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Use of organosolv lignin in phenol–formaldehyde resins for particleboard production

I. Organosolv lignin modified resins

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Abstract

This paper describes the work considering the potential for partially replacing phenol with organosolv lignin in phenol–formaldehyde resin used as an adhesive in the production of particleboard. Lignin-based resins were synthesised with organosolv lignin using various percentages of lignin replacement for phenol. The lignin was introduced to the resin in two different ways. The first method was the replacement of a certain percentage of phenol (5–40%) with lignin (as supplied) directly into resins. In the second method, lignin was modified by phenolation prior to resin manufacture. Different degrees of phenol substitution (20–30%) were investigated for the production of lignin-based resins. The physical properties of the formulated resins were measured and compared to commercial PF resin.

Keywords: A. Phenolic; B. Wood; Gas chromatography; Physical properties of resins

1. Introduction

Phenol formaldehyde resins are used as adhesives for gluing together the veneer plies of exterior-grade (structural) plywood panels, the flakes of oriented strandboard (OSB) panels and particleboards. Phenol–formaldehyde (PF) resins provide high strength and are extremely resistant to moisture, which prevents delamination and gives excellent temperature stability. This is in part due to the more flexible nature of phenolic resins [1]. However, PF resins can be very expensive products, because of the fluctuating price of phenol. Therefore, investigations aimed at using natural products as substitutes for phenol gained favour on not only environmental but also economic grounds [2]. Lignin has tremendous potential for many industrial uses as replacements for what ultimately will be increasingly scarce and expensive petroleum-based materials.

Extensive studies have been made on the use of various lignins as a PF resin substitute or co-reactant in PF resins. These lignins are derived from kraft, lignosulphonate, steam-exploded, organosolv and bio-mass pyrolysis processes [3]. Lignins have an aromatic and highly cross-linked structure, similar to the network of PF resins. They can be used as a macromolecular material without previous treatments. They may reduce the cost of PF resins because of the high cost and toxicity of phenol [4].

In view of these advantages, a great deal of research has promoted its use as a substitute in PF resins. Recently, lignin has been successfully used to replace phenol in PF resin preparation, or has been added as an extender for current commercial PFs [5–8].

However, despite these advantages, lignin has found limited utilisation commercially because of its varying complex chemical and physical structure making industry wary about significant commercial usage. Variation in its material characteristics depends on many factors including variations in pulping conditions, the kind of wood being pulped and the conditions under which is recovered [9].

To overcome these disadvantages, chemical modification of lignin is one of the possible methods to improve its reactivity. One potential reaction is phenolation, which naturally increases the number of potential reactive sites. Such modified lignin may be used in high percentages for resin production.

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Part I of this work demonstrates that organosolv lignin when substituted for up to 30% of the phenol in lignin-modified PF resins would be a suitable raw material in particleboard-type resin formulations. The utilisation of organosolv lignin in PF resins was achieved through various approaches. Initially, lignin was used directly as a replacement for phenol. Secondly, lignin was modified by phenolation and then incorporated in the resin formulations. The physical properties of the formulated resins were measured and compared to commercial PF resin (PF-com).

2. Materials and methods

A commercial powdered organosolv lignin (trade name Alcell® lignin, from Alcell® Technologies, Ltd.) was obtained. Commercial grade phenol of 99% purity, formaldehyde solution (35 wt% aqueous solution) and sodium hydroxide (40 wt% aqueous solution) were used. Commercial resol-type liquid PF resin (code DPL 5681, which is a particleboard binder resin) was supplied by DynoChem Ltd.

2.1. Preparation of lignin-based resins

Lignin replacement in PF resins was evaluated in two different ways:

1. By substituting phenol with lignin at different percentages [Resin 5 (5% lignin substitution), Resin 10 (10% lignin substitution), Resin 20 (20% lignin substitution), Resin 30 (30% lignin substitution) and Resin 40 (40% lignin substitution)].
2. By substituting phenol with phenolated-lignin compounds at different percentages [LPF 20 (20% lignin substitution), LPF 25 (25% lignin substitution) and LPF 30 (30% lignin substitution)].

2.2. Manufacture of PF resol base combination

Phenol and formaldehyde (P:F, 1:1.4) were mixed together for 10 min. To these reactants, sodium hydroxide was added and allowed to mix for a further 10 min. The required pH was 10.2. If the pH was too high, it was adjusted with acid (para toluene sulphonic acid); if too low, NaOH was added until it was within specification. The lab apparatus was set up for reflux, and heated to 50°C. The temperature was raised to 50°C over 30 min. When the temperature reached 50°C, the heat was turned off and cold water was applied to the outside of the flask if the temperature continued to rise. The temperature was held at 50°C for 1 h. The base product was then quickly cooled down in an ice bath, divided into batches and frozen to prevent further reaction of the components to PF polymers.

2.3. Organosolv lignin in PF resins

The addition of a PF precondensate to lignin was used as a way to increase lignin reactivity. The replacement of phenol was calculated on a weight basis. This method was used to afford comparisons with novel methods devised in the work. Organosolv lignin at 5%, 10%, 20%, 30% and 40% of the original phenol content was incorporated into the PF base combination (produced as described) and then the temperature raised slowly to 80°C. Cold water was applied to the reaction flask at 75°C to prevent temperature overshoot. The temperature was held at 80°C and samples were removed every half an hour to check the viscosity. When the sample reached the required viscosity, a vacuum was applied and the flask cooled to 35°C. The pH was adjusted to 7 with para toluene sulphonic acid. (Doing this maximises the pot life of the resin since at pH 7, the polymerisation reaction rate at ambient temperature is minimal.) Each batch was distilled under vacuum at a temperature of 40–50°C. Water was removed from the reaction mixture until the viscosity reached a set specification (200–300 cP). The flask was cooled and the vacuum released. All resins were stored in a fridge to reduce any further reactions occurring. When required for analysis or use they were warmed to 25°C, stirred and used. These candidate resins were assessed as adhesives, after adjustments were made to percent non-volatile solid content (50–55%), viscosity (200–300 cP), pH (10.2).

2.4. Preparation of phenolated-lignin base combinations

Initially, lignin was allowed to react with phenol before the phenolated lignins were combined with formaldehyde. Lignin was added to a mixture of phenol dissolved in industrial methylated spirit (IMS), such that the lignin/phenol weight ratio was varied and known. The phenolation reaction was allowed to proceed with continued stirring of the mix at 70°C, so that the maximum amount of phenol was added to the lignin for the given lignin/phenol weight ratio. IMS was evaporated off under a reduced pressure at 40–50°C from the mixture. The lignin–phenol product did not precipitate out of the phenol solution but the product viscosity varied, depending on the phenol/lignin weight ratio used. The lignin–phenol product was analysed for free phenol content by using gas chromatography (GC) to ensure that the reaction had gone to the expected completion.

2.5. Preparation of phenolated-lignin–formaldehyde resins

Since all the comparisons were made against the PF-com resin, it seemed from preliminary data, that 50% free phenol in the base combination was a good starting point. Therefore, the base combinations were prepared

Table 1
Parameters for phenolated-lignin resin formulations

Base resins	P/L mole ratio	Free phenol content (wt%) in base combinations	Formaldehyde solution added (wt%) to base combinations
Base LP 20	19	50	70
Base LP 25	14	50	70
Base LP 30	9	50	70

Table 2
Typical lignin–phenol co-polymer formulations using organosolv lignin

	Ingredients	Weights (g)
Phenolated-lignin–formaldehyde resins		
Base LP 20	Lignin	250
	Phenol (99%)	700 + 320
Resin LPF 20	Base LP 20 + formaldehyde (35%)	1270 + 890
Base LP 25	Lignin	250
	Phenol (99%)	550 + 275
Resin LPF 25	Base LP 25 + formaldehyde (35%)	1075 + 752.5
Base LP 30	Lignin	500
	Phenol (99%)	550 + 542
Resin LPF 30	Base LP 30 + formaldehyde (35%)	1592 + 1114.4

as explained above with the target of 50% free phenol content. Table 1 shows the required P/L mole ratio and free phenol content in the base combinations, and the amount of formaldehyde solution that was added to the base combinations to produce the phenolated-lignin–formaldehyde resin formulations. In the LP 20, LP 25 and LP 30 base combinations, the free phenol contents were less than the desired 50%. Therefore, extra phenol (320, 275 and 542 g) was added to the LP 20, LP 25 and LP 30, respectively, to bring the free phenol content up to the required 50%. The required extra amount of phenol was added at the same time as the calculated amount of formaldehyde solution (35%) (based on the total weight of lignin–phenol–extra phenol) and the NaOH (10 N) to catalyse the reaction. pH of the mixture was adjusted to 10.2. The reaction was heated up to 50°C and held at that temperature for an hour. A sample was taken from the resin and cooled at the end of the hour in order to determine its viscosity and free phenol content after the reaction. The reaction temperature was then increased to 80°C and maintained there until the required viscosity was achieved. After this, the reaction was cooled. Final viscosity and the free phenol content of the resin were determined. The excess water was removed under reduced pressure at 40–50°C until the desired end-point viscosity (200–250 cP) was reached and the product was used for further study. Table 2 shows the formulations of these resins. In instances, when the measured free phenol content in the phenolated-lignin–formaldehyde resins was found to be out of specification (i.e. ±6%), the mixture was heated up to 80°C again for a period and re-tested for free phenol content. If the viscosity started to rise, the phenol content had to be accepted as the nearest possible within the viscosity limits.

2.6. *The quantitative determination of phenol content in resins by GC*

The free phenol content for all the resin types was measured by GC using a flame ionisation detector (FID) on a glass column RTX-1 (7.5 m × 0.53 mm). The FID oven and injector oven temperatures were 350°C and 320°C, respectively, and oven temperature programmed from 100°C to 190°C at 2°C min^{-1} with a 10 min hold at 190°C. Helium was used as a carrier gas at a flow rate of 36 ml min^{-1}. A sample of resin (about 0.1 g) and known quantity of naphthalene (acting as internal standard, 500 ppm) were dissolved in 10 ml acetone.

3. Results and discussion

3.1. *Lignin–phenol–formaldehyde resins without modification*

Five types of lignin resins were prepared (i.e., 5–40% lignin addition) as explained in Section 2. PF-com and lignin–phenol–formaldehyde (i.e., where lignin was added to PF resin) resins were characterised for their physical properties, free phenol, free formaldehyde, hardening time and specific gravity. These results are presented in Table 3. All the resins had 200–250 cP viscosity and 50–55% solid content. The hardening times of lignin-based phenolic resins were carried out at 150°C. In these hardening experiments, no additional hardener was used. It was confirmed that hardening could take place without a curing agent, though the hardening time was longer. Curing agents were not used to determine the hardening time of the resins and were not added to resins in particleboard production. Fig. 1 shows the relationship between hardening time at 150°C and lignin content.

3.2. *Phenolated-lignin–formaldehyde resins*

In order to distinguish and clarify the characteristics of the phenolated-lignin–formaldehyde resins studied, it is necessary to compare certain important properties with those of the other similar resins. The resulting phenolated-lignin–formaldehyde resins were characterised for their free phenol, free formaldehyde, hardening time and specific gravity. The physical

Table 3
Physical properties of the lignin–phenol–formaldehyde resins

Resins	Free phenol (%)	Free formaldehyde (%)	Hardening time (min, at 150°C)	Specific gravity
PF-com	0.1	0.2	3.2	1.2
Resin 5 (5%)	14.1	2.40	3.3	1.2
Resin 10 (10%)	14	3.40	3.36	1.19
Resin 20 (20%)	16.8	3.87	3.49	1.17
Resin 30 (30%)	21	5.21	4.53	1.18
Resin 40 (40%)	22	5.76	6.45	1.19

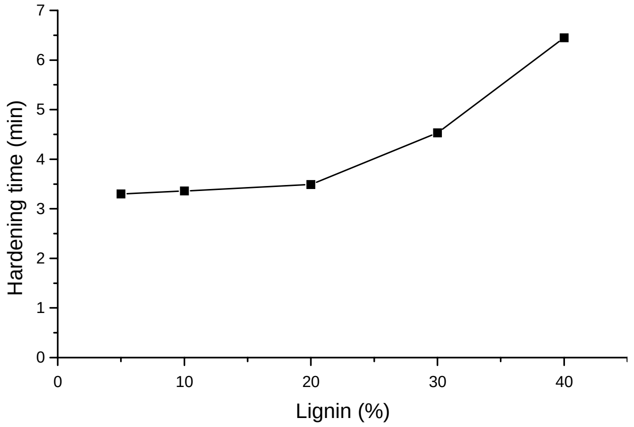

Fig. 1. Hardening time versus lignin (%) for lignin–phenol–formaldehyde resin.

Table 4
Physical properties of the phenolated-lignin–formaldehyde resins

Resins	Free phenol (%)	Free formaldehyde (%)	Hardening time (min, at 150°C)	Specific gravity ($g\,cm^{-3}$)
Resin LPF 20	9.4	0.77	1.30	1.18
Resin LPF 25	8.2	0.86	1.35	1.19
Resin LPF 30	6.4	0.92	1.56	1.17

characteristics of these phenolated-lignin–formaldehyde resins are summarised in Table 4. Table 4 shows the free formaldehyde content for some of the phenolated-lignin–formaldehyde resins to be less than 1%, which is considered to be acceptable in industry as indicated by the specifications reported for the control resin. Low levels of free formaldehyde and free phenol in PF-type resins indicate that these materials are condensed into other polymeric compounds reducing and/or eliminating potential health hazards. The physical properties of these resins such as hardening time, indicated that resins (LPF 20, LPF 25 and LPF 30) had good curing properties, if compared to the properties of initial lignin resins (Resins 5–40). The viscosity of phenolated-lignin–formaldehyde resins was 200–250 cP, which is a suitable range for resin distribution by high-pressure spray or high-speed disc application.

4. Conclusions

The synthesis of a lignin-based resin was developed to conform to the existing production of PF resin. The utilisation of organosolv lignin in PF resins was achieved through various approaches. Initially, lignin was used directly as a replacement for phenol. Secondly, lignin was modified by phenolation and then incorporated into the resin formulations. These lignin-based resins were characterised and compared to a commercial PF resin (PF-com). Phenolated-lignin–formaldehyde resin formulations exhibited satisfactory resin properties. The physical analysis of these resins such as hardening time, indicated that the resins (LPF 20, LPF 25 and LPF 30) had good curing properties, if compared to the properties of initial LPF resins.

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