fiber Mat의 Composite Board製造에 관한 研究(第一報). 목재공학 12(6): 34-38.
17. 辛東韶, 李華珩 外, 1983. 林産化學, 卿文社, p. 57-116, p. 172-255.
18. 趙南奭, 1987, 木材化學製品의 첨단技術과 展望(하) 製紙界, 117(6): 39-48.
19. 日本 木材學會, 木材科學實驗書, p. 190-199.