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## Technical soda lignin dissolved in urea as an environmental friendly binder in wood fiberboard

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The application of lignin as binder in wood composite panel is not only environmentally friendly but also commercially attractive. The dissolving of technical soda lignin is the most premier challenge in its application. In this study, the effect of different key factors on soda lignin solubility in urea was investigated. The maximum solubility of 60.16 g/L was obtained under the temperature 70 °C, urea concentration 8 M, lignin content 7%, and pH 8.8. Then, different kinds of wood fiber material were mixed with the dissolved lignin solution to make fiber board separately. The results showed that the lignin can enhance the tensile strength of particleboard and can be used as a binder in wood material, but the strength will be different with different materials. The optimal tensile strength obtained was 44.63 MPa with the sample made from oriented cotton linter sheet.

**Keywords:** soda lignin; polysaccharides; composite; binder application

### Introduction

Lignin, which comprises approximately 30 wt.% of the wood biomass,[1,2] is one of the most abundant natural biopolymers on Earth, as one of the main components in plant cell walls. It works as a cementing and curing agent covalently and non-covalently, cross-linking the cell wall polysaccharides cellulose, hemicelluloses, and pectins components together, thereby making the cell wall stiff and limiting its swelling in water.[3,4] The covalent bonds between lignin and polysaccharides, the lignin-carbohydrate complexes (LCCs), serve as anchoring points where the carbohydrates and lignin are covalently bonded to each other. The covalent attachments are important for the unique physical properties that wood exhibit as a natural composite material, but there are also possibilities for non-covalent interactions based on aromatic interaction and hydrogen bonds. In chemical pulping of wood, the lignin is partly degraded and solubilized, and is produced as a by-product from the process liquors. Due to the large volumes of wood and other plant material that are chemically pulped, such technical lignin represents one of the largest quantities of natural resources. However, technical lignin has a very complex structure. Lignin is, *in vivo*, formed by an uncatalyzed oxidative radical polymerization process, in contrast to other biopolymers such as cellulose,

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hemicellulose, and proteins, which are formed by enzymatic catalyzed condensation. [1,5] Lignin is constituted by hydroxyphenylpropane units that are connected with each other by ether and partial carbon-carbon bonds with a heterogeneous, 'chaotic' structure.[5,6] Furthermore, during chemical pulping, the lignin undergoes complicated chemical modification resulting in a branched, very heterogenic structure containing not only aromatics and hydrophobic structures, but also hydroxylated hydrocarbon structures and carboxylic acids.[7] This complexity has limited the technical uses of lignins. The largest technical uses of lignins are as lignosulphonates – a class of water soluble anionic derivatives. Lignosulphonates are mainly used for various bulk applications, such as dispersing agents in oil drilling, additives to concrete, and dust binder on roads. It is obtained as a by-product of the sulfite pulping process. This process is, however, being replaced by the alkaline kraft process of pulping, and to some extent by soda antraquinone pulping. The technical lignins produced from these alkaline processes are water- and solvent-insoluble products that dissolve in alkali owing to their high concentration of phenolic hydroxyl groups. Efficient techniques have been developed for the collection of technical lignin from kraft and soda pulping liquors,[8] but it has been difficult to develop advanced commercially feasible applications of the lignin. Presently, most of the lignin in pulp mills is burned as fuel. It has been estimated that only 1–2% of lignin is isolated from pulping liquors and used for speciality products, which amount to 1 million tons per year worldwide.[9,10]

However, in the laboratory, many potentially interesting applications of lignin have been reported,[11–13] for instance, technical lignin can be used as an efficient and relative humid resistant binder for wood and pulp fiber, and can therefore be used in the construction of fully bio-based novel materials.[14,15] In the wood composite industry, urea formaldehyde (UF) and phenol formaldehyde (PF) are the two most commonly used binders, but the two major disadvantages of using formaldehyde-based resins are: (1) Its formaldehyde emission is harmful to human health and (2) petroleum for producing formaldehyde is limited.[16] Both academic groups and industry have been trying to find sustainable alternative binders for wood composite panel products for many years,[17] and utilization of natural lignin, a phenolic heteropolymer, as a wood adhesive has attracted a lot of attention.[9,18,19] One important advantage of such materials is that they will be free of formaldehyde emissions, which today is a common problem with wood-based composite materials.

Using lignin as an adhesive instead of or as a partial replacement for UF or PF is not only a way to recycle the vastly under-utilized lignin in the black liquor, but such an approach also has the advantage of using low toxicity and renewable resources. The main objective of this study was to use technical soda lignin as a binder with different fibers to make fiber board. Meanwhile, the urea solution as a prospective solvent for technical soda lignin was also investigated. Mechanical properties and surface morphology of fiber board were evaluated.

## Experimental

### Materials

Technical soda flax lignin with 5.0% moisture content was provided from the Granit International Lignin Institute (Lausanne, Switzerland). Even quality spruce sawdust with moisture content 8.29% was supplied from Setra Company (Stockholm, Sweden). Kraft cotton linter provided from Crane AB Company (Tumba, Sweden) was obtained in the form of pulp sheet with 4.79% moisture content, and milk box paper was offered from

Tetra Pak Company (Lund, Sweden). Unbleached chemithermomechanical pulp (CTMP) with about 6.28% moisture content was obtained from the wood division of the fiber and polymer department in KTH (Stockholm, Sweden). Sterile gauze dressing used as textile was purchased from Akla Sweden AB (Ängelholm, Sweden). ACS reagent grade urea was bought from Scharlau Chemie S.A. (Barcelona, Spain). Activated carbon, 50–200 mesh, was purchased from Fisher Scientific and used without further treatment. All other chemicals were of analytical grade.

### ***Lignin solution preparation***

The urea was dissolved in different buffer solution with different pH thoroughly. Then, the lignin was added in the urea solvent and mixed with magnetic stirrer for 24 h until the limitation of solubility. After 24 h treatment, there was always some lignin not dissolved. The mixture was under centrifugation (Hettich, D-78532 Tuttlingen) with speed 4000 rpm for 30 min.

The lignin dissolved amount was calculated as following:

$$D = \frac{W_{\text{add}} - W_{\text{sed}}}{V_{\text{urea}}}$$

where  $D$  is the lignin dissolved amount, g/L;  $W_{\text{add}}$  the weight of added lignin;  $W_{\text{sed}}$  the weight of sedimentation in centrifugation tube; and  $V_{\text{urea}}$  the volume of urea solvent.

### ***Panel preparation***

The fiber board preparation procedure is illustrated in Figure 1. Firstly, 10 g of dry content of lignin was added in 100 mL of 8 M urea solvent at pH 8.8 and temperature 70 °C, the solution was then mixed with 90 g of dry content of different wood and fiber materials. The mixture was homogenized evenly with a IKA-Werke stirrer for 20 min, and then was left in hood overnight to control the moisture content between 15 and 20%. After that the mixture was loaded into a round steel mold with diameter 210 mm and thickness 3 mm, then pressed into a particle board using a Fontune Hot-Press TP400 (Fontijne Grotnes, the Netherlands) as shown in Figure 1(c) with temperature 180 °C, pressing time 5 min, and pressing force 400 kN. A programmed water cooling system was used to reduce the temperature to 25 °C after the pressing was completed. The final thickness of the particleboard was about 3 mm, as shown in Figure 1(d). The

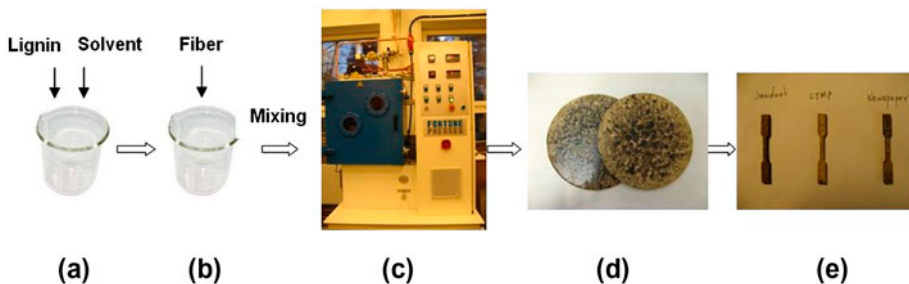


Figure 1. Scheme of fiber board preparation procedure.

particleboard was placed in a constant humidity room with 50% relative humidity at 23 °C for 48 h before the characterization of mechanical properties.

### **Characterization**

Mechanical properties, including tensile strength and internal bonding strength, were determined following ASTM standard method D1037, standard test method for evaluating properties of wood-base fiber and particle panel materials, using an Instron 5566 testing system (Instron Corp., Bucks, UK). Tensile strength was obtained by applying the load continuously throughout the test at a uniform rate of motion of the movable cross head at 2 mm/min. Figure 1(e) shows the specimens in dumbbell shape with size  $3.8 \times 15.2$  cm for the tensile strength test. For the internal bonding strength test, the alumina alloy cylinder with diameter 5.6 cm was first mechanically abraded by sand and blown with air under high pressure; then the specimens were bonded to the fresh cleaned alumina alloy by Araldite 420 A/B (1.0: 0.4) epoxy adhesive and was clamped as soon as the adhesive has been applied. After 24 h, the testing was implemented with the cross-head speed at 1 mm/min. The loading fixtures, which grip the specimen, were attached to the Instron device, and tension was applied perpendicular to specimen surface until the specimen failed. The data were processed with Bluehill software. A mean data were obtained from five individual specimens for each test sample.

The microstructure of the panel surface was observed with scanning electron microscopy (SEM) (Hitachi S-4800, Hitachi Science Systems, Ltd, Ibaraki, Japan). The specimens were first mounted on alumina stubs, and then fracture surfaces were coated by a sputter coater (Cressington 208HR) with a mixture of 60% gold particles and 40% palladium.

## **Results and discussion**

### **Lignin solubility in urea solution**

A major problem with the application of technical soda lignin is its poor solubility in water except under strongly alkaline conditions. Dissolving lignin in an appropriate solvent is the premier challenge in the application of lignin. In this study, replacing conventional organic solvent, the urea solution was employed as a mild and environmentally friendly solvent for the technical soda lignin. Different factors effect on the lignin solubility in urea solution. Figure 2(a) demonstrates the effect of pH on the lignin dissolved amount. It is obvious that the lignin dissolved amount increased with the increase of pH. Since high pH accelerates the hydrolysis of urea, pH 8.8 was batter after balancing the lignin dissolved amount and hydrolysis of urea. Figure 2(b) shows that the solubility of lignin increased significantly under high temperature, however, urea is not stable under high temperature. Under 70 °C, it is better for urea to modify lignin through Mannich reaction. Considering this, 70 °C is enough for the lignin dissolving. This urea solvent system for lignin has a very high technical potential. It is relatively cheap and gives no large environmental or fire problems. From Figure 2(c), we can see that the higher the urea concentration, the larger the lignin dissolved amount. Under high urea solution, high polarization was obtained. High polarized solution was good for lignin dissolving.

Figure 2(d) shows that the lignin dissolved amount increased with the added lignin content in urea solution under 70 °C below 7%. The maximum dissolved amount was 60.16 g/L, which was also the maximum value obtained in this experiment and used for

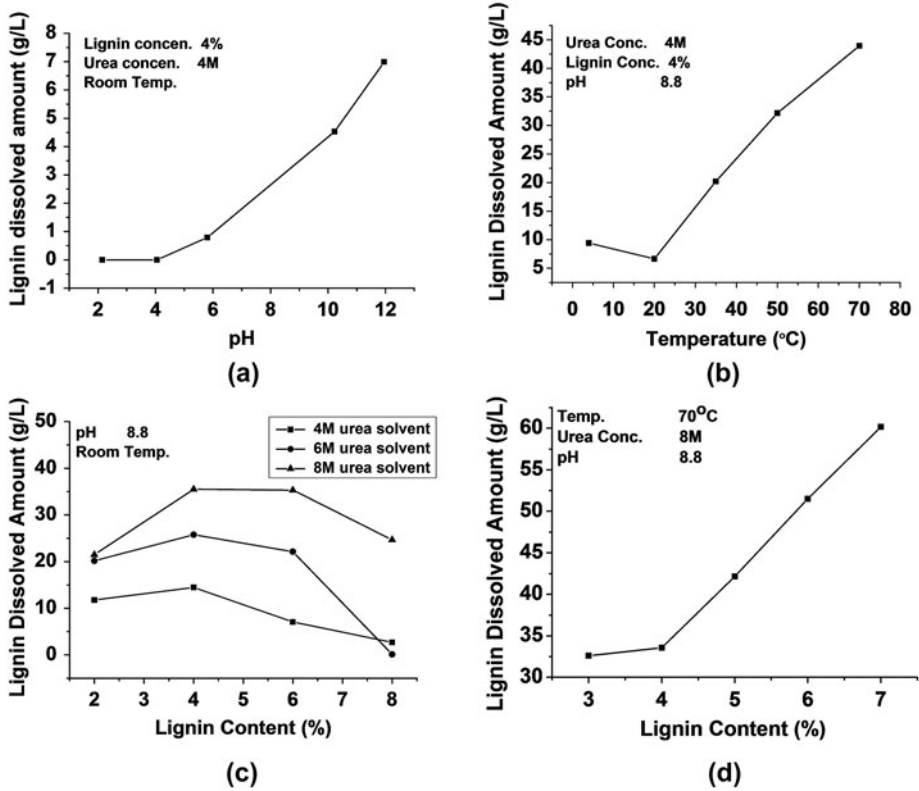


Figure 2. Effect of different factors on the lignin solubility in urea solution: (a) pH, (b) temperature, (c) urea concentration, and (d) lignin content.



Figure 3. Lignin dispersed in water (left) and dissolved in 8 M urea (right).

the subsequent board preparation. Lignin dissolved in urea solution to form uniform dark liquid, as shows in Figure 3.

### Mechanical properties

Hot-pressing of wood fibers in the presence of lignin solution generated materials that appear to have interesting properties. The lignin solution was prepared in 8 M urea at pH 8.8 and temperature 70 °C. To compare sample 1 (90% CTMP, 10% lignin) with sample 2 (only CTMP, without lignin), the tensile strength of sample 1 was approximately twice that of sample 2, and the internal bonding strength of sample 1 was almost triple that of sample 2. A similar result also can be concluded from the sample 3 (90% sawdust, 10% lignin) and sample 4 (only sawdust, without lignin), in which both the tensile strength and internal bonding strength were doubled after the addition of 10 wt.% lignin. The covalent bonds (such as benzyl ether, benzyl ester, glycoside and acetal types) can be formed between lignin and carbohydrates and fibers with lignin rich-surfaces could improve the mechanical properties of binderless board by mechanical entanglement of the softened lignin molecules under high pressure and temperature.

This urea solvent system for lignin has a very high technical potential for several reasons. It is relatively cheap, gives no large environmental or fire problems, and furthermore, the urea may possibly form resins together with lignin. One can also perform other types of reactions, as cross couplings of lignin in order to increase the molecular weight of lignin. So, the lignin can enhance the mechanical strength of particle board and can be used as binder in wood material, but the strength will be different with different material.

In Table 1, compared with sawdust and Tetra Pak milk box paper, the fiber board made from CTMP possessed better strength. We concluded that, firstly, compared to other material used in this experiment, CTMP contains a larger percentage of lignin, which may work together with the added lignin to enhance the mechanical strength. Secondly, the CTMP fiber has larger relative surface area, which increases the contact area between fiber and lignin. Based on the second reason, the sample 10 was made of 87% CTMP, 3% active carbon, and 10% lignin. The purpose of adding active carbon was to increase the contact area between fiber and lignin by the large surface area of active carbon. The active carbon possesses a high degree of fine pores, which allow it to be efficiently employed as structured binding support. The binder can partly anchor the fine pores near to the external surface of active carbon and thereby created more joint points between fiber and lignin, and to some extent create a rough surface for the

Table 1. Mechanical properties of particle board.

Sample	Composition	Tensile strength (MPa)	Internal bonding strength (Mpa)	Tensile strain (%)	Thickness swelling (%)
1	CTMP + lignin	14.36	1.1437	1.49	31.24
2	CTMP	7.21	0.4312	1.26	37.61
3	Sawdust + lignin	3.56	0.2395	1.70	46.31
4	Sawdust	1.87	0.1521	1.34	50.04
5	Milk box paper + lignin	3.29	0.3101	2.34	32.52
6	Milk box paper	3.30	0.3112	2.39	33.74
7	Lintner sheet + lignin	44.63	1.3289	5.56	28.13
8	Lintner chip + lignin	5.36	0.8947	0.80	37.25
9	CTMP + textile + lignin	7.76	1.0015	1.27	32.14
10	CTMP + active carbon + lignin	17.15	1.5286	1.56	30.47

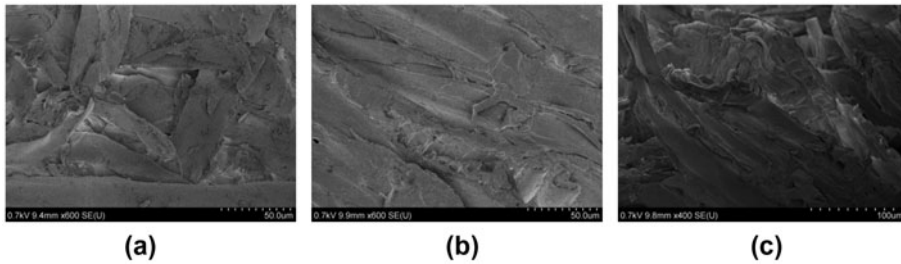


Figure 4. SEM images of fractured surface morphology of wood particle board (a) CTMP and lignin, sample 1; (b) sawdust and lignin, sample 3; and (c) sawdust without lignin, sample 4.

adhesive. Compared to sample 1, the tensile strength of sample 10 was increased 19.4% and internal bonding strength increased 33.6%.

Comparing sample 5 with sample 6, both the tensile strength and the internal bonding strength showed no increase with lignin addition. Based on the fact of Tetra Pak milk box paper containing large percent of plastic film, we deduced that the fiber surface was covered with the plastic film, which prevented the lignin from contacting with cellulose fiber. For the further comparison, in sample 9, the sterile textile was employed to wrap the fiber layer by layer and then pressed, and the sample's strength was also reduced measurably.

Sample 7 shows a sample that was made from cotton linter sheet which possessed the maximum tensile strength of 44.63 MPa in this study. It is better than the conventional UF-bonded particleboard with tensile strength 7–15 MPa. But the mechanical strength of sample 8, which was made from the linter chip, was much lower than sample 7. We presume that oriented fiber is helpful to the product's mechanical strength.

The fiberboard made from different material shows significant different thickness swelling in water after 24 h. The sample made from the pure sawdust without lignin has the largest thickness swelling, and the sample made from linter sheet added with lignin has the most excellent shape stability. The result is quite consistent with the mechanical strength.

### *SEM image*

Representative samples were selected to characterize with SEM. Sample 1 was composed of 90% CTMP fiber and 10% lignin. As illustrated in Figure 4(a), after hot-pressing, the shape of a CTMP fiber became to flat. Lignin filled the space between fibers making the adhesion between fibers stronger. Sample 3 was composed of 90% spruce sawdust and 10% lignin, and sample 4 was pressed with only spruce sawdust. Comparing sample 3 with sample 4, the surface of sample 3 was much smoother and more gelatinous than sample 4. Obviously, the lignin in sample 3 played a role of binding, which made sample 3 much stronger than sample 4.

### **Conclusions**

An 8 M urea solution under pH 8.8 and temperature 70 °C worked as an excellent solvent for technical lignin, and this can be valuable for the structural modification of plant biomass for technical uses. The mechanical strength of the lignin-containing fiber board



related closely with the forming procedure, including the material composition, contact area between fiber and lignin, and the fiber orientation. Fiber board made from cotton linter sheet possessed the maximum tensile strength of 44.63 MPa and internal bonding strength of 1.33 MPa. Technical lignin can be used as binder and can enhance the mechanical strength of fiber board and similar materials. The usefulness of renewable lignin-based binder could be further explored to assist in manufacturing environmentally friendly wood composite panels.

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