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Studies on Lignin-Based Adhesives for Particleboard Panels

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Abstract: The ultimate aim of this work was to develop a phenolic resin for partially replacing phenol with modified organosolv lignin in phenol-formaldehyde (PF) resin production. The lignin-formaldehyde relationship was determined in a reactivity test. Organosolv lignin-phenol-formaldehyde (LPF) resins were produced in a two-step preparation with different additions of lignin. The method selected for the manufacture of lignin resins dealt with modification of the lignin by the methylolation route. The effects of different substitution levels of organosolv lignin on strength properties were evaluated by testing lignin resin impregnated paper strips. A comparison of the tensile properties of organosolv lignin formulations, impregnated and cured onto glass fibre paper strips, was made with those of PF resin. Organosolv lignin-based resins showed comparatively good strength and stiffness. The tensile strength properties of test samples made from organosolv lignin resins were equal to or better than those of test samples made from PF resin only. The physical properties (solid content, specific gravity, viscosity and gel time) of formulated resins were also determined before use and compared to a control PF resin used to bond particleboards. The particleboards were manufactured using liquid phenolic resins. The particleboards were tested for their physical strength and dimensional stability properties. The properties of particleboards bonded with LPF resins were comparable to those of the control-bonded particleboards. The results indicated that organosolv lignin was a feasible replacement for up to 30% of the phenol in particleboard-type PF resins.

Key Words: Organosolv lignin, lignin-phenol-formaldehyde resin, methylolation, tensile strength, physical properties, particleboard.

Yongalevha Üretiminde Kullanılan Lignin Kökenli Tutkallar Hakkında Çalışmalar

Özet: Bu çalışmanın amacı, fenol-formaldehit tutkal üretiminde modifiye edilmiş organosolv ligninin bir kısım fenol yerine kullanılması ile fenolik tutkal geliştirmektir. Ligninin formaldehit ile aktivitesi belirlendikten sonra, organosolv lignin-fenol-formaldehit tutkalları farklı oranlarda ligninin eklenmesi ile iki aşamada hazırlanmıştır. Lignin tutkallarının yapılması için lignin metilolasyon denilen modifikasyon metodu ile modifiye edilmiştir. Farklı lignin ikame oranlarının direnç özellikleri üzerine etkisi, lignin tutkallarına batırılmış cam lifli kağıt şeritlerin test edilmesi ile değerlendirilmiştir. Organosolv lignin-fenol-formaldehit tutkallarının çekme direnci özellikleri fenol-formaldehit tutkalının çekme direnci ile karşılaştırılmıştır. Lignin-fenol-formaldehit tutkalları fenol-formaldehit tutkalı ile karşılaştırılabilir iyi çekme direnci özellikleri göstermiştir. Ligninden yapılan tutkalların test örneklerinin çekme direnci özellikleri lignin kullanmadan yapılan PF tutkallarına eşit ve daha iyi sonuçlar göstermiştir. Ayrıca, formüle edilen tutkalların fiziksel özellikleri (katı madde miktarı, özgül ağırlık, viskozite, jelleşme zamanı) tutkallar yonga levha yapımında kullanılmadan ve kontrol fenol formaldehit tutkalı ile karşılaştırılmadan önce tespit edilmiştir. Fenolik tutkallar kullanılarak yongalevhalar üretildi. Yongalevhaların fiziksel direnç ve boyutsal sabitliklik özellikleri test edildi. Lignin fenol formaldehit tutkalları ile yapıştırılan yongalevhaların özellikleri kontrol tutkalları ile yapılan yongalevhalar ile karşılaştırılabilir olduğunu ortaya koymuştur. Sonuçlar ligninin fenol-formaldehit tutkallarında % 30 oranına kadar fenol yerine kullanılması ile yongalevha üretiminde kullanılan fenol formaldehit tipi tutkallarda uygulanabilir olduğunu göstermiştir.

Anahtar Sözcükler: Organosolv lignin, lignin-fenol-formaldehit tutkalı, metilolasyon, çekme direnci, fiziksel özellikler, yongalevha.

Introduction

The adhesives used in commercial wood composite products are usually synthetic polymer resins, based on the condensation reaction of formaldehyde with phenol, urea, resorcinol or melamine. All these thermosetting resins adhere well to wood and when cured form bonds at least as strong as the wood itself. Phenol-formaldehyde (PF) resins are characterized by their high strength and moisture resistance. The costs of PF resin, the main factor limiting its use, have been the subject of considerable fluctuation, largely as a result of variability in the world oil market, but there is no trend indicating any long-term reduction of phenol costs (Hughes, 1996). An alternative, cheaper source of phenols would be of

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great interest to all users of PF resin. There has been a great deal of research performed concerning lignin. An important field of application is in the wood-working industry, especially in plywood and particleboard production in which PF resins are almost exclusively used as the binder (Danielson, 1998).

Lignin is one of the most abundant, renewable natural products on earth and technical lignins are produced in tremendous quantities every year as a by-product of the pulping process. Extensive work has been conducted to include organosolv lignins and other lignins with their polymeric structure of phenolic units in PF resins (Danielson, 1998; Nimz, 1983; Olivares et al., 1995; Sellers, 1993; Shimatani and Sano, 1995).

The objective of this study was to investigate the extent to which organosolv lignin could replace phenol in PF resins designed for application as an adhesive to bond particleboards. The tensile strength properties of lignin-phenol-formaldehyde (LPF) resins were characterised and the physical and mechanical properties of particleboards bonded with lignin resins were evaluated. Lignin-modified resins were compared with control PF resin.

Materials and Methods

The essential raw materials used in the preparation of phenolic resins were: a commercial powder organosolv lignin [trade name ALCELL® lignin, Alcell Technologies, Ltd. This material was produced from a mixture of hardwoods that included 50% maple (*Acer rubrum*), 35% *birch* (*Betula papyrifera*) and 15% poplar (*Populus tremuloides*)]; a commercial grade phenol of 99% purity; formaldehyde solution (50 weight % aqueous solution); sodium hydroxide solution (NaOH, 50 weight % aqueous solution); and commercial resol type liquid PF resin (control) (code DPL 5681) supplied by DynoChem Ltd., Mold, Clwyd, UK.

Reaction of Lignin with Formaldehyde

The formaldehyde reactivity of the organosolv lignin was determined in accordance with the method described by Wooten et al. (1988). Lignin was methylolated by reaction for 5 h at 55 °C with formaldehyde [formaldehyde/lignin ratio 0.38 (w/w)] in the presence of sodium hydroxide [NaOH/lignin ratio 0.2 (w/w)]. The reaction vessel was equipped with a stirrer, a thermometer, a reflux condenser, a sample port and a mantle. In this method, the optimum solvent to dissolve a 3 g sample (lignin, NaOH, formaldehyde and water) without excessive precipitation was a mixture of 20 ml of methanol and 30 ml of distilled water. The concentration of formaldehyde in samples taken periodically from the reaction mixture was determined by the hydroxylamine hydrochlorite method as explained below.

Methylolated Lignin-Phenol-Formaldehyde Resin Preparation

Methylolated LPF resins were prepared using the procedure of Sellers (1993) with some modifications. The addition levels can be seen in Table 1.

Table 1. Typical lignin-phenol co-polymer formulations using organosolv lignin.

Ingredients	Lignin/Phenol Ratio (20%)
Methylol-Lignin Condensation Step (Parts by Weight)	
Water	68
Sodium hydroxide, 50%	48
Lignin	58.1
Formaldehyde, 50%	130.3
Methylol-Lignin, Phenol-Formaldehyde Co-Condensation Step	
Phenol (90%)	290.5
Sodium hydroxide	70.6
Formaldehyde, 50%	310
Urea	45

A wide-necked, round-bottom reaction vessel with a five-socket lid was used to synthesise the resin. The multi-socket lid allowed the addition of chemicals and the extraction of samples, so both methylolation and condensation reactions could be performed sequentially. The relevant quantities of water and sodium hydroxide were placed into the reaction vessel equipped with a reflux reactor and heated to 55 °C with stirring. The organosolv lignin was slowly added to the sodium hydroxide solution and allowed to stand for 10 min. A partial amount of formaldehyde (as shown in Table 1) was added to the solution, and the reaction temperature was increased to 70 °C. The lignin solution was allowed to react with the initial formaldehyde for about 1h at 70 °C. At this point in the cook, phenol, sodium hydroxide and formaldehyde are added over a 30 min period to prevent a rapid increase in temperature due to exothermic reactions. The resin is cooked at 85 °C for 1 to 3 h depending on the desired viscosity (250-300 cP). Urea was added as the cook cooling at the end of the cook at about 5% based on total solution.

Testing of Phenolic Resins

Preparation of Dumb-Bell Shaped Specimens

Dumb-bell shaped samples were cut out with a die cutter (Figure 1). The idea for this experiment came from a thesis by Irle (1986), who used glass filter strips to estimate the durability of wood adhesives. The cross-sectional area of each sample was measured at the failure zone; thickness was measured to ±0.005 mm and width to ±0.05 mm, and stress at failure was calculated from the load/deflection curve, which was drawn and integrated automatically on a recorder.

Resin Impregnated Paper Filter Strips

The experiments were carried out using a Whatman GF/C glass microfibre filter. The inert glass fibre substrate will not swell in water and any change in physical properties would be wholly attributable to the resin rather than the substrate. The glass microfibre filter paper strips were approximately 95 mm long, with the length being cut along the machine direction of the paper.

The oven dry mass of each sample of strips was determined so that resin uptake could be determined. The strips were completely immersed in resin and left for 5 min. Excess resin was removed from each strip by running the sample between the thumb and finger. A hand-operated, electrically heated press was used to cure the samples at 180 °C. PF resins should be heated in the region of 145 to 175 °C to obtain complete cure (Irle, 1986). Therefore, a platen temperature of 180 °C was chosen to cure the strips.

The samples were placed on smoothed aluminium foil, to prevent sticking to the caul plates during the hot pressing stage. The strips were covered by another layer of smoothed aluminium foil. A gap of 0.25 mm was maintained between cauls with stainless steel spaces, to prevent the resin from being squashed out of the filter when the press closed. After 10 min the samples were removed from the press and foil. The samples were reweighed and resin uptake was calculated.

Conditioning and Strength Measurements

The samples were conditioned at 20 °C ± 2 °C and 65 ± 5% relative humidity until constant mass was achieved, before being tested. The tensile strength of each sample was measured using an Instron Universal machine (Model 4301), with a cross head speed of 2 mm per min. The samples were held by pneumatic rubber faced jaws at 10 mm span, operating at 2.11 kg cm^{-2}.

Ultimate tensile strength (UTS), total energy (TE), and strain and modulus of elasticity (MOE) were calculated for each strip. A comparison of properties was

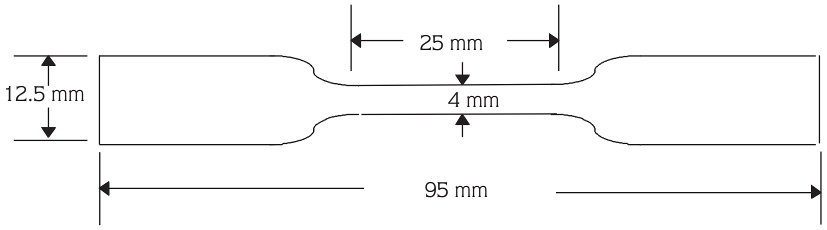

Figure 1. A plan of the dumb-bell shaped die cutter used to make the tensile strength test samples of resin.

made with the control resin; a sample of the Whatman GF/C glass microfibre filter paper, not impregnated by resin, was tested as an indication of the properties of the paper substrate.

Physical Properties of Resins

Phenolic resins are made to a specification, which means that the properties of the resin are controlled within certain limits. The main tests made are explained below.

Solid Content

This was determined by weighing the resin into a dish placed in an oven for a fixed period of time at a set temperature (120 °C, 3 h), and then cooled and re-weighed. The residue is solid cured resin and the solid content was calculated by the difference and quoted as a percentage.

Specific Gravity

The specific gravity of a resin solution was obtained by dividing the weight of the resin solution by the weight of an equal volume of water.

Viscosity

The viscosity of the resin samples was measured using a low-shear, rotating spindle apparatus (Model DV-II+ Viscometer). Viscosity was estimated (cP) at a constant temperature (25 °C).

pH

The alkalinity or acidity of solutions has a major effect on many adhesives properties. Properties such as viscosity, aging stability of the liquid adhesive, and properties of the adhesive bond such as water resistance are highly pH dependent.

Gelation Time (Disc Method)

In order to determine gel time, a Techne automatic gel timer was used. The sample to be measured was introduced into a dry glass beaker. The beaker was then immersed in boiling water and set. Polymerisation was observed.

The Determination of Free Formaldehyde Using Hydroxylamine Hydrochloride

The reaction product resins were analysed for free formaldehyde content. The weight of the sample to be taken depends on the expected free formaldehyde level, as indicated by the mid-point of the formaldehyde specification for the resin under test. If the specification mid-point was in the range of 0-5%, 2 g of sample was taken. Twenty-five millilitres of industrial methylated spirit (IMS) were added to the resin samples and stirred until dissolved. Two or three drops of 0.1% bromo phenol blue were added and the solution was then carefully neutralised with 0.5 N sodium hydroxide, or 0.5 N hydrochloric acid, as required. Ten millilitres of 10% hydroxylamine hydrochloride aqueous solution was added and the mixture was then heated to 50-55 °C in the water bath for 5 min. The mixture was cooled to room temperature and titrated with 0.5 N sodium hydroxide solution. A blank was carried out on 25 ml of neutralised IMS and 10 ml of hydroxylamine hydrochloride under the same conditions. The calculation and expression of the results were formulated as follows:

$$\textit{Free Formaldehyde}\ (\%) = \frac{(V_1 - V_2) \times f \times 1.5}{W}$$

where

V_1 = Volume of 0.5 N sodium hydroxide required for sample

V_2 = Volume of 0.5 N sodium hydroxide required for blank

f = Factor of normal (N) sodium hydroxide = 0.5

W = Weight of sample

Particleboard Production and Testing

Industrial woodchip furnish, comprised of a variety of principally softwood species was used for producing test panels. The resins used for the manufacture of boards were PF-com and lignin-based resins. No resin hardener or wax was added. Resins were applied at a rate of 10% (resin solids based on the oven dry weight of wood particles). Particles were dried to approximately 3% moisture content prior to the application of resin. Board target thickness was 12 mm; target density was 650 kg m^{-3} in all cases. The hot-press temperature was 180 °C. Particleboards were made under 15 min press time. Three replicates were made for each resin type. Test samples were prepared and conditioned at 65 ± 5% RH and 20 ± 2 °C until weight stability was reached. After conditioning, sample weight and dimensions were determined.

All tests were carried out to the appropriate European standards. The tests performed on the specimens were internal bond (IB) strength perpendicular to the plane of the board (EN 319:1993), static bending [modulus of rupture (MOR) and modulus of elasticity (MOE)] (EN 310:1993), thickness swelling and water absorption (EN 317:1993).

Results and Discussion

Determination of Reacted Formaldehyde

The purpose of this experiment was to evaluate the formaldehyde reactivity of lignin materials and demonstrate how lignin might be used in resin systems. The best way to make LPF adhesive is by first reacting it with formaldehyde to form methylol lignins (Wooten et al., 1988). In order to avoid unreacted lignin or a high amount of free formaldehyde in a finished LPF adhesive, it is necessary to know the reactivity of the lignin prior to the formulation of the resin (Jin et al., 1990). When substituting lignin for phenol, as was done in this research, it is desirable to define how much formaldehyde was needed to react with organosolv lignin because each lignin type can differ. The lignin-formaldehyde relationship was determined in a reactivity test, which defines the equivalent moles of formaldehyde per 100 g of lignin to be used in the experimental resins. The plot of lignin with formaldehyde reaction at 55 °C is shown in Figure 2.

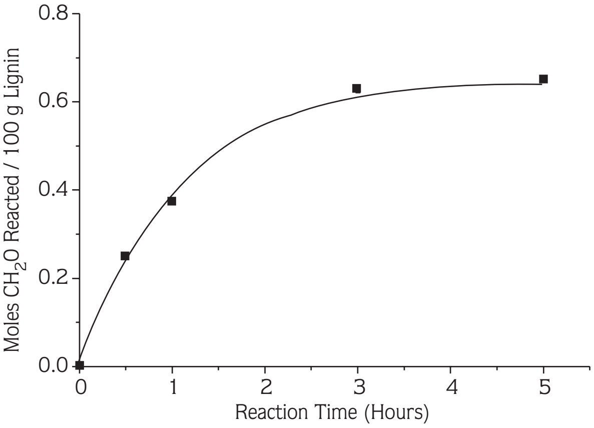

Figure 2. Lignin-formaldehyde methylolation.

As can be seen in Figure 2, an increase of reaction time from 1 to 5 h showed an increase in the moles of reacted formaldehyde. There was a curvilinear relationship between the reacted formaldehyde and reaction time. As the LF reaction proceeds, the rate increases. Gardner and McGinnis (1988) showed that as the phenolic molecule becomes partially substituted, there is a subsequent increase in the rate of reaction of the partially substituted molecule with formaldehyde.

The Results of Tensile Strength of Phenolic Resins

The resin preparations made at different organosolv lignin contents were examined with respect to tensile strength properties. The results are presented in Table 2 together with the results obtained for a PF commercial resin (control) without lignin addition. At replacement levels from 10 up to 30% organosolv lignin (LPF 10, LPF 20, LPF 30.), the tensile strength of the resins was equal or better than that observed for the pure PF resins. At a replacement of 40%, a considerable strength reduction was obtained. The resin impregnated paper strips were very brittle and weak.

Physical Properties of Phenolic Resins

In order to distinguish and clarify the characteristics of the lignin modified formaldehyde resins studied in this work, it is necessary to compare certain important properties with those of other similar resins. The resulting resins were characterised for their free formaldehyde, hardening time and specific gravity. The physical characteristics of these LPF resins are summarised in Table 3.

As can be seen from Table 3, the free formaldehyde for the lignin modified resins was less than 0.4%, which is considered to be acceptable in industry. Low levels of free formaldehyde in PF type resins indicate that these materials are condensed into other polymeric compounds. The viscosity of LPF resins was 250-300 cP.

Particleboard Properties

The results from the tensile strength tests looked promising for the use of organosolv lignin at 20% and 30% substitution for phenol in PF resins. Therefore, this study was designed to produce particleboards from two

Table 2. The tensile strength of PF and lignin-phenol-formaldehyde (LPF) resins.

RESINS	U.T.S** ($N\ mm^{-2}$)	T.E.** ($Nmm\ mm^{-3}$)	STRAIN** (%)	M.O.E.** ($N\ mm^{-2}$)
No resin	1.07	0.02	1.13	28.33
	(0.14)*	(0.005)	(0.29)	(14.03)
Control	13.71	0.16	1.4	520
	(1.84)	(0.06)	(0.52)	(57.26)
LPF 10 (10%)	20.93	0.24	2.1	780
	(3.49)	(0.17)	(0.42)	(103.03)
LPF 20 (20%)	18.13	0.2	1.75	650
	(2.29)	(0.06)	(0.34)	(65.38)
LPF 30 (30%)	15.78	0.17	1.5	557
	(2.54)	(0.25)	(0.49)	(86.58)
LPF 40 (40%)	10.35	0.11	0.98	364
	(3.06)	(0.07)	(0.24)	(106.76)

*Figures in brackets represent standard deviations
**: U.T.S.: Ultimate Tensile Strength; T.E.: Total Energy; M.O.E.: Modulus of Elasticity

Table 3. The physical properties of resins.

Resins	Viscosity (cP)	Solid Content (%)	pH	Free Formaldehyde (%)	Specific Gravity	Gel Time (min)
Control	270	42.09	10.2	0.18	1.19	27.0
LPF 10	248	39.10	10.8	0.16	1.18	25.0
LPF 20	265	40.98	10.4	0.25	1.17	29.0
LPF 30	256	41.80	11.0	0.21	1.19	30.5
LPF 40	260	43.60	11.3	0.38	1.20	35.3

types of LPF resins and control resin (PF). Table 4 shows the effect of lignin substitution in resins on the particleboard IB strength perpendicular to the plane of the board, static bending [MOR and MOE], thickness swelling and water absorption.

The results listed in Table 4 clearly indicate that the LPF resins do provide proper bonding of particleboard. The larger proportion of lignin used with the PF resin, however, showed a decrease in IB strength. The poor performance of the adhesive mixture containing the

Table 4. Particleboard test results.

Resin Type	IB** ($N\ mm^{-2}$)	MOR** ($N\ mm^{-2}$)	MOE** ($N\ mm^{-2}$)	Thickness Swelling (%)		Water Absorption (%)	
				2h	24 h	2 h	24 h
Control	1.1	14	2175	12	13.5	68	75
	(0.2)*	(0.3)	(40.2)	(1.1)	(1.2)	(1.5)	(2.1)
LPF 20	1.02	16	2267	10.6	12.9	65.8	73.2
	(0.2)	(0.4)	(30.4)	(1.4)	(1.3)	(1.7)	(2.4)
LPF 30	0.96	12.7	2224	9.5	14.7	69.5	72.9
	(0.2)	(0.3)	(45)	(1)	(0.4)	(2.3)	(1.8)

*Figures in brackets represent standard deviations
** IB: Internal Bord; MOR: Modulus of Rupture; MOE: Modulus of Elasticity

largest proportion of PF resin can probably be attributed to degradation of the PF component. The IB strengths of the boards, presented in Table 4, show that smaller amounts of lignin can produce acceptable boards. The resin type had some effect on particleboard MOR in this study. There is a relationship between the increased addition of lignin and a reduction in MOR. The presence of lignin in resins typically resulted in increases in MOE. Particleboards bonded with the control PF resin had higher thickness swell after 2 h absorption than particleboards bonded with the LPF resins. There were some differences in particleboard thickness swells after 24 h of water soaking between the resin types. Particleboards bonded with the PF control resin had higher 2 h and 24 h water absorption than boards made with the two types of LPF resins.

Conclusions

The synthesis of LPF resins was developed to conform to the existing production of PF resin. The utilisation of organosolv lignin in PF resins was achieved by methylolation. The results of this work showed that it is possible to partially replace phenol by organosolv lignin in PF resin. The tensile properties of a number of organosolv lignin resins were assessed by impregnation and curing onto glass fibre paper. This method was used to develop and assess LPF formulations. The strength properties were compared to those of a commercial PF resin. The tensile testing of resin-impregnated strips showed that the properties of modified lignin resins were at least as good as those of PF resin. The physical analysis of the LPF resins exhibited equal properties, if compared to the properties of control PF resin. Particleboards were bonded with control PF resin and LPF resins (LPF 20 and LPF 30). The particleboards bonded with LPF resins exhibited comparable physical properties when compared to particleboards with the control PF resin. These physical properties included IB, MOR and MOE. The thickness swell and water absorption properties of particleboards bonded with LPF resins gave comparable results to particleboards with control PF resin. The substitution of lignin for phenol at levels of 30% in cooked LPF co-polymers was considered practical. The study demonstrates that renewable resources such as lignin have potential as a substitute for phenol in PF resin systems.

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