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Lignin based adhesives for particleboard production.

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Lignin Based Adhesives for Particleboard Production

A thesis submitted to the University of Wales Bangor for the degree of *Philosophae Doctor* in Wood Science

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DEDICATION

To my family with love and thanks

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ABSTRACT

The purpose of this study was to utilise lignin as a partial substitute for phenol in PF resins. To achieve this, initially brown rot lignin was produced by a bioconversion technique. During the course of the study, it became clear that the production of brown rot lignin had a limited success.

Since brown rot lignin could not be obtained in sufficient quantity and purity by a bioconversion method, other alternative lignin production methods, as well as commercially available lignin, were chosen; namely production of lignin from black liquor and Alcell® (organosolv) lignin. Before performing production of resin formulations, the lignin sources were characterised in terms of reactivity and physical properties of lignins. Both lignins had a similar reactivity, but organosolv lignin was found to be more pure, with a low ash content. Since isolation of lignin from black liquor in laboratory conditions is more complex and requires more time, it was decided to use organosolv lignin for subsequent production of lignin-based resins.

The lignin was introduced to the resin in two different ways. The first method was the replacing of a certain percentage of phenol with lignin (as supplied) directly into resins. In the second method, lignin was modified prior to resin manufacture by phenolation. Different degrees of phenol substitution (from 5% to 60%) were tried for the production of lignin-based resins.

Bond qualities of lignin-phenol-formaldehyde (LPF), phenolated-lignin-formaldehyde, commercial phenol-formaldehyde (PF_com) and laboratory made phenol-formaldehyde (PF_made) resins were assessed by using an Automatic Bonding Evaluation System (ABES), prior to production of particleboards, in order to eliminate some of the poor quality resins. The effect of press temperature and time on bond strength appeared to be highly significant, as the lignin substitution levels increased. Up to 30% phenol substitution was achieved without sacrificing bond strength. The bond strength values of phenolated-lignin-formaldehyde resins were similar to commercial phenol-formaldehyde and laboratory made phenol-formaldehyde resins, but better than the LPF resins. It was apparent that resins containing a high level of lignin substitution gave the poorest bond strength values. From these results, some of the resins were eliminated, prior to particleboard production.

In order to evaluate the quality of lignin-based resins, particleboards were produced and mechanical and physical tests performed. Effect of press platen temperature (140°C, 160°C, 180°C) and press cycle time (5 min, 8 min, 15 min) on the mechanical properties of particleboard, produced by using lignin-based resins, were investigated. It was found that particleboards bonded with up to 30% lignin content resins gave similar mechanical and physical properties to commercial phenol-formaldehyde resin, as long as a sufficient heating regime and time were applied.

List of abbreviations

ABES	Automatic bond evaluation system
aq	Aqueous
CP-MAS	Cross polarisation magic angle spinning
DI	Diisocyanates
DMSO-d_6	Hexadeuterodimethyl sulfoxide
DS	Dimensional stability
DSC	Differential scanning calorimetry
FID	Flame ionisation detector
FTIR	Fourier transform infrared
GC	Gas chromatography
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
IB	Internal bonding strength
IMS	Industrial methylated spirit
KBr	Potassium bromide
LPF	Lignin phenol formaldehyde
MF	Melamine formaldehyde
Mn	Number average molecular weight
MOE	Modulus of elasticity
MOR	Modulus of rupture
Mw	Weight average molecular weight
NMR	Nuclear magnetic resonance
OSB	Oriented strand board
PF	Phenol formaldehyde resin
PF_com	Commercial phenol formaldehyde
PF_made	Laboratory made phenol formaldehyde
RF	Resorcinol formaldehyde
Tg	Glass transition
RPM	Revolutions per minute
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TS	Thickness swelling
UF	Urea formaldehyde
UV	Ultraviolet

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CHAPTER 1

INTRODUCTION

This study of lignin based adhesives was initiated to develop a renewable alternative raw material source for wood adhesives.

The current adhesive market for wood is dominated by urea-formaldehyde (UF), phenol-formaldehyde (PF), and isocyanate resins. Early pre-cursor PF resins were developed in the beginning of this century and were the first example of fully synthetic polymers. Important applications of this material, besides the wood working industry, were for moulding and insulation compounds.

Urea-formaldehyde resins are popular because the produced particleboards cure quickly, are strong, have a low cost and they do not colour the board. They are not resistant to moisture, and therefore are not suitable for exterior use.

Boards produced using PF resins are resistant to cold/boiling water and high temperatures, and are not attacked by fungi, insects and chemicals to the same extent as UF. The quality of joints glued with PF is very good, therefore these boards are suitable for exterior applications; however, they have some disadvantages. The boards are more expensive, have a darker colour, many have a phenolic odour and, can cause skin irritation.

Lignin-based resins can be used as alternatives to synthetic resins for particleboard production. Currently, such plant-derived adhesives show similar performance to synthetic resins but not better. It might be considered that the cost disadvantages of the PF resins can be avoided by the development of a new type of adhesive.

During the oil based energy crisis of the 1970's, increasing costs and decreased availability of phenol drastically disrupted the wood industry's efforts to supply much needed panel products for construction. Even after this shortage was overcome, it was apparent that the wood industry's almost total dependence upon petrochemicals for durable wood adhesives was a situation badly in need of correction (Gillespie, 1986).

The wood products industry has a long successful history of utilising adhesives based on renewable resources. The pulping industry produces millions of tons of by-product lignin annually, which it normally burns for energy. This large volume of potentially useful material has attracted the attention of numerous investigators over the years, attempting to develop products of commercial value, particularly adhesives for use in the manufacturing of wood-based panel materials.

With growing concern about global ecological changes and environmental problems, future emphases will be on the more effective use of renewable resources of which forest products are a subset. In this context, wood adhesives and adhesion play a tremendously important role. This will only occur if the adhesives themselves are effective and environmentally acceptable.

Lignins have been considered as replacements or substitutes for phenol in PF resin systems used to bond wood composites for many years. The major driver here is that the use of lignin poses less threat to the environment and may have large cost benefits compared with petrochemically derived phenol.

The replacement of phenol requires that the replacement substance will take part in the chemistry of either the resin manufacture process or resin curing process, or even in both processes (Kambanis *et al.*, 1985). The interest in using lignin as a starting material for the formulation of a durable adhesive is based on the fact that its basic chemical structure is phenolic, with repeating phenylpropane units combined in various ways.

Therefore, the objective of this project was to investigate whether or not lignin recovered as a by-product from a pulping process or a composting process could replace phenol in a commercial synthesis of PF resin, and if so whether adequate performance could be achieved at an acceptable level of the replacement.

The focus in this project was intended to assess the performance of different lignins to produce resins. An initial investigation involved producing lignin by biological degradation of wood, which would give one type of lignin for resin synthesis.

Two types of fungally released lignin were isolated and screened. Brown rot fungi were utilised to isolate and modify lignins from (i) hardwood (poplar) (ii) softwood (pine and spruce). This work was to include isolation of these lignins, characterisation and then utilisation in resin formulations. Unfortunately, this procedure did not yield sufficient quantity of the lignin to carry out the proposed work.

Another approach to lignin utilisation involved its extraction from black liquor, derived from hemp/flax alkali sulphite pulping, in laboratory conditions. However, the alkali sulphite lignin had a high ash content and low purity, when compared to organosolv lignin, even though both lignins had a similar reactivity.

Therefore, this work narrowed down its focus to pay particular attention to the effective formulation of readily available organosolv hardwood lignin (Alcell® lignin), for the partial substitution of phenol in particleboard PF resin adhesives.

Different lignin-based resin formulations were designed. The lignin-based resin batches in this study were made to substantiate their feasibility in comparison to a commercial PF (PF_com) resin. The physical properties of lignin-based resins were characterised prior to use and compared to PF_com resin used to bond particleboards. Assessment of resin physical properties included: free phenol content, free formaldehyde content, non-volatile solids content, viscosity and gel time.

All the resins were tested for their bonding strength using an automatic bonding evaluation system (ABES). The tests were conducted at various temperatures and times to determine the optimum parameters and eliminate the poor resins, before producing particleboards.

The physical properties of particleboards bonded with the lignin-based resins were compared to the physical properties of particleboard bonded with the PF_com resin. The particleboards were subjected to various physical property tests including internal bond strength (IB), modulus of elasticity (MOE) and modulus of rupture (MOR). Thickness swell and water absorption properties of panels were measured after 2 hours and 24 hours water soak test.

The thesis describing this work is broken down as follows:

Chapter 2 contains a review of relevant literature.

Chapter 3 describes the attempts to isolate lignin from wood using brown rot fungi. This work was not successful and was not continued.

Chapter 4 describes the isolation of alkali sulphite lignin from black liquor and analyses the alkali sulphite lignin and organosolv (Alcell®) lignin to characterise the properties of these lignins before production of LPF resins.

Chapter 5 studies the activity of organosolv lignin and incorporation of this lignin material into a phenolic resin blend using different resin applications.

Chapter 6 determines the bonding strengths of the resins. Resins were evaluated for ability to bond lap-joint specimens under the conditions chosen.

Chapter 7 evaluates the strength properties of particleboards bonded with lignin-based resins and PF_com resin. The relevant results from each of these chapters are brought together and discussed in Chapter 8.

CHAPTER 2

LITERATURE REVIEW

2.1 LIGNIN

The structure and chemical composition of wood has been widely studied and reviewed, for example by Fengel and Wegener (1989). The structure of woody tissue is composed primarily of the three major polymeric compounds; cellulose, hemicellulose and lignin. Lignin is a characteristic chemical component of the tissues of higher plants such as softwoods and hardwoods, where it typically occurs in the xylem (Fengel and Wegener, 1989).

The word “lignin” originated from the Latin “Lignum” meaning wood. Next to cellulose, lignin is the second most abundant and important polymeric organic substance in the plant world and an agricultural product that is available for industrial use (Kirk and Harkin, 1973).

Always closely associated with cellulose, most lignin is bound to plant polysaccharides, especially the hemicelluloses. The incorporation of lignin into the cell walls of woody plants gave them the ability to conquer the Earth’s land surface. At a microscale lignin acts as a stiffener surrounding the cellulose microfibril in the plant cell wall and at a grosser level it binds plant cells together (Fengel and Wegener, 1989).

The main function of lignin is therefore to provide rigidity and unique mechanical and elastic strength properties to the plant cell wall. Lignin acts as a cementing agent to bind the cellulosic microfibrils together into a rigid woody structure. It also provides considerable protection from attack by fungal enzymes, which degrade the polysaccharides of the cell walls. (Northey, 1990).

2.1.1 Basic chemical structure of lignin

Lignin is considered to be a random, amorphous, three-dimensional network polymer, which does not posses a uniform, homogenous structure. It is comprised of various types of phenylpropane units (Figure 2.1) possessing a variety of functional groups (Northey, 1990). The principle difference is in the number of methoxyl groups on the aromatic ring (Eaton and Hale, 1993). p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol are the primary precursors and building units of all lignins.

Lignin polymers are synthesised by free-radical coupling of these three major C6-C3 (phenylpropanoid) units (Figure 2.1) (Pizzi and Mittal, 1994). The phenylpropane units principally differ in the nature of R_1 and R_2 giving p-coumaryl alcohol (R_1 = H, R_2 = H), coniferyl alcohol (R_1 = H, R_2 = OCH_3), sinapyl alcohol (R_1= OCH_3, R_2= OCH_3) (Figure 2.1). Thus, the major difference in the chemical structure of these monomers is the presence or absence of an electron donating methoxyl ($-OCH_3$) group at the 3 or 5 positions of the phenol ring.

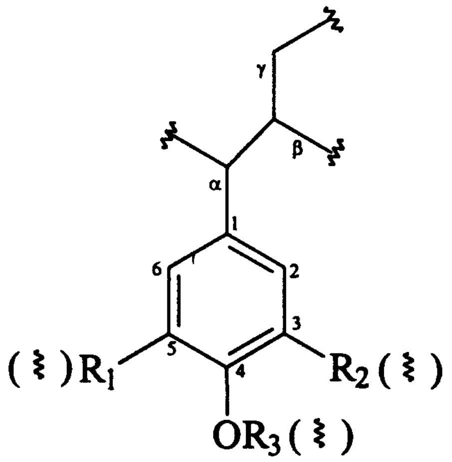


Figure 2.1 Phenylpropane - the basic structure of lignin. Phenylpropanoid units of lignin: R_1, R_2 = H, OCH_3; R_3 =H, CH_3, CH_2.

The lignins of grasses, softwoods and hardwoods differ with regard to their content of p-coumaryl (C), guaiacyl (G), or syringyl (S) units. This can be readily shown by nitrobenzene oxidation, which yields different amounts of the corresponding aldehydes: p-hydroxybenzaldehyde, vanillin or syringaldehyde (Fengel and Wegener, 1989). Figure 2.2 shows that corresponding alkaline nitrobenzene oxidation products of the basic phenylpropanoid units of lignin and the most common acid derivatives.

Grass lignins are classified as guaiacyl-syringyl lignins, as are hardwood lignins. However, unlike hardwood lignins, grass lignins additionally contain small but significant amounts of structural elements derived from p-coumaryl alcohol. Grass lignins also contain p-coumaric acid (Figure 2.2.7), and ferulic acid (Figure 2.2.8) (Lin and Dence, 1992).

"Guaiacyl lignin" which occurs in most of the softwoods, is largely a polymerisation product of coniferyl alcohol. "Guaiacyl-syringyl lignin" typical of hardwoods is a copolymer of coniferyl and syringyl alcohols in addition to small amounts of p-coumaryl (p-hydroxyphenol) units (Sjostrom, 1993).

In addition to the phenylpropanoid units, smaller amounts of C_6-C_1 units are found in some lignin samples, especially p-hydroxybenzoic acid (Figure 2.2.4), which may be linked via ester and ether bonds to the rest of the lignin molecule (Sjostrom, 1993).

2.1.2 Lignin structural formulae

Phenylpropane units are joined together via both C-O-C (ether) and C-C linkages with the ether linkages dominating (Sjostrom, 1993). The most prominent type of linkage in softwood and hardwood lignins is the β-O-4 linkage, which comprises more than one half of all interunit linkages. Other important linkages are 5-5, β-5, and α-O-4 (Fengel and Wegener, 1989). Figure 2.3 shows the prominent inter-unit linkages connecting phenylpropane units in softwood and hardwood lignins.

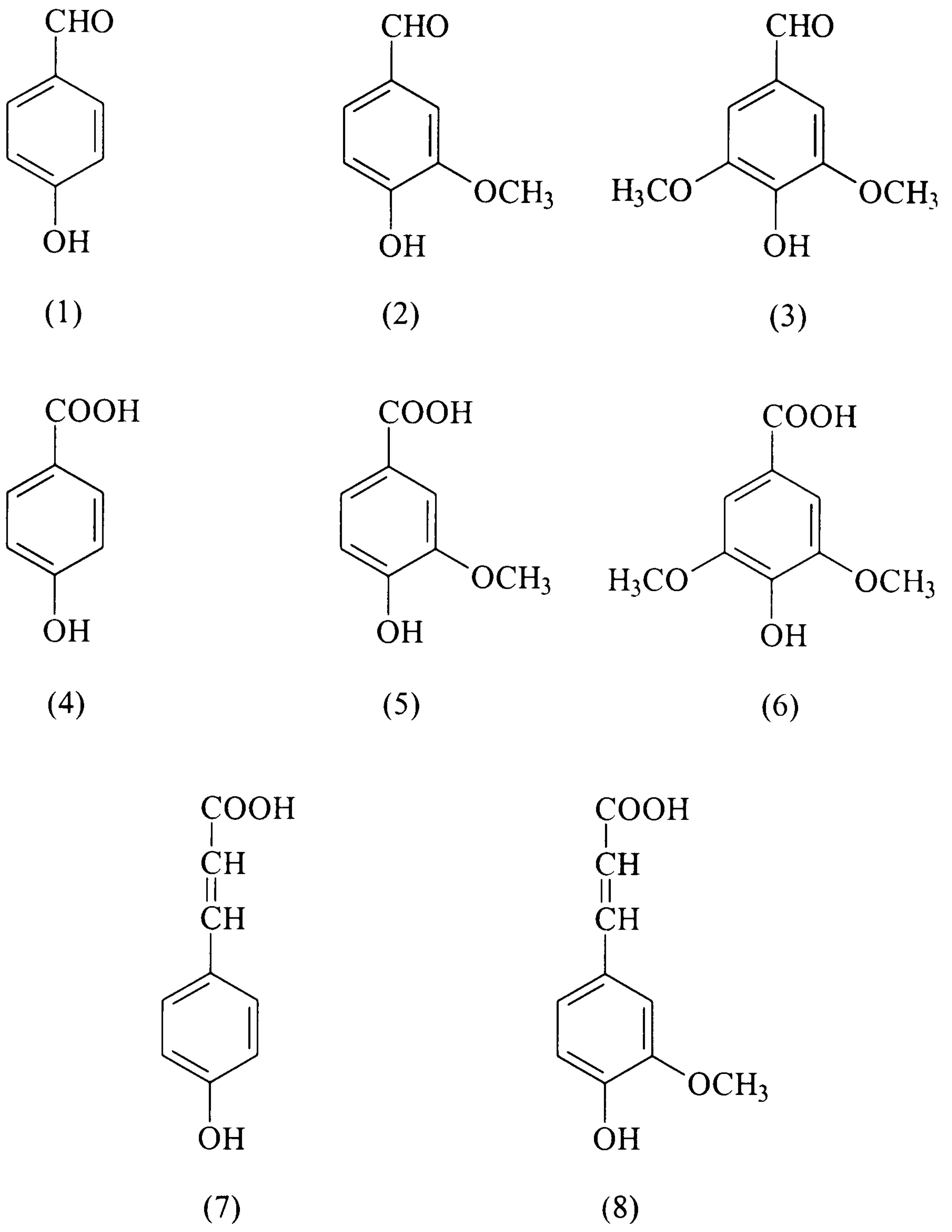


Figure 2.2 Alkaline nitrobenzene oxidation products of lignin precursors: (1) p-hydroxybenzaldehyde, (2) vanillin, (3) syringaldehyde, (4) p-hydroxybenzoic acid, (5) vanillic acid, (6) syringic acid, (7) p-coumaric acid, (8) ferulic acid (Lin and Dence, 1992).

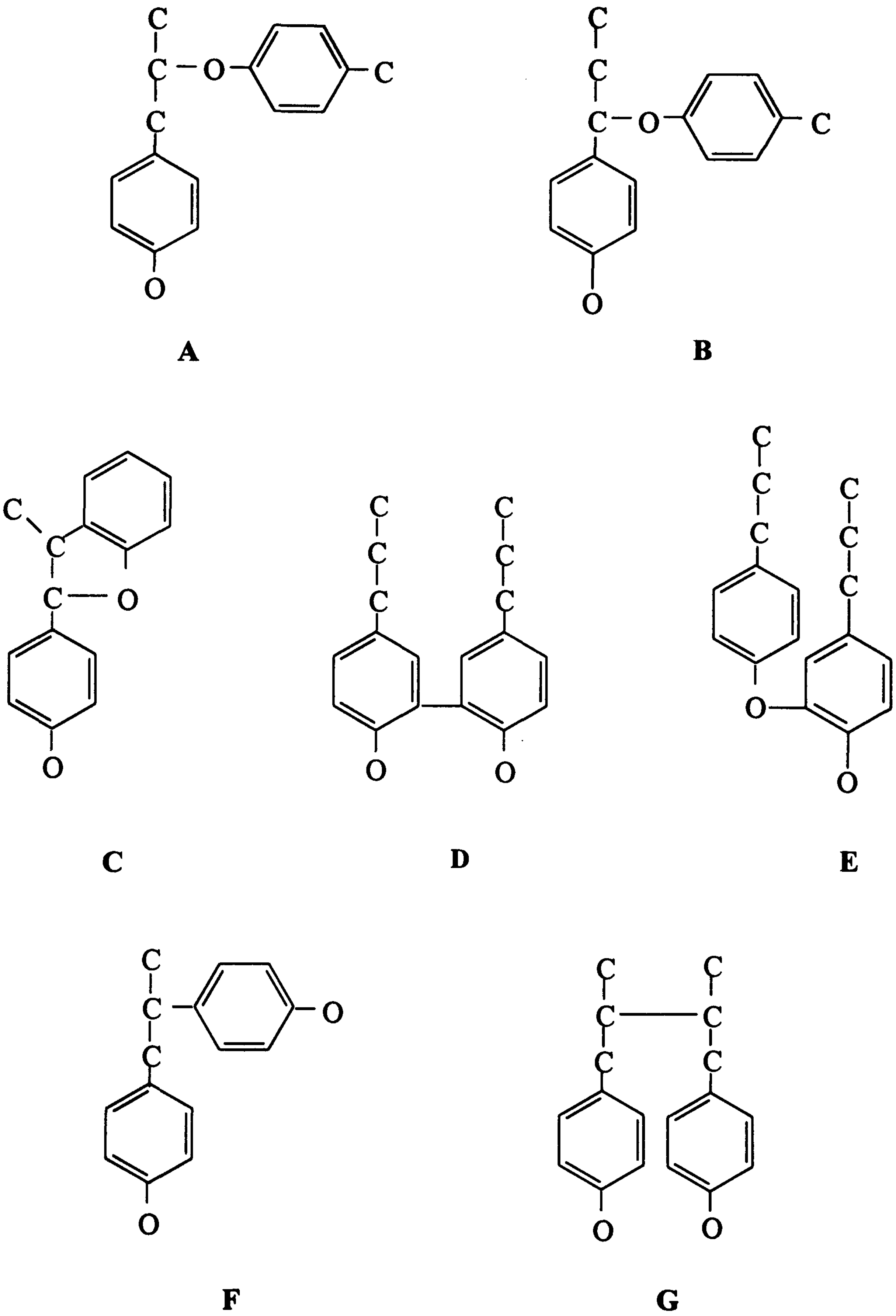


Figure 2.3 The main linkage types in softwood and hardwood lignin (Adler, 1977). A: β-O-4 (phenylpropane β-aryl ether), B: α-O-4 (phenylpropane α-aryl ether), C: β-5 (phenylcoumaran), D: 5-5 (biphenyl), E: 4-O-5 (diaryl ether), F: β-1 (1-2-diaryl propane), G: β-β (lignan-like).

Although the basic lignin unit appears to be simple, its complete polymeric structure is very complicated. This complexity is due to the number of different ways the three units bond can combine, as a result of radical polymerisation during biosynthesis and its structure is not completely understood. Various models of its structure have been proposed (Kharade and Kale, 1998). Based on the information obtained from studies of biosynthesis as well as analysis of various linkage types and functional groups, structural formulae for hardwood and softwood lignins have been constructed. A schematic structure for a softwood lignin is shown in Figure 2.4. This consists of 16 phenylpropyl units and it represents only a small segment of the lignin macromolecule (Adler, 1977).

These models should not be regarded as depicting the true structural formulae for lignin in the usual sense, but should be used as examples for illustrating the type and linkage modes of the constituent structural elements and the proportions in which they are believed to occur in lignin (Lin and Dence, 1992).

2.1.3 Lignification of different cell wall layers

Lignin is not uniformly distributed throughout wood cell wall, and the use of ultraviolet microscopy shows that it is concentrated in the inter-cellular spaces (i.e. the middle lamella) and is also present, but at lower concentrations, in the secondary cell wall layers. Although the middle lamella is rich in lignin, because of its relatively small volume, it is not the region in which most of the lignin is located. The secondary cell wall is lignified to a significant degree and, because of its relatively large tissue volume in comparison to the middle lamella, most of the lignin in wood is in fact located here (Roberts, 1996).

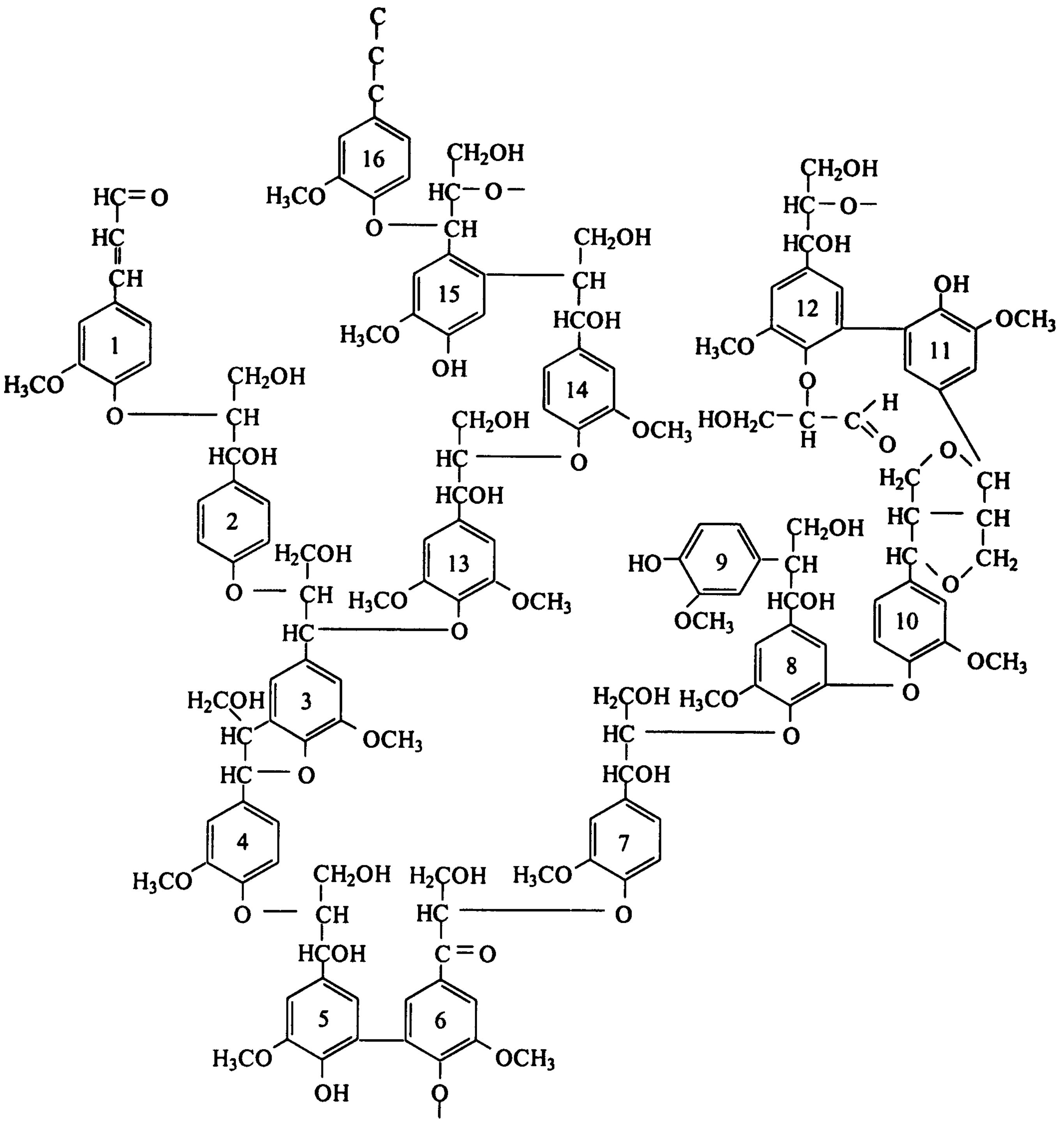


Figure 2.4 A structural segment of softwood lignin proposed by Adler (1977).

2.1.4 Distribution and primary sources of lignin

Trees are the most abundant source of lignin. Lignin exists as one of the essential wood components ranging in amount from 20% to 30% e.g. *Pinus sylvestris* (26.3%), *Acer rubrum* (22.8%). In non-woody fibre sources, the lignin contents are typically in the 11 to 27% range.

Although present in all woody material, the proportions of each of the different monolignols and the compositions of the lignins vary according to tree species (Northey, 1990). The variability of lignin composition is much greater in hardwoods than softwoods.

While the lignin content ranges from 20 to 40% in aquatic and herbaceous hardwoods, many monocotyledons (e.g. horse-tail species) are less lignified. Softwoods generally contain more lignin than temperate hardwoods. Normal softwoods contain 26-32% lignin, while temperate hardwoods have 18-25% lignin. Tropical hardwoods have higher lignin contents than temperate hardwoods (Fengel and Wegener, 1989).

Wood is sometimes formed with abnormal lignin contents. In softwoods this is known as compression wood, which has 35-40% lignin. In hardwoods, tension wood is formed which contains amounts lower than in normal wood (Fengel and Wegener, 1989).

2.1.5 Bulk sources of isolated lignins

The majority of lignin can be separated from cellulose-rich fibres, either by strong alkaline, or by a high-pressure steam treatment, followed by extraction with aqueous alkali or organic solvents. There are two major types of pulp and paper derived lignin by-products, kraft (alkali) and sulphite (lignin sulfonates) lignins. Table 2.1 gives a very conservative idea of annual lignin production in the United States and Worldwide (Lewis and Lantzy, 1989).

In addition, there are several different types of lignins from potential biomass-to-chemicals conversion processes. These include process schemes based on the involvement of the water and steam at various temperatures and pressures (autohydrolysis and steam explosion lignin) and organic solvent mixtures (organosolv lignin) (Glasser and Jain, 1993).

Table 2.1 Estimated annual production of lignin (millions of tons) (Lewis and Lantzy, 1989)

Type	United States	Worldwide
Kraft lignin	20	75
Lignosulphonates	1.5	15

2.1.5.1 Kraft lignins

The term kraft lignin refers generally to the lignin material, which typically is refined from alkaline pulping black liquors. Other black liquors such as those produced in the soda and other well known alkaline pulping operations are also produced (Doering, 1993).

Kraft pulping is the major wood pulping process and potentially represents the most abundant source of technical lignin (Lewis and Lantzy, 1989). In the kraft pulping process, delignification occurs on the ether linkages in the lignin molecule. Cleavage of these bonds liberates phenolic hydroxyl groups which increases the hydrophilicity and thus dissolution of lignin in the alkaline solution (Northey, 1990).

Kraft lignins can be utilised in ways similar to lignosulfonates, and high refinement costs make kraft lignins typically more expensive. These high costs have prevented any major use of kraft lignin use in wood adhesives (Pye and Lora, 1991).

Kraft lignins have low polarity and are water insoluble. These compounds are therefore rather unattractive as feed stocks for polymer production and little progress has been made in this direction so far.

In addition, kraft lignin is more degraded and thus possesses a lower molecular weight than lignosulfonate lignin produced in sulphite pulping. The high alkalinity utilised in kraft pulping causes condensation reactions, resulting in the formation of new carbon-carbon bonds (Northey, 1990). Also, the lignin residues in black liquor are combusted, which is an essential part of the kraft chemical recovery cycle. Furthermore the energy content contained in the black liquor makes the kraft pulping process energy self-sufficient. Hence, there are powerful economic and technical arguments for not utilising this lignin in other processes.

2.1.5.2 Lignosulfonates

Lignosulfonates are by-products of the sulphite pulping process. Sulphite pulping has been in a steady decline for many years because of environmental concerns and the inferior physical properties of the pulp (Pye and Lora, 1991). However, there are certain products (e.g. grease-proof paper) where this pulping method is preferred.

Delignification in these processes is the result of ester and ether bond cleavage, in addition to sulfonation, reactions which solubilise the lignin molecule. Sulfonation occurs primarily at benzyl aryl ether, and benzyl alkyl ether linkages on the side chain of the phenyl propane units (Northey, 1990).

Lignins from the sulphite process (lignosulfonates) are extremely polar, owing to the presence of sulfonate groups and are highly water-soluble.

2.1.5.3 Organosolv lignins (Alcell® lignin)

In recent years, alternative pulping methods have been investigated worldwide in an effort to provide a raw material source for the production of higher value added products such as useful low-molecular weight chemicals and polymeric materials.

Several methods have emerged as strong candidates for commercialisation (Thring *et al.*, 1996).

One of these alternatives is the Alcell® process; an organosolv pulping technique developed by Alcell Technologies Inc. Alcell® was a subsidiary of Repap Enterprises Ltd. (Montreal, P.Q, Canada) based at its semi-commercial facility in Newcastle, N.B., Canada.

The general operating principles of the Alcell® (organosolv lignin) process can be described as follows: Initially wood chips are loaded into a batch digester, which serves as an extractor. Liquor from the primary accumulator, after being used as a secondary liquor in the previous cook, is rapidly circulated through the extractor and through a peak load heat exchanger. This procedure brings the temperature up to 190-200°C in a few minutes and generates a vapour pressure of about 2758 kPa (400 psi). The liquor contains approximately 50% (weight/weight) denatured ethanol/water mixtures. Once at full temperature, the primary cooking cycle begins, which lasts a predetermined time, usually in the range of one hour. The primary liquor, now loaded with dissolved solids consisting mostly of low-molecular weight lignin, hemicellulose saccharides, furfural and acetic acid, is displaced from the extractor into a recovery feed accumulator by secondary liquor, which is finally replaced by a tertiary liquor, each having a lower solids content. No acids or alkali are added to the cooking liquor, which maintains a natural pH of about 4. This acidity derives from the acetic acid released through hydrolysis of acetyl groups associated primarily with the hemicelluloses present in the wood during the early stages of the cook. The first liquid performs mostly heating, while the last two liquors serve mostly to wash the cooked chips.

Once the extractor is drained, it is vented, and alcoholic vapours are condensed and recycled. Then the pulp left in the extractor is stripped with low-pressure steam, until only trace amounts of alcohol remain. After steam stripping, the pulp remaining in the extractor is sluiced with water, and after screening, is sent to the bleach plant.

Alcell pulps use conventional oxygen bleaching. The effluent process water contains about 0.02% (200 ppm) ethanol. The start-to finish time for the extraction process is about three hours for lower density hardwoods, and longer for high-density hardwoods, and depends in part on pH, ethanol concentration, and temperature.

In the solvent recovery system, the hot black liquor accumulated from the three liquor cycles is flashed from the recovery feed accumulator into a tank. The alcohol-rich vapours obtained are condensed and recycled. Lignin is precipitated from the liquor and recovered by a liquid/solid separation system consisting of a settler and a centrifuge. The lignin cake obtained from the centrifuge is then dried and bagged for sale. The liquor is further processed to recover additional by-products and /or burned for process energy (Sellers, 1993).

The Alcell process lignin (organosolv lignin) is a co-product of the recycled ethanol solvent pulping of a mixture of Canadian hardwoods that includes 50% maple (*Acer rubrum*), 35% birch (*Betula papyrifera*) and 15% poplar (*Populus tremuloides*) (Sellers *et al.*, 1994b).

This pulping method has many advantages over kraft and sulphite pulping. High purity lignin can be obtained by organosolv pulping processes (Vazquez *et al.*, 1997a). The environmentally benign (because it is sulphur free) organosolv process produces high quality, fully bleached pulps from hardwoods and annual fibres (Pye and Lora, 1991). The process has low chemical, water and energy requirements and uses a simple solvent for by-product recovery. In addition, it has overall a lower capital cost requirement, which is a major advantage (Tjeerdsma *et al.*, 1994).

Organosolv lignin is different from the kraft lignin and lignosulfonate. Unlike lignosulfonates, this lignin is water insoluble and therefore it contributes to bond durability when used as an additive in PF resins. Unlike kraft lignin, powdered organosolv lignin flows under hot-pressing conditions and is therefore well suited for applications that frequently require powder binders e.g. oriented strandboard (OSB) (Senyo *et al.*, 1996).

These lignins are very pure, having low ash and low sugar content and they do not contain formaldehyde. They are also characterised by their hydrophobicity, low glass transition temperature, low molecular weight and narrow molecular weight distribution (Senyo *et al.*, 1996).

2.2 ADHESIVES

2.2.1 The development of synthetic resins for the wood panels industry

Artisans in early Egypt depended on natural adhesives to glue a variety of natural materials. More recently, natural adhesives have been largely replaced by synthetic adhesive polymers developed from low-cost petrochemicals. In a review of the history of adhesives (Skeist, 1977), it was stated that the reaction of phenol and an aldehyde (acetaldehyde) in the presence of an acid catalyst yielding a resinous product, was discovered in the late nineteenth century by a A. Bayer. The use of an alkaline catalyst was developed by Michael, and the use of formaldehyde by Kleeberg. The oldest commercial product made of a purely synthetic plastic is Bakelite, consisting of a PF resin (Danielson, 1998).

Adhesives, used for the manufacture of wood-based panels, are principally composed of five major synthetic thermoset resin groups (Table 2.2). However, various blends of the groups are being increasingly used by industry e.g. MUPF. Particle and medium density boards as well as hardwood plywood are mainly bonded with UF resins, DI resins and MUF resins, whereas PF and RF resins are the main binders for OSB, softwood plywood and laminated beams, respectively. These binders are considered to be conventional adhesives for wood-based panels (Roffael and Dix, 1991).

Table 2.2 Major conventional and potential alternative adhesives in wood-based panels

Conventional wood adhesives	Potential alternative adhesives
Urea Formaldehyde (UF)	Carbohydrates
Phenol Formaldehyde (PF)	Tannins
Resorcinol Formaldehyde (RF)	Lignins
Melamine Urea Formaldehyde (MUF)	-
Diisocyanates (DI)	-

However, some alternative and renewable resins like carbohydrates, tannins and lignins have been of great historical importance to the adhesive industry. They have been replaced in most applications by petroleum-based adhesives, because the synthetic adhesives show improved performance or better economics. Some natural adhesives remain important in certain speciality areas and there has been recent interest in non-petrochemical adhesives as they are seen as being "green" or environmentally friendly.

Table 2.3 Main requirements for today's adhesives

- Costs
- Reactivity
- Performance
- Homogeneity of chemical composition
- Environmental issues

Particleboard adhesives have to meet many criteria for use in wood based panels (Table 2.3). In order to produce a competitive product, industry must keep the price down by using the least expensive but acceptable raw materials. However, the reactivity of the adhesive and the end-use applications of the product also have to be taken into consideration. Therefore, binder cost is a critical but not overriding factor in acceptance. Lignin-based adhesives therefore have the potential advantage of producing a relatively inexpensive but reactive product (Roffael and Dix, 1991).

2.2.2 Concepts of synthesis/structure/property relationships

The identification of variables that correlate with resin performance is the prime objective of resin synthesis and characterisation studies. Because of the complexity and quantity of synthesis and structural properties, the identification of key variables is difficult. The variables involved in resin synthesis-structure-property relationships are shown in Figure 2.5 (Gollob, 1989).

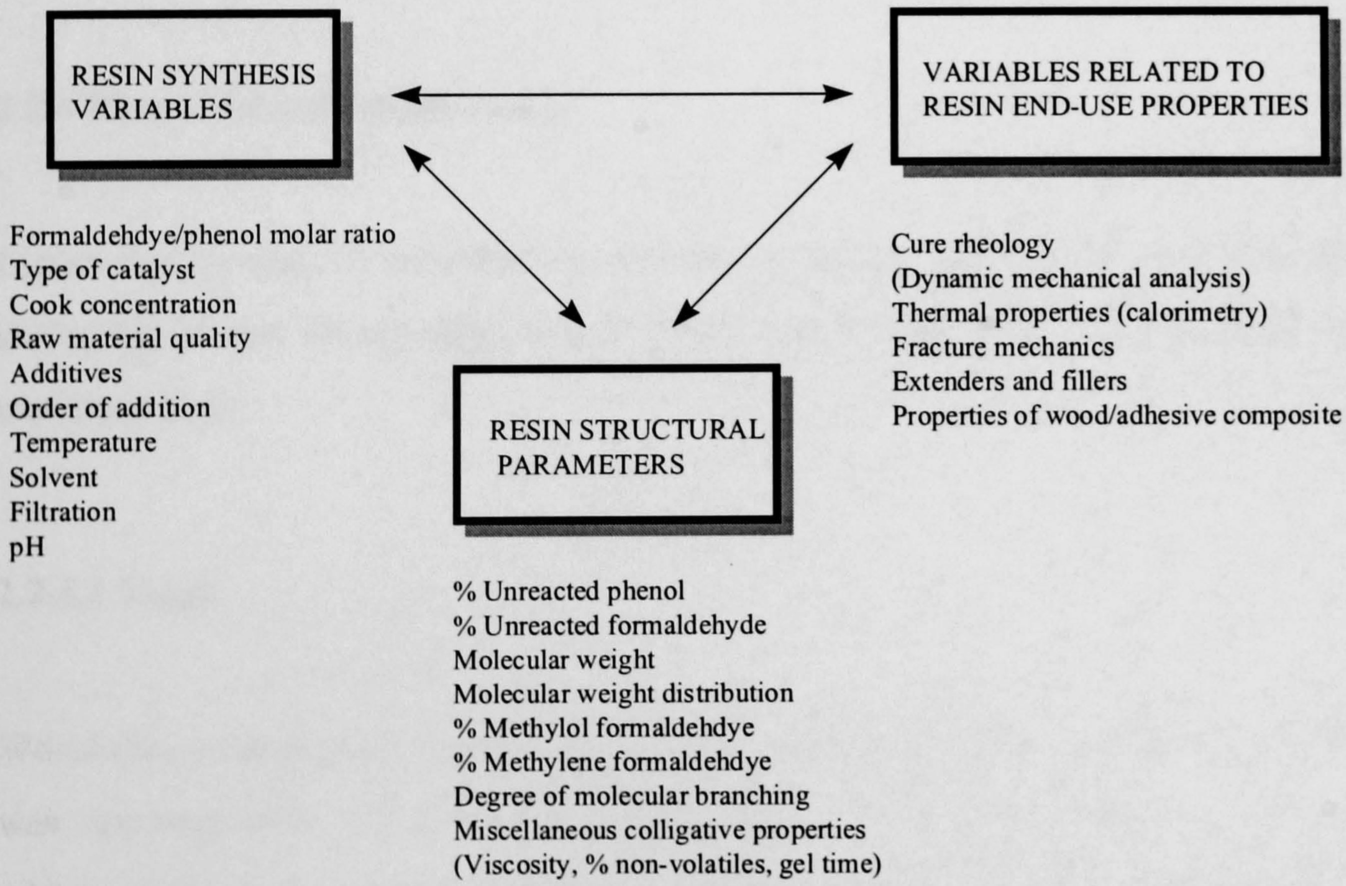


Figure 2.5 Interaction of PF resin synthesis, structure and property relationships (Gollob, 1989).

2.2.3 Adhesion

Adhesion is the state in which two surfaces are held together by chemical or physical forces with the aid of an adhesive. When two pieces of wood are glued together for structural purposes, the basic objective is to hold the two pieces in a fixed position so that when an applied stress reaches a critical value, the failure occurs with the wood rather than with the adhesive.

To be a satisfactory adhesive, a material must be capable of both wetting the wood substrate (polar attraction) and being converted into a rigid solid through either evaporation of the solvent, physical cooling of a thermoplastic-type adhesive, or a chemical reaction that may require a catalyst and/or heat to complete (Pizzi and Mittal, 1994).

2.2.4 Phenol-formaldehyde resins

Lignin can be used in combination with resins such as PF and UF resins. In this study, lignin was incorporated with phenolic resins. Therefore, only PF resins are explained here.

2.2.4.1 Usage

Worldwide consumption of PF resin solids for wood composite adhesives in 1992 was approximately 770,000 tons (Himmelblau, 1996). The adhesives used in commercial and composite products are usually synthetic polymer resins based on the polycondensation reaction of formaldehyde with phenol (Pizzi, 1983). PF resins were the first completely synthetic polymeric materials synthesised in the early twentieth century and found wide application in a variety of different areas. All these thermosetting adhesives adhere well to wood and, when cured, form bonds at least as strong as the wood itself (Pizzi, 1983).

PF resins are used as adhesives for gluing together the veneer plies of exterior-grade (structural) plywood panels and the flakes of oriented strandboard (OSB) panels and particleboard. 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.

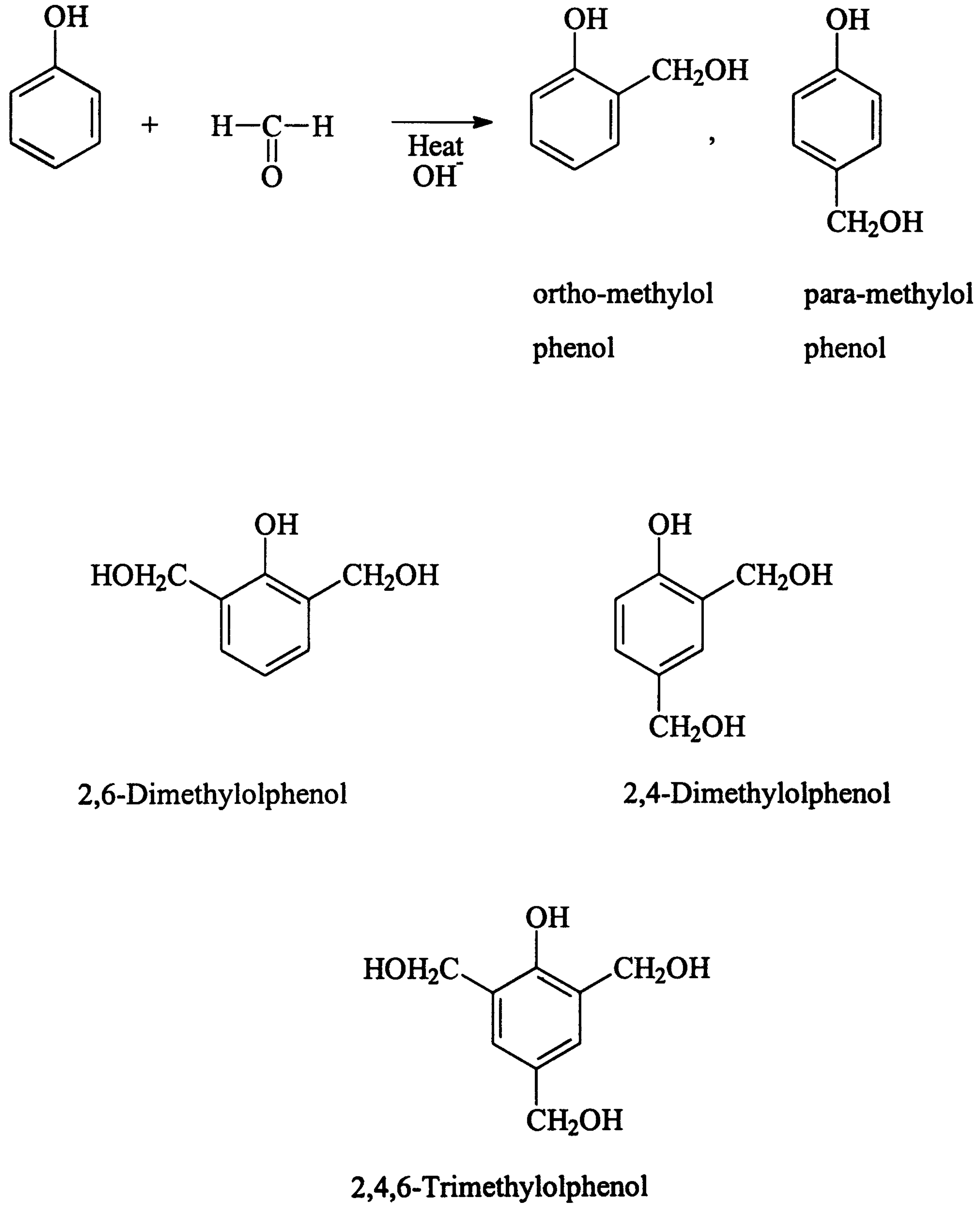
PF thermoset resins are normally applied in an aqueous media, and then polymerised *in situ* to afford a solid, highly cross-linked system with a durable wood adhesive interface (Steiner, 1975).

2.2.4.2 Chemistry

PF resins are the complex final products of many reactions involving formaldehyde and phenolic compounds, producing a variety of substances ranging from simple methylol and methylene derivatives, to the complex resins (polymers), in which large numbers of phenolic molecules are linked together by methylene groups (Walker, 1964).

Formaldehyde attacks the active *ortho-* and *para-* positions of a phenol ring to form methylol groups (Figure 2.6). The first products are monomethylol phenols. If two or three molecules of formaldehyde attach to the ring, dimethylolphenols or trimethylolphenol are formed (Figure 2.6).

The hydroxymethyl groups on these compounds can react with unreacted positions on other phenolic rings, or with activated hydroxymethyl groups on different phenolic rings. These condense together by splitting off water to form diphenylmethanes and ethers (Figure 2.6). These condensation reactions build up the molecular weight and lead to branching and cross-linking (Martin, 1956; Pizzi, 1983).



ortho-methylol phenol

para-methylol phenol

2,6-Dimethylolphenol

2,4-Dimethylolphenol

2,4,6-Trimethylolphenol

Figure 2.6 Active positions of a phenol ring to form methylol groups.

Phenolic resins fall into two main categories: novalacs and resols. The differences between these two basic types are determined by the P/F molar ratio, the type and amount of catalyst used, time and temperature of reaction.

- **Novalacs**

Novalacs are often referred as two stage resins since they need to be heated with additional formaldehyde in order to cross-link to their final infusible form. Novalacs are produced from a reaction that uses an acid catalyst (e.g. sulphuric acid, oxalic acid) and which is highly exothermic. Novalacs are synthesised with a formaldehyde/phenol molar ratio less than one, otherwise total cross-linking will occur during manufacture. Because of their linear structure, novalacs have a thermoplastic nature. They are soluble in various organic solvents (Sellers, 1985).

In novalac synthesis, formaldehyde reacts with phenol through electrophilic substitution in the *ortho* and *para* positions of the phenol ring. The methylol groups are unstable under aqueous acidic conditions and readily hydrolyse, affording stable methylene bridges. The reaction proceeds, yielding linear oligomers with molecular weights of less than 2000. Because novalacs are not branched, they tend to be water soluble at high molecular weights and tend to be more thermoplastic in nature than resols (Rowell, 1996). Figure 2.7 shows the formation of PF resin under acid conditions. The oligomers are then cross-linked further in the presence of the substrate (e.g. wood) by the addition of formaldehyde (normally hexamethylenetetramine-hexamine or paraformaldehyde), further catalysis and heat.

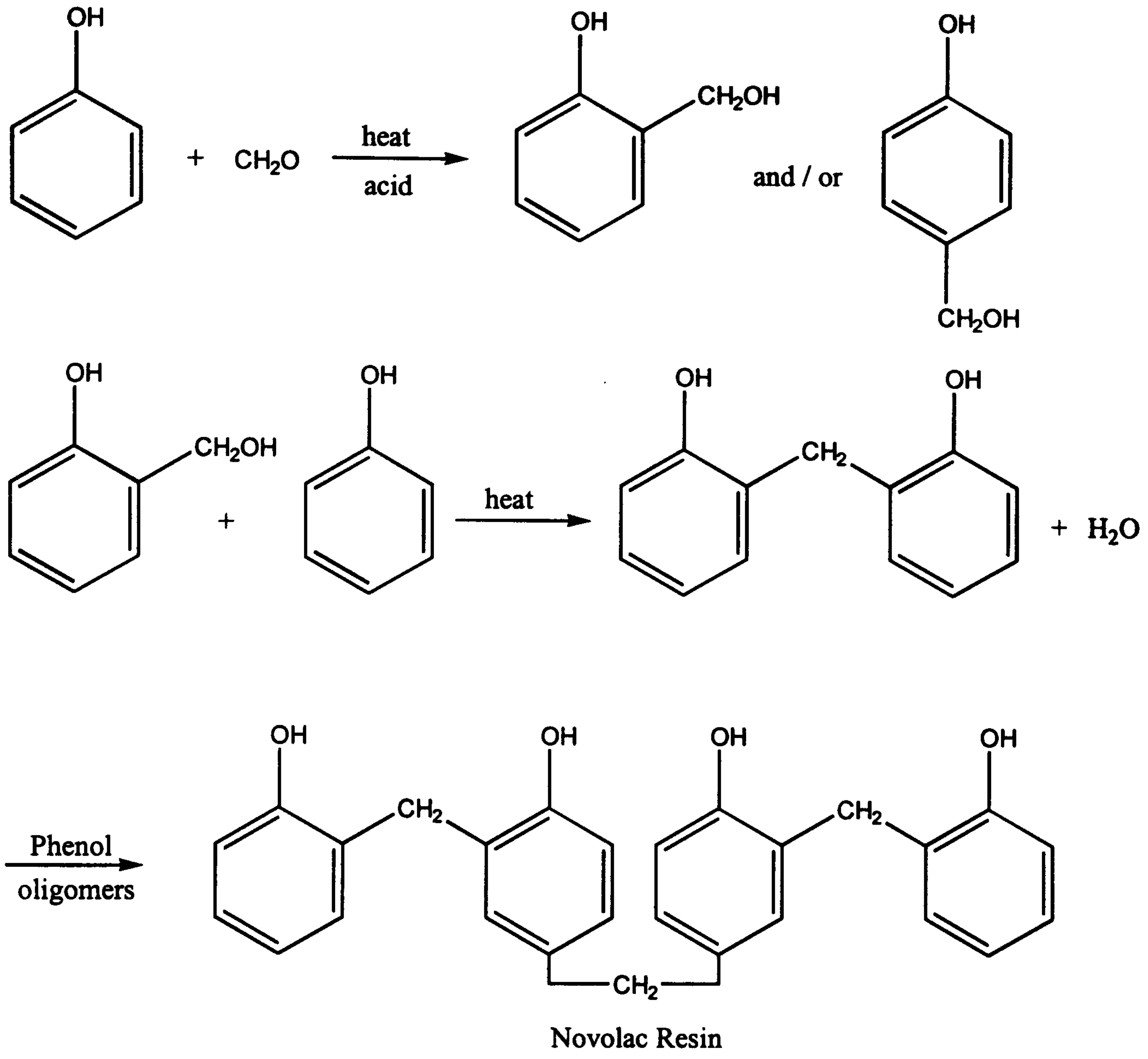


Figure 2.7 Phenol-formaldehyde reaction under acidic conditions.

- **Resols**

Resols are different from novalacs. These are referred to as one-stage resins. Resols are obtained as a result of alkaline catalysis (usually caustic soda for water-soluble resins and ammonia or an amine for electrical grade laminating resins) and an excess of formaldehyde (Figure 2.8). A resol molecule contains reactive methylol groups, (CH_2OH) that are oligomerised further to methylene ether groups (–CH_2-O-CH_2-) or methylene bridges. Resols are irreversibly hardened at higher temperatures without added cross-linkers. They are made in a very wide range of viscosities and molecular weights for specific end-uses (Sellers, 1985).

Resols have a sufficiently high formaldehyde ratio for them to cross-link on further heating without additional formaldehyde into their final infusible form. Alternatively, resols may be cross-linked through the addition of strong acids. This reaction is extremely exothermic e.g. as is experienced in felt bonding or in foam production.

Resols obtained at low F:P ratios have a relatively linear structure whereas resols prepared at high F:P ratios have a highly branched form due, in part, to a greater cross-linking density caused by the higher methylene content (Wang, 1992). Figure 2.8 shows example of dimers and pre-oligomers formed during resol synthesis.

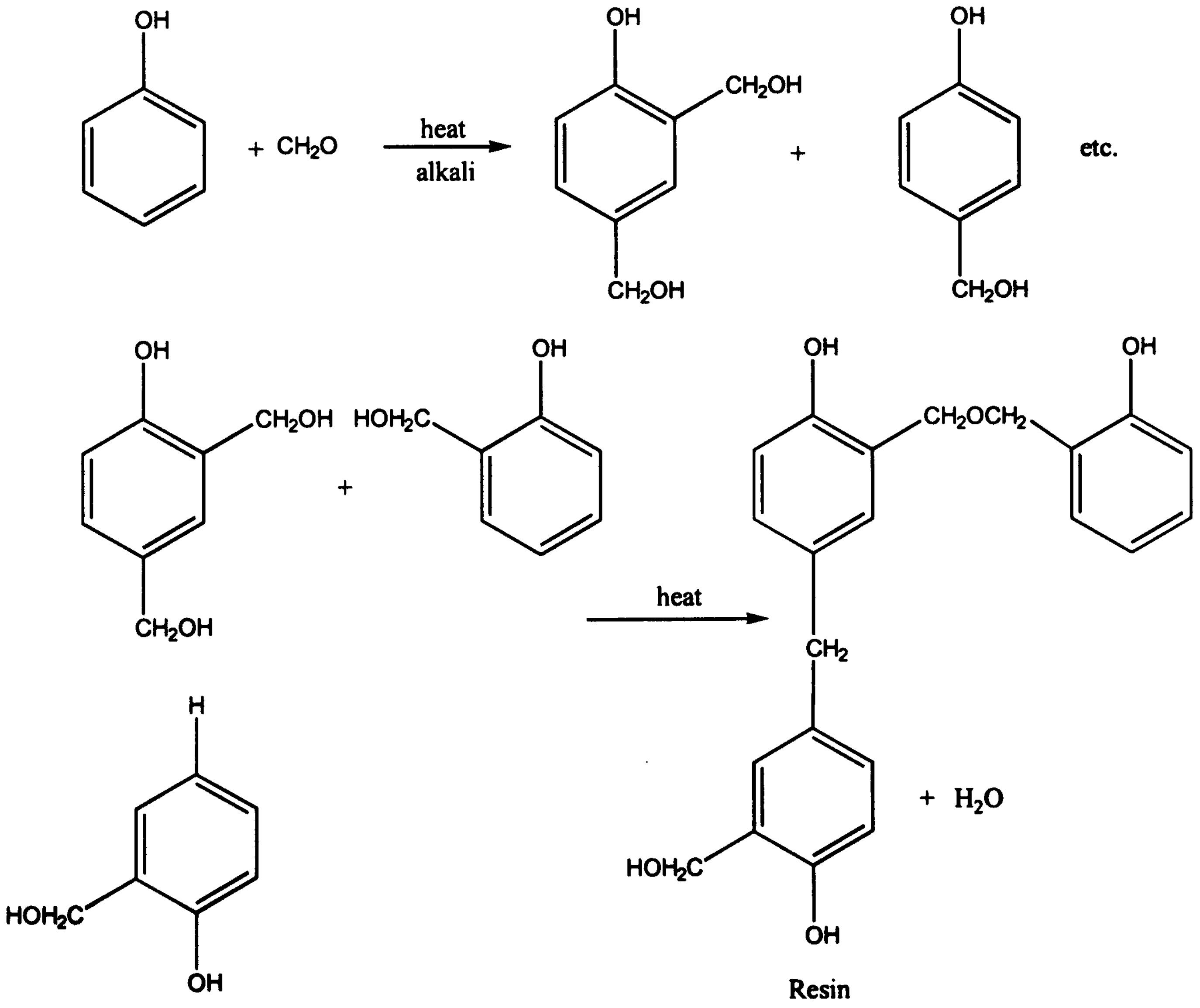


Figure 2.8 Resols formed via alkaline catalysis.

In the resols, the addition of formaldehyde to the phenol takes place at the *ortho* and *para* positions on the phenol ring only, due to the destabilising effect of the OH group on the meta position carbon. There are three types of resols that can be obtained at various stages in the PF resin condensation reaction:

- Initial resol -------- A stage resol
- Resitol -------- B stage resol
- Resite -------- C stage resol

The initial resol known as the A stage resol, commonly has a low molecular weight of less than 200. The product of an A stage resol reaction consists primarily of methylol substituted phenol. When initially produced, A stage resols are soluble in organic solvents such as alcohols and ketones (Webster and Charleston, 1965). When an A stage resol is heated further, it is turned to a resitol or B stage resin. Resitols are an intermediate stage in the phenol resin reaction, where cross-linking is only partially complete. So they are insoluble, but may be rubbery when swollen by solvents, or softened when heated. On further heating, the resitol stage is converted to the highly cross-linked resite or C stage. Resites are resins of high molecular weight. They are thermosets and completely insoluble (Martin, 1956; Pizzi, 1983).

A strong alkaline water solution, such as 50% sodium hydroxide, is used to maintain the solubility of PF resins and act as a catalyst for the majority of synthetic PF resin formulations. Under alkaline conditions, the formation of methylene linkages is rapid, but can be slowed down by cooling if the proper concentrations are used. This cooling during batch reaction in the vessel reactor is an important plant consideration. In such a way, synthetic resin solutions are obtained which can be more easily formulated to 45 to 50%, concentrated to 60% by vacuum distillation at temperatures below 45°C or dried to 90% non-volatile content under appropriate temperature conditions. The level of alkali in the resin formulations may vary, depending on the PF polymer desired. Apart from its catalytic effect, the sodium hydroxide improves the solubility of the resin in aqueous solution. When sodium hydroxide is used in large excess, it may retard the gelation time of phenol resins and increase resin penetration into wood tissue (Sellers, 1985).

On the other hand, if the sodium hydroxide concentration is lowered too much, the release of free-formaldehyde can increase to unacceptable levels. However, one of the most important facts is that the amount of sodium hydroxide in phenol adhesive is related to the hydroscopicity of particleboard bonded with phenol resins, due to its substantial proportion of hydroxyl groups (Wang, 1992).

2.2.4.3 Applications for phenolic adhesives

The applications for phenolic resins are shown in Table 2.4.

Table 2.4 The application of phenolic adhesives. Materials foams and application areas for phenolic resins (Ren, 1988)

Phenolic Resins						
Liquids	**Solutions**		**Solids**			
Neat	**Aqueous**	**Organic**	**Lumps**	**Flakes**	**Pulverised**	**Dispersions**
	Laminates		Coatings	Foundry	Fibre bonding	Friction
	Foams		Adhesives		Grinding wheels	Adhesives
-	Foundry	-			Wood bonding	Coated abrasives
	Coated abrasives				Friction	Coatings
	Coatings					
	Fibre bonding					

2.2.5 Lignin-phenol-formaldehyde resins

The worldwide crude oil crisis in 1973 interrupted access to cheap raw materials, such as phenol from petrochemicals and emphasised the need for alternatives based on renewable raw materials. 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 (Klasnja and Kopitovic, 1992). Lignin has tremendous potential for many industrial uses as replacements for what ultimately will be increasingly scarce and expensive petroleum based materials.

As lignin is one of the largest waste products in pulp mills, it is an attractive raw material for adhesives; it has been since the beginning of the sulphite pulping of wood (Pizzi and Mittal, 1994). Disposal of the lignin is a serious environmental problem and thus a number of studies have been devoted to its utilisation. A process that would make rational use of the liquors would be highly desirable, not only from the aspect of environmental protection, but also from that of the optimum consumption of raw materials.

Briefly summarised, lignins can be used as an extender or as a component in phenol-formaldehyde resins and have the following advantages:

- Lignins are renewable, natural and abundant raw materials,
- High cost and toxicity of phenol,
- Lignin is a phenolic-based material,
- They 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 (Benar *et al.*, 1999).

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 PF's (Nimz, 1983; Van der Klashorst, 1989; Gillespie, 1989; Sellers, 1990).

However, despite these advantages, lignin has found limited utilisation commercially because of its a complex chemical and physical structure and industry has been wary about large 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 (Hollis and Schoenherr, 1981).

According to its structure as a polyphenol (Figure 2.4), lignin as an adhesive should be similar to phenol-formaldehyde resins. This is true for native lignin in wood, while technical lignins (lignosulfonate and black liquor) have to be additionally cross-linked, in order to transfer them into insoluble resins. However, cross-linking condensation reactions in lignin by heat cannot be as effective as in synthetic phenol-formaldehyde resins, due to a lower quantity of free positions in the aromatic nuclei of lignin and their considerably lower reactivity than in PF resins. There are several reasons for this.

- First, there are only 0.5 free 5-positions (*ortho* to the phenolic groups) per C_9 unit, while the 6-and 2-positions are less reactive. Industrial lignin is usually fairly condensed, hence does not contain a high number of unsubstituted 5-positions on phenolic C_9 units to contribute in cross-linking reactions with formaldehyde.

- Second, there is less than one benzyl alcohol or ether group per C_9 unit in lignin, while in synthetic PF resins up to three methylol groups can be introduced into one phenolic ring.

- Third, the aromatic nuclei in lignin are in a precondensed, rigid state, which hinders their reaction with benzyl alcohol groups in adjacent C_9 units. Finally, the aromatic nuclei in lignin are considerably less reactive toward hydroxybenzyl alcohol groups than phenol, due to the presence of methoxy or methoxy-equivalent groups rather than hydroxyl groups on the lignin aromatic rings (Nimz, 1983).

Not only the reactivity issues have to be addressed. Lignin-based adhesives for use as in wood composites need:

- to produce a strong resin with a high density of cross-linking in its cured state,
- to be fast-curing, thus to tolerate very fast pressing-times compatible with standard panel products in manufacturing processes,
- to be able to be used with existing equipment with little or no plant retooling (Stephanou and Pizzi, 1993).

2.2.5.1 Cross-linking of lignin by condensation

Higher percentages of cross-linking can be achieved only if the reactivity of the lignin is chemically enhanced. The most promising reactivity-enhancing processes are methylolation, phenolation or demethylation.

Lignin can be incorporated into phenol-formaldehyde resins in several ways:

- It can be reacted with formaldehyde to provide methylol functionalities, therefore introducing more reaction sites,
- It can be reacted with phenol to enhance its reactivity in PF resins (Gardner and McGinnis, 1988).
- It can also be directly condensed into a resin with phenol and formaldehyde.

Reactivity of different lignin preparations with formaldehyde will vary, according to the severity of their isolation procedure (pH, temperature, pressure on the pulping conditions), and also, with the plant species origin of the lignin. Hardwood lignins, which contain a high percentage of syringyl units and highly condensed lignins, have been shown to have limited reactivity with formaldehyde (Gardner and McGinnis, 1988). The apparent reactivity of lignins with formaldehyde may also be affected by the quantity of extraneous materials such as carbohydrates and inorganics contained in the lignin preparations and by competing side reactions (Gardner and McGinnis, 1988).

The reaction of lignin with formaldehyde (hydroxymethylation) is a first step in the synthesis of lignin-phenol-formaldehyde resins. Lignin can react with formaldehyde under alkaline conditions introducing methylol groups at the *ortho* positions of the aromatic ring (Benar, 1999). On increasing the temperature, the methylol groups react with free positions of other lignin units to form methylene bonds (cross-linking).

Reaction of lignin with formaldehyde, introduces methylol groups (which can condense with other lignin molecules or phenol-formaldehyde pre-polymers) at position C5 of the guaiacyl units (the Lederer-Manasse reaction), at side chain positions α to a carbonyl group (the Tollens reaction) and on the β carbon of α- β double bonds conjugated to free phenol units (the Prins reaction) (Vazquez *et al.*, 1997a). Figure 2.9 shows methylolation, and condensation of lignin sub units with formaldehyde.

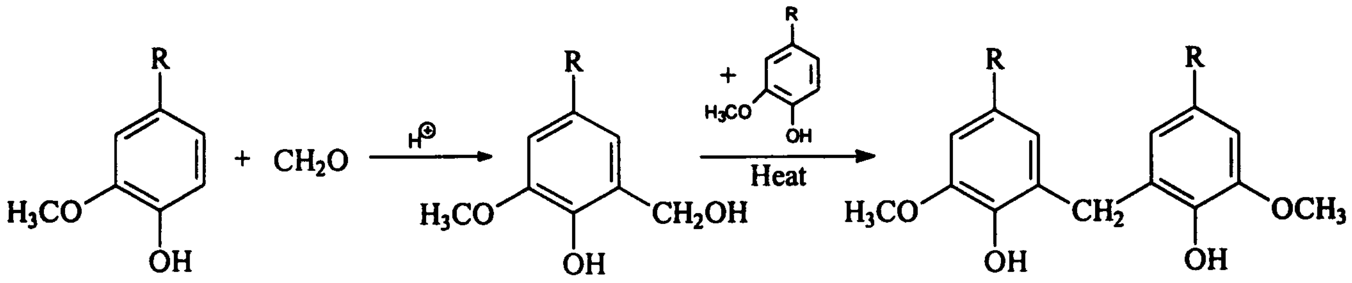


Figure 2.9 Reaction of lignin with formaldehyde (Nimz, 1983).

Alkali lignin contains a substantial number of benzylic hydroxyl (α-carbinol) groups owing to the cleavage of arylalkyl ether linkages (e.g. β-O-4, Figure 2.3) during pulping. α-carbinol groups react with phenol in a manner similar to the hydroxymethylated lignin intermediates to give a methylene linkage (Figure 2.10) (Van der Klashorst, 1989).

Under very alkaline conditions and high temperature, most of these groups can be expected to react with reactive lignin units, especially with the long pulping times normally used. The only reactive sites left are therefore unsubstituted 5-positions on phenolic C_9 units (also 3-positions for grass lignin). The occurrence of unsubstituted 5-positions on phenolic C_9 units in industrial alkali lignin is however low (Van der Klashorst, 1989).

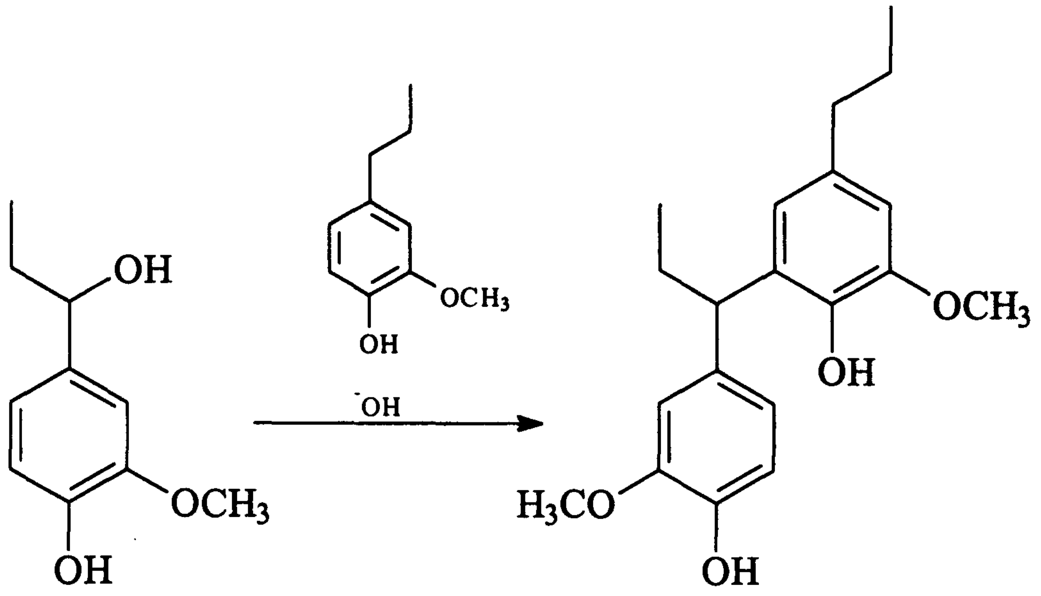


Figure 2.10 Reaction of α-carbinol groups on phenolic C_9 units with a reactive lignin fragment to afford a methylene linkage (Van der Klashorst, 1989).

Lignin can also be chemically modified to increase its reactivity toward formaldehyde, through simple substitution with phenol. This reaction naturally increases the number of potential reactive sites. Under acidic conditions, phenol reacts with oxysubstituted α-carbons to afford a phenolised lignin adduct (Figure 2.11) (Van der Klashorst, 1989).

In a two step process, chemical modification by phenolysis, in which the lignin was treated with phenol to form a phenol-lignin derivative was evaluated for the manufacture of resins by Ysbrandy *et al.* (1992).

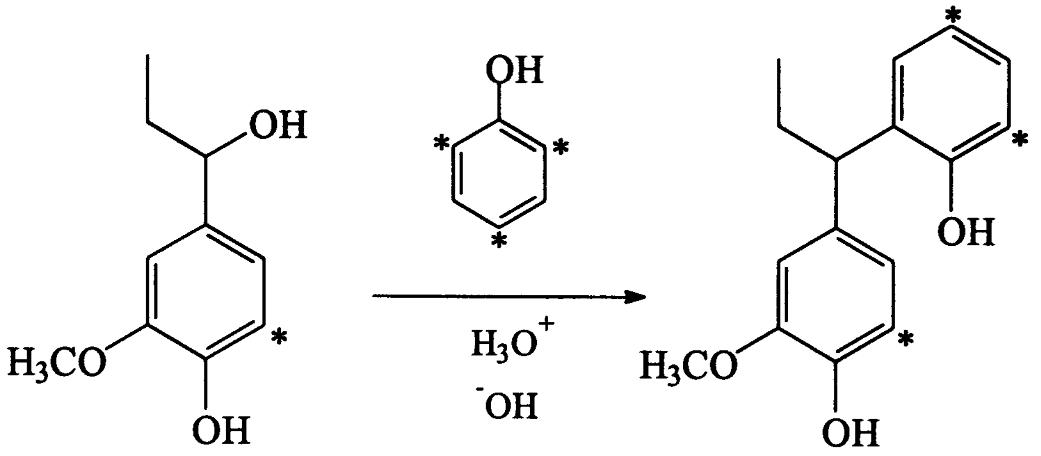


Figure 2.11 The increase of reactive sites (*) on lignin fragments by phenolysis (Van der Klashorst, 1989).

In stage one, the lignin was treated thermally in an acid medium with phenol, which leads to condensation of phenol into the lignin aromatic ring and side chain. In this process bonds were cleaved, which decreased the molecular weight of the lignin structure, as was evident by a drop in viscosity after a set reaction/residence time. Thus, the flow properties were enhanced under heat and pressure to a range more suitable for further processing purposes during resin manufacture.

In stage two, formaldehyde was added, either to make novolac or resol resins. In the case of resol resins, the medium had first to be neutralised and then made alkaline. Because of excess phenol in the reaction mixture, the combination with lignin most likely involved only one of the three reactive positions on the aromatic ring of the phenol being substituted. Consequently, the reactivity of the modified lignin towards formaldehyde was enhanced compared with pre-phenolated lignin material because, for every reaction position lost by combination, two new reactive positions were created by the added phenol unit (Ysbrandy *et al.*, 1992).

2.2.5.2 Application of lignin-phenol-formaldehyde as an adhesive for wood composites

It is known that lignins are reactive toward formaldehyde and thus various attempts have been made to use these paper mill by-products in resins as phenol replacement rather than just as an extender. The lignin-containing portion of these materials may be used in PF resin systems, intended for use as adhesives in the manufacture of pressed wood products.

Extensive studies have been reported on the use of lignin as a PF resin substitute or co-reactant in PF adhesives. These studies have examined lignin co-products originating from several process sources: kraft, lignosulphonate, organosolv, steam-exploded, biomass pyrolysis. The results of previous work have suggested that lignin could replace up to 40% of the phenol in PF adhesive, which are used to bond wood composites without extending the curing time, or worsening the board properties (Pizzi and Mittal, 1994). Some of these applications which are related to the LPF used, are reviewed below. Table 2.5 presents published information for many of these resins which have been studied.

- **Kraft lignin-based resins**

Kraft lignin, obtained from crude black liquor derived as a by-product in the pulping process, was successfully chemically modified to form resin precursors. When combined with a suitable one-stage PF resol, it produced a thermosetting resin, which demonstrated potential as a waterproof adhesive for wood products (Dolenko and Clarke, 1978).

In U.S. patent application 4, 303, 562 (1981), LPF resins were made in two steps. Lignin was obtained by pulping of Douglas fir wood chips by the sulphate process. A partially condensed alkaline PF was reacted with sodium hydroxide, formaldehyde and a lignin concentrate having at least 40% solids. The lignin concentrate comprised lignin dissolved in phenol and water; or phenol, water and sodium hydroxide. The second stage of the method was conducted at reflux temperature initially, after which it was conducted below reflux temperature to control the degree of condensation. In the resulting resin, lignin was employed to extend the PF resin and from about 10 to 30% phenol was replaced by the lignin. The resulting resins was found to exhibit superior wood bonding properties when compared to resins produced without first partially condensing phenol and formaldehyde (Hollis and Schoenherr, 1981).

The utilisation of kraft lignin from *Pinus radiata* black liquor, as a copolymer in LPF resin binders has been studied (Olivares *et al.*, 1988). Different modified lignins were tested in the preparation of LPF resin binders. The mechanical properties and water resistance was evaluated through testing particleboard panels manufactured with the resins obtained. The best resin had properties comparable with typical commercial PF resins.

Hse and Hong (1989), studied the performance of structural quality flakeboard panels made with kraft LPF. Flakeboard was bonded with an adhesive mixture containing 75% hydroxymethylated kraft lignin and 25% PF resin. The test boards showed an improved bond strength and reduced thickness swelling with an increase in the formaldehyde:phenol ratio from 0.2 to 0.7. Panel strength properties decreased with increasing resin solid content. Adhesives formulated with 75% of methylolated lignins as a substitute for phenolic resins, were used to make structural flakeboards with acceptable properties.

In further work (Kuo *et al.*, 1991) *Sweetgum* flakeboards bonded with LPF resins containing 50% hydroxymethylated lignin, prepared from some of the alkali treated southern pine kraft lignins, showed a satisfactory bending strength. Boards bonded with resins prepared by reacting lignins with phenol and formaldehyde had better internal bond strength and durability properties, especially thickness swell, than those bonded with lignin-extended resins.

Table 2.5 Lignins used in LPF resins

Lignin Type	Lignin Content (%)	Resin Type	Pre-treatment	Boards Type	References
Lignosulfonate	25-30%	Resol	-	Plywood	Ludwig and Stout (1971)
Lignosulfonate		Resol	-	Particleboard	Roffael (1975)
Kraft lignin	40-70%	Resol	Hydroxymethylation	Waferboard/plywood	Dolenko and Clarke (1978)
Kraft lignin	10-30%	Resol	-		Hollis and Schoenherr (1981)
Lignosulfonate	30%	Resol	-	Fibreboard	Janiga (1983)
Kraft lignin		Novalac	-	Particleboard	Yaunlu *et al.* (1983)
Lignosulfonate	35-45%	Resol	-	Waferboard	Kambanis *et al.* (1985)
Steam exploded hardwood lignin	30%	-	Methylolation	Plywood	Gardner and Sellers (1986)
Ammonium spent sulphite liquor	Up to 50%	Resol and novalac	-	Waferboard/ OSB	Calve *et al.* (1988)
Kraft black liquor	20-45%	Resol	Methylolation/ Demethylation/ Ultrafiltration	Particleboard	Olivares *et al.* (1988)
Organosolv lignin	35%	Resol	Methylolation	Waferboard Strandboard	Cook and Sellers (1989)
Kraft lignin	75%	Resol	Hydroxymethylation	Flakeboard	Hse and Hong (1989)
Brown-rot lignin	35%	Resol	Methylolation	Flakeboard	Jin *et al.* (1990a)
Kraft lignin	50%	Resol	Hydroxymethylation	Flakeboard	Kuo *et al.* (1991)
Organosolv lignin	20%	Resol	-	Waferboard OSB	Lora *et al.*(1991)
Kraft lignin	30-70%	Resol	-	Plywood	Klasanja and Kopitovic (1992)
Autohydrolysis bagasse lignin	33%	Novalac	Phenolation	Laminates	Ysbrandy *et al.* (1992)
Wood acid hydrolysis lignin	30%	Resol	Methylolation	OSB	Sellers (1993)
Wood acid hydrolysis lignin	35%	Resol	-	OSB	Oh *et al.* (1994)
Organosolv lignin	35%	Resol	Methylolation	OSB	Sellers *et al.* (1994b)
Kraft and Lignosulfonate	15%	Resol	Methylolation	Plywood	Olivares *et al.* (1995)
Kraft lignin	20-40%	Resol	-	Plywood	Chen (1995)
Acetosolv lignin	30%	Resol	Methylolation	Plywood	Vazquez *et al.* (1995)
Sugarcane and bagasse lignin	40%	Resol	Methylolation	Molded resins	Piccolo *et al.* (1997)

Kraft lignin from hardwood, obtained by the sedimentation of acidified semi-thickened black liquor, replaced 30-70% of the phenol in the resin production of resin intended for plywood production. Resin made with a high lignin addition contained relatively high contents of free formaldehyde, and panels pressed at high temperatures, at long press times showed acceptable results, when tested according to standard methods. When using lignin levels of up to 50% to substitute for phenol in resin composition, plywood exhibiting satisfactory shear strength properties was obtained. The addition of accelerator (10% substitute of $Al_2(SO_4)_3$) resulted in an additional increase in shear strength (Klasnja and Kopitovic, 1992).

Shimatani *et al.* (1994) investigated the preparation of moderate-temperature setting lignin adhesives. Softwood kraft lignin was isolated from a commercial concentrated kraft pulping waste liquor and a mixture of the isolated softwood kraft lignin, and phenol was reacted with formaldehyde under alkaline conditions. To the resulting lignin-phenol resin solution, were added small amounts of resorcinol and paraformaldehyde.

Resol type, liquid LPF resins were synthesised by substituting 15% phenol with kraft and sulphite derived lignins. The lignins were a precipitated kraft type and sodium, calcium, or sodium-ammonium lignosulfonate types. Lignin-formaldehyde reactivity tests were used to aid in resin synthesis. PF formulated with 15% phenol substitution was successfully used to bond exterior-grade plywood of radiata pine (*Pinus radiata*) veneers (Olivares *et al.*, 1995).

Shimatani and Sano (1995) investigated the preparation of softwood kraft lignin-based thermosetting (LPF) and cold-setting (LPRF) wood adhesives. The LPF resins solutions obtained from lignin -phenol were acidified with 5% aqueous hydrochloric acid (HCl) and the water insoluble precipitate was collected. These were reacted with small amounts of resorcinol to produce LPRF resins. The LPRF adhesives were equivalent to RF in terms of bonding abilities. However, high reaction temperatures of LPRF resins were required, as compared to those of RF resins; improvements may therefore be necessary for fast-curing.

Alkali treated kraft lignin was used to synthesise copolymer resins with phenol and formaldehyde. The copolymer resins were evaluated for bonding southern pine plywood. The lignin to phenol ratio, formaldehyde to lignin ratio, and hot press time requirements of the copolymer resin were also investigated. The bond quality of copolymer resins, having a lignin, to phenol weight ratio of 20/80 and 40/60, was generally comparable with that of the commercial PF resin, in bonding southern pine plywood. The curing rate and flow property of lignin copolymer resins deteriorated. The greater the quantity of lignin, the longer the hot press time needed. The bond quality of the copolymer resin with a weight ratio of lignin to phenol of 60/40 was not acceptable for bonding this plywood (Chen, 1995).

- **Lignosulfonate-based resins**

Ludwig and Stout (1971) used lignosulphonate, which was first reacted with phenol under alkaline conditions, and then with formaldehyde in the presence of an alkali metal hydroxide to condense the lignosulfonate-phenol product. By this method, up to about 50% of the phenol could be substituted by the lignosulfonate without basically changing the adhesive properties of an adhesive prepared from the product.

Roffael (1975) looked at employing sulphite spent liquor in the particleboard industry with a major focus being on resin properties. Sulphite spent liquors have been employed along with diisocynates and tannin resins as extenders with binders, but these require long pressing times and high temperatures. The employment of lignin sulfonate in the adhesion process made it possible to leave out 50% of the expensive PF resin, and substitute the cheaper sodium sulphite liquor, without lowering the physical and chemical properties of the boards. However, the lignin sulfonate binder still does not participate actively in adhesion.

In U.S. Pat. No. 4, 105, 606 (1978), the lignin derivative was a lignosulfonate produced from spent sulphite liquor, which was the by-product of pulping natural lignocellulose material with bisulphite. The lignosulfonate was dissolved in water and was mixed with a resol-type PF in the manufacture of adhesive. The adhesive was used for manufacture of plywood, fibreboard, particleboard, and similar products (Forss and Fuhrmann, 1978).

Lignosulfonates blended either with a PF resin in a separate step during the synthesis, or mixed with the resin, accomplish satisfactory cross-linking during the hot pressing of the final product. Panels like plywood, particleboard and fibreboard were successfully produced using the LPF resin, although the resin required longer press times or higher press temperatures compared with commercial PF resins (Forss and Fuhrmann, 1979; Calve *et al.*, 1988).

Haars and Huttermann (1984) described a process in which phenolic substances, particularly lignin sulfonate, were used to produce a binder for wood materials. The phenolic substance was activated with enzymes e.g. laccase. Phenolic groups of the lignin became oxidatively polymerised by a radical mechanism, so that the phenolic substance was changed into an active binder. The phenolic material treated with enzymes can then be used in the manufacture of particleboard. Such a board can be compressed under very low pressures and stacked for curing at room temperature. Phenol-oxidizing enzymes securely bond the lignin sulfonate in the sulphite liquor to the wood by oxidative polymerisation during this curing process.

Kambanis *et al.* (1985) described an improved modified phenol-formaldehyde resin, and a process for its preparation, which contained 35% to 45% lignosulfonates and potassium ferricyanide. Typically, the lignosulfonates were in the form of black liquor. There was some indication that potassium ferricyanide modifies, in some way, the lignin sulfonate-phenol reaction. Unlike the known processes utilising black liquors and the like, this process appeared to be far less susceptible to the inherent variability of these liquors. These resins can be easily converted into a solid by spray drying, and find use as adhesives in board products.

A resin adhesive based on spent ammonium sulphite liquor waste material from a pulping operation, has shown good potential for replacing some of the phenolic resin adhesive used in the manufacture of waferboard/OSB. This resin can be obtained in a one step operation by blending NH_4SSL (ammonium spent sulphite liquor), an alkaline PF resin, and an acid catalyst. This study indicated that an economical NH_4SSL-PF resin containing up to 50% of NH_4SSL can be used as a face adhesive in the manufacture of 3-layer waferboard without lessening board quality (Calve *et al.*, 1988).

Allan *et al.* (1989) studied the high temperature phenolysis of commercially available, spray-dried, spent ammonium sulphite liquor from the pulping of softwood as a phenol substitute in PF resins. They selected the phenolysis reaction as a means of modifying the structure and reactivity of lignin sulfonate. The phenolysis process suggested that it was a feasible route to an economically attractive and marketable replacement for phenol.

U.S. Pat. No. 5, 202, 403 (1993) disclosed the preparation and use of a lignosulfonate-modified PF resin as an adhesive in the manufacture of plywood and particleboard. According to Doering (1993), phenol and formaldehyde were first reacted under alkaline conditions, and then lignosulfonate was added to form 'so-called' lignin-modified phenol-formaldehyde (PFL) precursors. The final lignin-modified phenol-formaldehyde resol resin (PFLF) was prepared by further alkaline reaction of the (PFL) precursor with more formaldehyde. This method made resins that apparently overcome most of the press time, assembly time, and penetration problems associated with other lignosulfonate modification methods. A lignin-modified phenol-formaldehyde resol resin made by this method was practically useful for bonding plywood veneer sheets, or for the other laminated wood products together, for laminating wood veneers, or for bonding wood chips together in particleboard. This product also had improved curing characteristics and superior bond strength. In addition, less wood failure occurred and water resistance improved, as compared to products made with adhesives based on the other lignin-modified phenol-formaldehyde resins not made in this way.

- **Organosolv lignin-based resins (OSL)**

Red Oak OSL has also been used to replace 35% to 40% of the phenol in PF resins for laminated maple blocks and to bond southern pine flakeboards (waferboard and/or strandboard), without adversely affecting the physical bond properties (Cook and Sellers, 1989). They found promising results using organosolv lignin at a phenol substitution level of 25%, in PF resins for flakeboards.

Industrially produced organosolv lignin (Alcell® lignin) has been successfully used in liquid PF resin as a direct replacement for resin solids, or as a partial replacement in resins for the manufacture of structural wood panels including plywood, oriented strandboards and waferboards (Lora *et al.*, 1991).

Sellers *et al.* (1994b) also produced a substitute PF resin formulation for Southern pine strandboards, which included hardwood OSL (partial phenol substitution 20% to 35%). These LPF resins were characterised and compared to commercial PF binders. The results indicated that OSL was a feasible replacement for up to 35% of the phenol in OSB type PF resins. The control resin and modified phenolic resins had similar physical properties.

Piccolo *et al.* (1997), recovered lignin from sugar cane bagasse and studied it for use in molded materials. Resols were prepared with the partial replacement of phenol by organosolv sugar cane bagasse lignin (10, 20, 40, 100% w/w). The modifications were introduced in the formulations used, in order to replace phenol by lignin at a substitution level higher than 40%. The results showed that lignin can be incorporated into the phenol polymer chain where it acts as a chain extender, rather than as a filler. The results indicated that replacement of phenol by organosolv sugar cane bagasse lignin, in the preparation of phenolic molded resins, is possible.

LPF adhesives for plywood were prepared using lignin obtained by (acetic acid) acetosolv delignification of *Eucalyptus globulus* wood. The percentage of substitution of phenol by lignin was between 20 and 40%. The reactivity of the resins and the quality of the pine and eucalyptus plywoods manufactured with them, increased with F/P ratios and decreased with increasing lignin percentage. It was observed that the LPF resins were much better than the commercial PF resin on a basis of both cost and quality benefits (Vazquez *et al.*, 1995).

- **Brown rot lignin-based resins**

Jin *et al.* (1990a) presented an adhesive system for flakeboard, in which 35% of the phenol in a PF resin was replaced with brown rotted lignin (BRL). It has been demonstrated that the BRL has higher formaldehyde reactivity than a purified kraft lignin. This result showed that it might be useful as a partial replacement for phenol in PF adhesives. They also compared the formulation characteristics of the BRL-PF resin with a control resin. The results of this study demonstrated that BRL could be used as a partial substitute for phenol in structural wood adhesives. On the other hand, the use of the BRL from brown rotted wood residues for modifying PF resin is not very practical. BRL lignin is not readily available in industrial quantities.

- **Autohydrolysis bagasse lignin-based resins**

Ysbrandy *et al.* (1992) reported on the use of "autohydrolysis bagasse lignin" for incorporation into a lignin phenolic novalac systems for bonding wood-like materials. Crushed sugarcane bagasse lignocellulose was used for the manufacture of furfural, which mainly finds its application in the manufacture of foundry sand resins. After the furfural extraction process, a partially stripped lignocellulosic residue remains. From the residue, lignin can be recovered as 'so-called' "autohydrolysis lignin", by dissolving the lignin in sodium hydroxide and removal of the insoluble residue, whereafter the lignin was precipitated by hydrochloric acid and subsequently dried to form a fine bulky powder. The phenolic raw materials selected were phenol and cresylic acids to confer special properties to the resins. The method selected for the manufacture of lignin resins dealt with modification of the lignin by the phenolation route (Section 2.2.5.1). The effect of substitution levels of different phenolic components with lignin on physical properties was evaluated by testing of lignin resin impregnated paper laminates. A 33% lignin level substitution did not seriously affect the tensile stress at failure and produced laminates with higher modulus of elasticity. The incorporation of lignin into the resin system produced a stiffer and better material.

- **Wood hydrolysis lignin-based resins**

Lignin-resins may also be obtained by direct condensation of lignin with phenols at high temperatures (150-170°C) in the presence of catalysts such as sulphuric acid, hydrochloric acid and certain salts. In carrying out this process, the lignin (effectively dilute acid hydrolysis lignin) was dissolved in a large quantity of the phenol and the lignin-resin was recovered as a residue after the surplus phenol was distilled off (Apel, 1958).

Yaunlu *et al.* (1983) carried out a study of LPF resins with high temperature hydrolysis lignin. The raw lignin was provided as a residue from hydrolysis of soft and hardwood waste residues with dilute sulphuric acid at high temperature. It was observed that the total consumption of phenol can be considerably reduced if the chosen raw material is of high lignin content, because it avoids side reactions and reduces phenol consumption. Therefore, from the point of view of lignin resin synthesis, the purity of starting lignin was very important. They illustrated that the strength of LPF resins made from Korean pine and white birch lignin obtained by strong sulphuric acid hydrolysis, was somewhat higher than that of the high temperature lignin hydrolyses by dilute sulphuric acid method. This showed that different methods of lignin preparation could influence the strength properties of lignin resins significantly. In addition, it was shown that wood species used to provide the lignin source could also affect the strength properties of the lignin resins.

Lignin, extracted from the residues of acid hydrolysis of waste newsprint, was utilised in the formation of a LPF allowing a 35% replacement of phenol. The resin was used in oriented strandboard (OSB) manufacture. The strandboards were tested for physical strength properties and the results showed that the strandboards bonded with the LPF were comparable to those bonded with a commercial control PF resin. This study also suggested that this source of lignin would be rather expensive and perhaps impractical for large-scale implementation (Oh *et al.*, 1994).

Lignins from four different TVA (Tennessee Valley Authority) wood hydrolysis residues, were successfully obtained by extraction with methanol and dioxane or sodium hydroxide. The lignins showed a satisfactory compatibility at a 30% phenol substitution level in PF resins used as wood binders. The resulting LPF resins had storage and application properties that would be acceptable in the strandboard manufacturing process. Some LPF resins performed better than others, which may be related to the residue source (acid hydrolysis process). Most of the LPF resins gave low IB properties, which may be traced to the low reactivity of lignin in comparison to phenol. However, the relatively good IB values for some of the LPF resins were promising, despite the widely held opinion that acid-hydrolysis lignins are ill-suited for resin uses (Sellers *et al.*, 1994a).

- **Steam-exploded lignin-based resins**

Gardner and Sellers (1986) chose steam-exploded mixed hardwood lignin to formulate an adhesive for southern pine plywood. Plywood shear strengths with steam-exploded lignin-based adhesives were at least as good as those of the PF control; wood failures, however were lower.

Ono and Sudo (1989) extracted the lignin from steam exploded pulp and phenolated it in the presence of sulphuric acid. The phenolated lignin was methylolated in order to prepare adhesive resins. Results revealed that the phenolated steam exploded lignin-based adhesives generally provided excellent bond strength, comparable to PF resin.

2.3 SUMMARY

Lignin is produced in tremendous quantities every year as a by-product of the pulping process. As can be seen from this literature review, considerable research has been carried out to exploit lignin as a substitute for phenol in PF adhesives for wood composites. Efforts have been made to develop its commercial uses, such as for lignin adhesives and binders, surface-active agents and so forth but success has been limited. Lignin adhesives have received little commercial attention for practical and economic reasons. Industrial use has been lagging (Shimatani and Sano, 1995).

A variety of effective lignin-phenol-formaldehyde formulations exist. Some of them have been used for periods of time in some particleboard or plywood mills. All these are not used today because all of them always come against some problems:

The formulation tends to be corrosive or hard on equipment in the plant, or the lignin in the formulation tends to noticeably slow down panel pressing time, with consequent loss of mill productivity. Their relatively low reactivities and their variation of molecular structure hinder the use of lignin in large-scale commercial practices. Additionally, the presence of lignin in phenolic resins reduces some properties of wood-based products made therefrom.

In North America, there are encouraging indications that pre-methylolated lignin (pre-reacted with formaldehyde) can be added up to 20 to 30% of synthetic phenolic resins for plywood without lengthening panel pressing times, and one or two mills already appear to be using such a system (Pizzi and Mittal, 1994).

To overcome some disadvantages inherent with the use of lignin, chemical modification of lignin is one of the possible methods to improve its reactivity. As mentioned earlier, the most studied of all chemical modification treatments for lignin has been methylolation. Such modified lignin may be used in high percentages for resin production. Although the literature relating to methylolation reactions of lignin is extensive, there have been few studies reported in the scientific literature on the phenolation reactions of lignin. For this reason, in this study, it was decided to investigate phenolation in more detail.

CHAPTER 3

PRODUCTION OF LIGNIN BY BIOCONVERSION

3.1 INTRODUCTION

As mentioned in Chapter 1, the ultimate aim of this work is to utilise lignin as a substitute for phenol in PF resin production. Various lignin types can be used for this purpose, such as black liquor and organosolv lignin. This chapter deals with the production of brown rot lignin by bioconversion of wood. In the literature, numerous studies are reported concerned with using white rot fungi for biopulping (Kirk and Chang, 1975; Jin *et al.*, 1990a). Production or modification of lignin by brown rot fungi has received little attention, compared to that of white rot fungi. As far as the author of this thesis is aware, there has been only one study of the utilisation of the brown rot lignin in order to produce lignin-phenol-formaldehyde resin (Jin *et al.*, 1990b). In the following paragraphs, a brief summary is given on brown rot fungi.

Wood decaying fungi are saprophytic, deriving their nourishment from dead organic materials. The three major types of wood decay fungi, white, brown, and soft rot fungi embrace a wide diversity of species of the Eumycota and are found within the sub-divisions: Basidiomycotina, Ascomycotina and Deuteromycotina (Ainsworth, 1973).

Fungal saprophytes produce the major depolymerising enzymes involved in cellulose and hemicellulose breakdown and thus utilise carbon, water and some mineral nutrients for their growth. Degradation of wood into monomeric sugars, which can be used as a source of energy and carbon skeletons for synthesis by a fungus, involves a number of enzymes. Some of these work by a hydrolytic mechanism (cellulases, hemicellulases) but it is thought that others generate free radicals which attach specific regions/chemical sites in the wood cell wall (e.g. in brown rot hydroxyl radicals are thought to be involved) (Blanchette, 1995).

The Basidiomycotina are of prime importance in the decay of wood and include both the brown and white rot decay types. These are the most destructive; brown rot in terms of rapid decay and strength loss, and white rot in terms of their ability to degrade all of the structural components of wood.

3.1.1 Brown rot decay

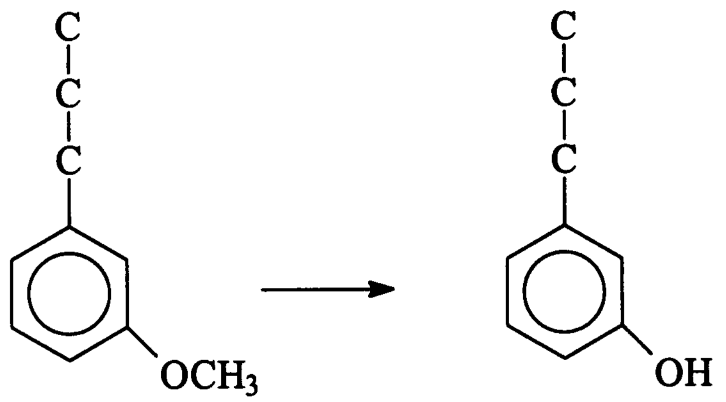
The effects of brown rot fungi on lignin differ from white rot fungi. White rot fungi utilise both the polysaccharides and the lignin. In contrast, brown rot fungi decompose and mainly remove the cellulose and hemicellulose in wood, leaving a modified brown lignin residue. It is apparent that degradation of cellulose and hemicelluloses occurs rapidly during brown rot decay, but lignin depletion is slow (Rowell, 1980; Eaton and Hale, 1993).

Brown rot fungi do not extensively change the lignin fraction of wood during the degradation of the holocellulose fraction. The main degradation reaction is demethylation, which increases the number of phenolic and aliphatic hydroxyl groups in the lignin structure (Rowell, 1980). In addition, the lignin to a very small extent is depolymerised (Cowling, 1961; Highley *et al.,* 1985; Kirk and Highley, 1973). In the final phase of degradation, only the lignin framework of the wood cell wall remains (Srebotnik and Messner, 1991).

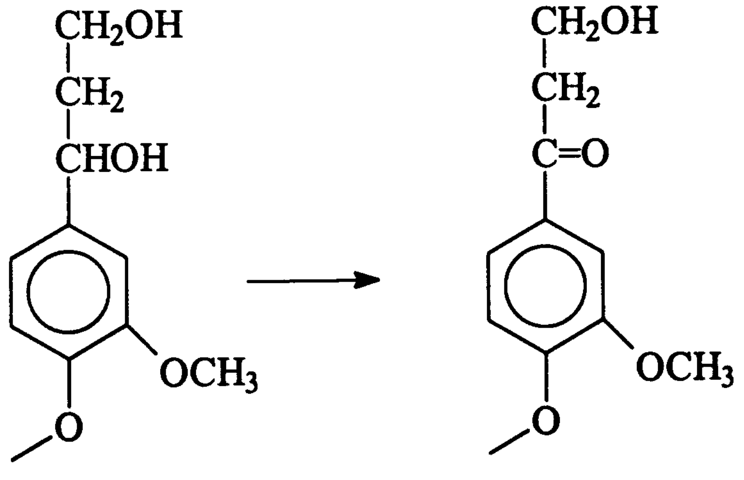
Even though brown rot fungi cannot metabolise lignin in wood, they do alter its structure as they decompose the wood polysaccharides. Specific changes in the polymer include:

- Demethylation of methoxyl groups, leaving phenolic hydroxyl groups
- Formation of carboxyl groups
- With at least one fungus, limited hydroxylation of aromatic rings (Kirk, 1973).

In the attack of lignin in wood by brown rot fungi, demethylation is very heavy in phenolic structural elements (Figure 3.1.1). Lignin degradation is primarily oxidative, evidenced by its increased oxygen content (Figure 3.1.2). The principal changes include decreased numbers of methoxyl groups, conversion of aldehyde groups to carboxyls, plus the introduction of some phenolic hydroxyls (Figure 3.1) (Kirk, 1975a). These changes make the lignin more reactive.



(1) Demethylation



(2) Oxidation of α-carbon atoms

Figure 3.1 Changes in lignin by brown rot fungi.

The influence of brown rot fungi on strength properties is directly associated with the rate at which the polysaccharides are affected. It is well established that the physical and chemical nature of the cell wall is of great importance in determining mechanical strength. Brown rot fungi reduce the strength of wood more rapidly than do white rot fungi (Clarke, 1935; Ifju, 1964).

The decay process rapidly involves S_1 and S_2 layers of the cell walls, but develops irregularly and in softwoods particularly lacks the hyphal-associated lysis zones typical of white rot fungi. There appears to be much less variation in the sequential attack of cell wall constituents by brown rot fungi, as compared to the white rotters (Zabel and Morrell, 1992). Whereas, the lignin monomer groups still remain generally linked, some fragmentation occurs, and their protective role for the carbohydrate is eliminated (Zabel and Morrell, 1992).

Studies of the chemical composition of decayed wood by brown rot fungi show an extensive depolymerisation of polysaccharides before much weight loss has occurred and subsequent degradation and removal occurs progressively. Analysis of decaying wood reveals that attack by brown rot fungi brings about a rapid decrease in the degree of polymerisation (DP) of the cellulose (Cowling, 1961; Kirk and Highley, 1973; Kirk, 1975; Ruel and Barnoud, 1985; Eriksson and Wood, 1985).

The rapid decrease in DP of the cellulose suggests a random splitting of the cellulose polymer into smaller units and x-ray diffraction and initial increase in crystallinity, suggesting that this occurs initially in the amorphous regions. Analysis of the individual sugars shows that all are used at essentially constant rates at all stages of decay, the rates being approximately proportional to the amounts of the sugars in sound wood (Cowling, 1961).

The modified lignin is typically dark brown and almost equal in weight to the lignin in the original. However, it was reported that most of the brown rot fungi examined, degraded the lignin to a significant extent (Enoki *et al.*, 1988). The decayed wood often cracks and checks into cubical fragments, when shrinkage occurs after drying (Blanchette, 1995). The lignin in the rotted wood is darkened by fungal attack, possibly as a result of oxidation of some o-diphenol structures, formed on demethylation of rings bearing free phenolic hydroxyl groups (Kirk, 1973).

3.1.2 Brown rot fungi

A number of fungi of the Basidiomycotina have been reported as being able to cause brown rot although the number of brown rot fungi is low in comparison to the numbers of white rot. For laboratory work a few brown rot fungi are favoured, namely *Coniophora puteana*, *Gloeophyllum trabeum*, *Postia placenta* and *Serpula lacrymans*. The easiest of these to handle are *C. puteana* and *P. placenta*.

Decay by *C. puteana* is rapid in softwood sapwood. According to Apenitis *et al.* (1951), 95% of the cellulose was decomposed in the sapwood of *Pinus sylvestris* at a weight loss of 68%. In seven strains of *C. puteana* tested by Gersonde, cited by Cardias (1992), it was found that the rate of decay was variable in pine sapwood, varying between 15-55% after 16 weeks at 20°C and 25-50% at 26°C.

Coniophora puteana is a cosmopolitan temperate basidiomycete having an optimal temperature for growth at 22°C. It is saprophytic on all kinds of wood, especially in sapwood of most European species. With *C. puteana,* the decomposition of cellulose occurs rapidly, whilst lignin is only very slowly altered (Kirk and Highley, 1973; Cardias, 1992).

Coniophora puteana is a wet rot fungus, since it needs high humidity for growth and has an optimal substrata moisture content of over 50%. It causes considerable shrinkage of wood and characteristic cubic cracking similar to that of dry rot i.e. deep longitudinal, as well as horizontal cracks, occurs in samples.

Postia placenta has an optimal temperature for growth at 28°C, maximum at ≤ 35°C. This fungus is an active decayer of softwoods and average weight losses of 50% in southern pine are reported after 12 weeks exposure in soil block tests (Eaton and Hale, 1993).

An early intention of this work was to obtain lignin from a variety of sources, including by decaying wood using a brown rot fungus. In order to utilise the lignin for resin production, it was necessary to obtain a large amount of brown rot lignin. For this purpose, the standard brown rot test method was modified. A large container method was conducted using two species of brown rot fungi. These are discussed below in more detail in the experimental section.

3.2 MATERIALS AND METHODS

3.2.1 Test fungi

Two brown rot fungi (Table 3.1) were selected as they are fungi that are commonly used in wood decay testing and due to their outstanding reputation as wood decomposers and ease of handling under controlled laboratory conditions.

- *Postia placenta* (Fries) M. Larsen et Lombard = *Poria placenta* (Fr) Cooke =*Poria monticola* Murr.
- *Coniophora puteana* (Fr.) Karst. = *Coniophora cerebella* (Pers.).

Table 3.1 Test fungi strains and their origins

Fungi	Strain No	Source
Coniophora puteana	11 E	BRE, Garston
Postia placenta	Hick 282	Hickson Timber Products

3.2.2 Agar-plate testing (malt-agar substrate)

For petri dish cultures of the fungi, a nutrient medium consisting of 4% malt-agar was used.

The medium was prepared using 20 g powdered malt, 15 g of agar in 500 ml water. The medium was sterilised at 103 kPa (15 psi, 121°C) of steam in an autoclave for 20 minutes and allowed to cool before inoculations. Plates were inoculated with plugs obtained from stock cultures maintained on slants of 4% malt-agar. Afterwards, the petri dishes were incubated for two weeks at 22°C.

3.2.3 Soil substrate

A soil substrate with a water holding capacity between 20-40% was used.

3.2.4 Wood

Sapwood blocks of a non-durable gymnosperm (softwood), Corsican pine and sapwood from a non-durable angiosperm (hardwood), poplar were used to produce test blocks, 40×25×10 mm (tangential × radial × longitudinal). These were free of knots and visible concentration of resins, and showed no visible evidence of infection by mold stain, or wood destroying fungi. All blocks were numbered with a waterproof marker. The wood blocks were dried at 105°C, cooled in a desiccator charged with silica gel and weighed. Prior to infection they were conditioned at 65% RH, 20°C in a conditioning room. In addition to wood blocks, Sitka spruce (*Picea sitchensis*) flakes were also decayed.

3.2.5 Preparation of test cultures

Wooden feeder strips, the soil and the containers were sterilised by autoclaving and then cooled. After sterilisation of the soil and feeder strips, the feeder strips were placed on the soil surface. Inocula obtained from actively growing malt-agar cultures were placed on the feeder strips so that each fungus was inoculated into bowls and incubated at optimal decay temperatures (22°C *C. puteana*, 27°C *Postia placenta*) for about three weeks, depending on the species of fungus used, to establish a satisfactory inoculum in the culture containers.

When the culture containers were ready to receive the weighed test blocks (i.e. the feeder strips were well covered with the mycelium) they were placed in each container on top of the feeder strips.

In the preparation of the test units, 500 mL wide mouth squat jars are used as decay chambers in order to decay the wood samples. However, in this study of fungal degradation, new large-scale set-ups were applied. The large-scale set-up was considered necessary to obtain a large yield of lignin and reduce the cost of the number of jars used. Figure 3.2 and Figure 3.3 show the examples of preparation of these large-scale set-ups. Pure culture conditions were maintained by autoclaving the test assemblies in autoclavable plastic bags and incubating the assemblies inside the bags.

3.2.6 Incubation and duration of test

The containers consisting of the test blocks were covered with bags and placed in the incubators and kept there for 36 weeks.

3.2.7 Handling test blocks after exposure to test fungi

At the end of the incubation period, the blocks were removed from the culture assembler, and the mycelium carefully cleaned off. Then the samples were evaluated for weight loss, moisture content and visually examined for decay.


Figure 3.2 An example of glass tank set-up preparation.


Figure 3.3 An example of polypropylene bowl set-up preparation.

3.2.8 Calculation of weight loss and moisture content

After mycelial removal, the blocks were immediately weighed (W_3) for moisture content and then dried in an oven at 105°C and cooled in a desiccator and reweighed (W_1).

The weight loss due to decay was calculated from the oven-dried block weight. Weight loss was expressed as a percentage of the initial oven dried weight of the sample.

$$\text{Weight loss (\%)} = [(W_2-W_1) / W_2] \times 100$$

where:

W_2= Oven dried weight before exposure
W_1= Oven dried weight after exposure to decay

The calculation of moisture content was expressed as a percentage of final oven dried weight of the sample.

$$\text{Moisture Content (\%)} = [(W_3-W_1) / W_1] \times 100$$

where:

W_3= Weight of block immediately after removal from the decay chamber and after removal of the adherent mycelium

3.2.9 Chemical evidence of decay

Chemical analysis was carried out on decayed and undecayed samples. Therefore the decayed wood blocks were dried and ground in a Christe mill and sieved to pass a 40-mesh (0.4 mm) screen. The samples were then analysed.

- ***Extractive content of solids***

Samples of approximately 10 g were extracted in a Soxhlet extraction apparatus using a 4:1:1 mixture of toluene, industrial methylated spirit (IMS) and acetone for eight hours. Resins, waxes, gums, fats and phenolics are soluble in this solvent mixture. The samples were oven dried at 105°C overnight, re-weighed and the extractives calculated by weight difference and expressed as a percentage of solids.

- ***Lignin determination (Jayme method)***

The standard method for lignin determination (Jayme *et al.*, 1958, 1959, 1967) involving acid hydrolysis (75% sulphuric : 89% orthophosphoric acid 6:1) was utilised for the samples. The acid mixture (15 mL) was added to 1 g samples of extractive free solids and stirred for 40 minutes in a water bath at 35°C. At the end of the initial hydrolysis, 400 mL of distilled water were added and the mixture boiled for 20 minutes. The mixture was cooled and then filtered through a pre-weighed oven dry glass fibre filter paper and dried overnight at 105°C. The samples were re-weighed and the lignin calculated as the percentage of the dried, extractive free solids.

- ***Holocellulose determination***

The holocellulose determination was according to the procedure described in Browning (1967). Approximately 1 g of the extractive-free dried, decayed, and undecayed, wood flour samples were weighed. Deionised water (160 mL), glacial acetic acid (0.5 mL) and 10 mL of a 15% solution of sodium chlorite were added into flasks. The contents were maintained at 70-80°C for 1 hour with occasional stirring. A further 0.5 mL of glacial acetic acid and 10 mL of the chlorite solution were added. Heating was continued for a further hour and the process was repeated two more times to give a total 4 hour, 4 addition cycle. The reaction vessels were cooled in a ice bath and filtered through a pre-weighed glass sinter crucible. The contents were washed with 100 mL of IMS and 20 mL of iced water and finally with 50 mL of acetone. The samples were dried in an oven at 50°C and re-weighed to obtain the amount of holocellulose.

- ***One percent sodium hydroxide solubility of wood samples***

The solubility of wood samples in 1% sodium hydroxide (NaOH) was determined according to the Tappi Standard T 212 om-93 (1996). The wood sample (about 2 g) was extracted with a hot 1% NaOH solution for 1 hour. At the end of 60 minute, the material was transferred to a tared crucible and washed with hot water (100 mL). Acetic acid (10%, 25 mL) was then added and allowed to soak for 1 minute before removal. This step was repeated with a second portion of acetic acid. The material was finally washed with hot water until acid free. The crucible and contents were dried in an oven (at 105°C) to a constant weight, then cooled in a desiccator, and weighed.

Calculation of percent solubility (S) was as follows:

$$S = \left[{}^{(A-B)}\!/_{A} \right] x\,100$$

where:

A= Oven dry weight of the test specimen before extraction (g)
B= Oven dry weight of the test specimen after extraction (g)

3.3 RESULTS AND DISCUSSION

3.3.1 Decay tests and evaluation of test results

Several decay tests were set up, such as large glass tanks (Figure 3.2), large polypropylene buckets, polypropylene bowls (Figure 3.3), and plastic bags (for spruce flakes). This was done in anticipation of setting up large pure culture decay systems.

There were a number of problems with the scale up:

- Maintaining a pure culture system
- Achieving and maintaining optimal conditions for decay, e.g. moisture, aeration, supply of mineral nutrients
- Monitoring the amount of decay present
- Choice of suitable fungus
- Size of vessel and incubation facilities at a suitable temperature

The results of fungus treated wood samples that were collected from the large scale experiments are illustrated below as visual and chemical evidence. Evidently, at the end of the decay cycle the results suggest that unfortunately, required optimum decay for wood samples was not achieved.

3.3.2 Visual evidence of decay

Naturally decayed wood samples were collected. The blocks were examined after they were weighed at the completion of the test. The physical properties indicated that the *Coniophora puteana* and *Postia placenta* did not extensively decay the wood. It has been reported (Cowling, 1961) that a brown colour has been attributed to the lignin enriched residue left by brown rot fungi as a result of preferential utilisation of the wood carbohydrates. In these wood samples, this evidence was only seen from the samples which were found at the bottom of the container contacting with the soil (Figures 3.4 a, b, c and 3.5 a, b, c). The other samples (in the middle or top of the container) kept their original colour (Figures 3.4 e, f and 3.5 e, f).

Distortion, shrinkage, and softening of the blocks should be considered as evidence of decay (Fengel and Wegener, 1989). The wood deterioration took place where the samples were in contact with the soil surface. Those that were not in contact with soil showed no, or only slight, deterioration (See Figure 3.4 and 3.5).

It has also been reported (Cowling, 1961) that brown rotted wood tends to shrink abnormally. Figures 3.4 and 3.5 show a comparison of the dimensional stability of pine and poplar wood blocks in the same chamber, after decay by brown rot fungi, respectively. As can be seen from Figure 3.4, all blocks were originally the same dimension and shape before attack. Blocks A through to F, show pine sapwood at various levels of decay in the same chamber. The dark coloured blocks were decayed (contacted with soil) (Figure 3.4 a, b, c). Most of the blocks (i.e. those not in contact with soil) kept their original dimensions (Figure 3.4 e, f).

As can be observed from the Figures 3.4 and 3.5, these changes are not the same on all the wood samples. Some wood samples were decayed well or half, on the other hand most of them were not decayed at all and did not produce the desired yield of lignin. It was apparent that blocks on the soil surface showed complete decay while those at the top of the incubation vessels were only partially decayed.

As can be seen from Figure 3.5, brown rot decayed poplar wood blocks also showed similar behaviour to brown rot degraded pine blocks. This strongly suggests that complete or nearly complete holocellulose degradation was not obtained. Thus, the lignin obtained was not readily useful for resin formulation. To be able to draw some conclusions, it was necessary to perform chemical analyses of the brown rotted samples, which are reported in the following section.

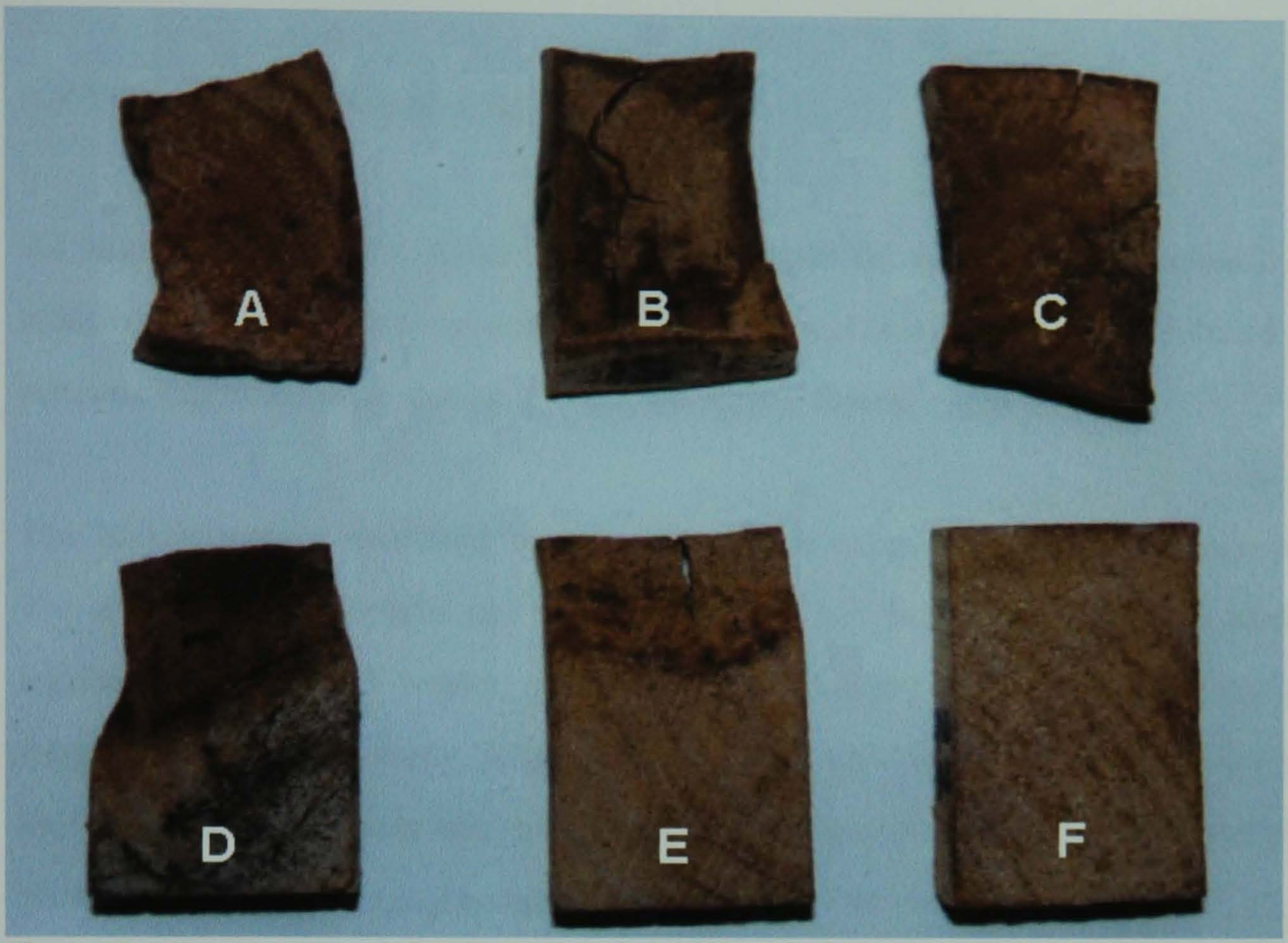


Figure 3.4 Comparison of the dimensional stability of pine wood blocks in the same chamber after decayed by brown-rot fungi (Samples were collected from the bottom of the container (a, b, c); from the middle of the container (d, e); and from the top of the container (f)).

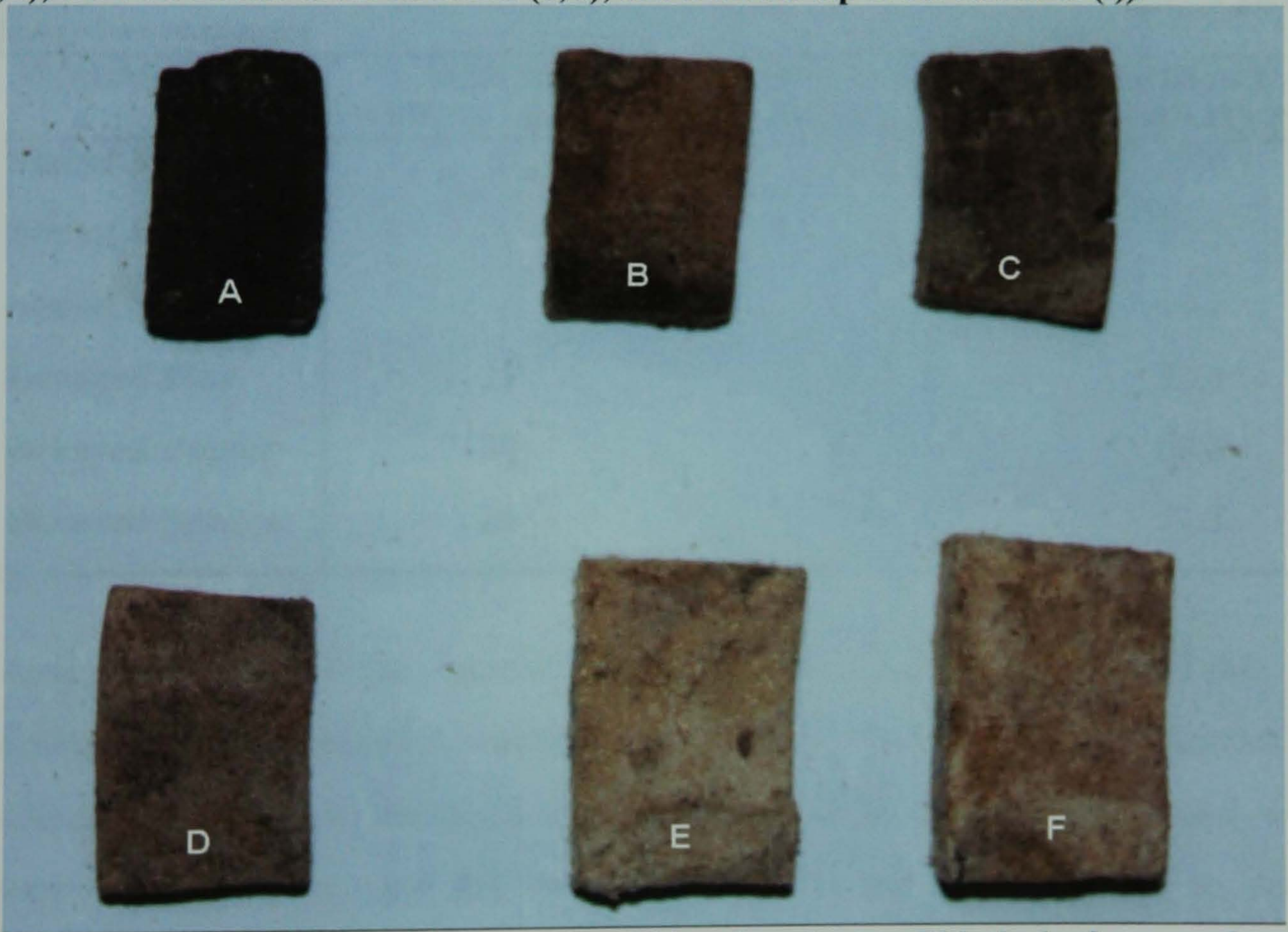


Figure 3.5 Comparison of the dimensional stability of poplar wood blocks in the same chamber after decayed by brown-rot fungi (Samples were collected from the bottom of the container (a, b, c); from the middle of the container (d, e); and from the top of the container (f)).

3.3.3 Chemical evidence of decay

As suggested from the visual evidence, adequate decay of wood samples was not achieved as was hoped. To confirm this, chemical analyses were performed on *C. puteana* degraded pine, poplar blocks and spruce flakes.

The loss in weight was used as a measure of the extent of decay in the test blocks. The average weight losses can be seen in Table 3.2. In Cowling's (1961) study, the incubation period (35 weeks) gave an average weight loss of 64% for brown rot fungi. In this present study, although appreciable time was permitted for incubation, the required weight loss was not achieved. The maximum weight loss, which was obtained with *C. puteana* degraded poplar blocks, was ≈ 34%.

Table 3.2 Solubility and weight losses and moisture contents of sound and *Coniophora puteana* decayed wood samples

WOOD SAMPLES	AVERAGE WEIGHT LOSS (%)	MOISTURE CONTENT (%)	1% NaOH ALKALI SOLUBILITY (%)
Sound Pine	-	-	13.6
Sound Poplar	-	-	17.5
Sound Spruce	-	-	17.1
Decayed Pine	25	75	32.8
Decayed Poplar	34	35	68.3
Decayed Spruce	24	70	57.3

Moisture contents of the samples after decay tests are presented in Table 3.2. Moisture content generally increases during decay, so final moisture contents are indicative of suitable decay conditions. Very wet blocks (>100% sound wood moisture content) or very dry conditions (<20%) are not conducive to decay. Decayed poplar samples reached average moisture contents of 35% during the tests whilst the pine and spruce wood samples reached higher moisture contents. These are adequate to support decay, but suggest that the poplar may have been drying during this incubation period.

Determinations of dilute alkali solubility (1% aqueous NaOH) provide one means of measuring the amount and nature of degradation products present in decayed wood. Brown rotted wood is more soluble than sound wood in aqueous NaOH. The increase in alkali solubility of brown rotted wood is attributed largely to carbohydrate degradation products (Cowling, 1961). This increased solubility of the wood is very evident even in early stages of brown rot decay where the increase is hemicellulose based. In later stages of decay, the partially degraded carbohydrate fragments are used by the fungi, but lignin becomes progressively more soluble in aqueous NaOH (Cowling, 1961). The results of the solubility determinations for the wood analysis are given in Table 3.2. The degraded wood blocks showed at least three times higher aq. NaOH solubility than the original sound wood samples. In addition, the results of the other chemical analysis of pine, poplar, and spruce wood samples before and after degradation are shown in Table 3.3.

Coniophora puteana degraded wood had higher lignin contents than sound wood. Even though the degraded wood samples had a higher lignin content, they still contained a high percentage of holocellulose. These are too high for lignin-phenol-formaldehyde resin production.

Table 3.3 Components of the sound and *Coniophora puteana* decayed wood samples

	Spruce		Pine		Poplar	
	Sound	**Decayed**	**Sound**	**Decayed**	**Sound**	**Decayed**
Extractives Content (%)	3.8	7.0	3.4	6.4	3.3	8.4
Lignin (%)	26.5	38.3	27.9	38.9	20.3	41.4
Holocellulose (%)	71.3	55.7	71.4	56.8	78.4	51.9
Ash (%)	0.3	0.8	0.3	0.4	0.4	1.0

3.3.3.1 FT-IR spectra analysis of wood decay

A description of this technique is given on page 72. The indicator of degradation by brown rot fungi can also be obtained by using FT-IR spectra. Figures 3.6 to 3.8 show the spectra of sound and decayed spruce, Corsican pine and poplar wood samples, respectively. The peak assignments for Figures 3.6 to 3.8 are shown in Table 3.4.

It can be seen from Figure 3.6, decayed spruce samples still possess a carbonyl peak in the region of 1739 cm^{-1}, which confirms that decayed spruce samples contain considerable amounts of holocellulose so, full degradation was not obtained, confirming the visual observations.

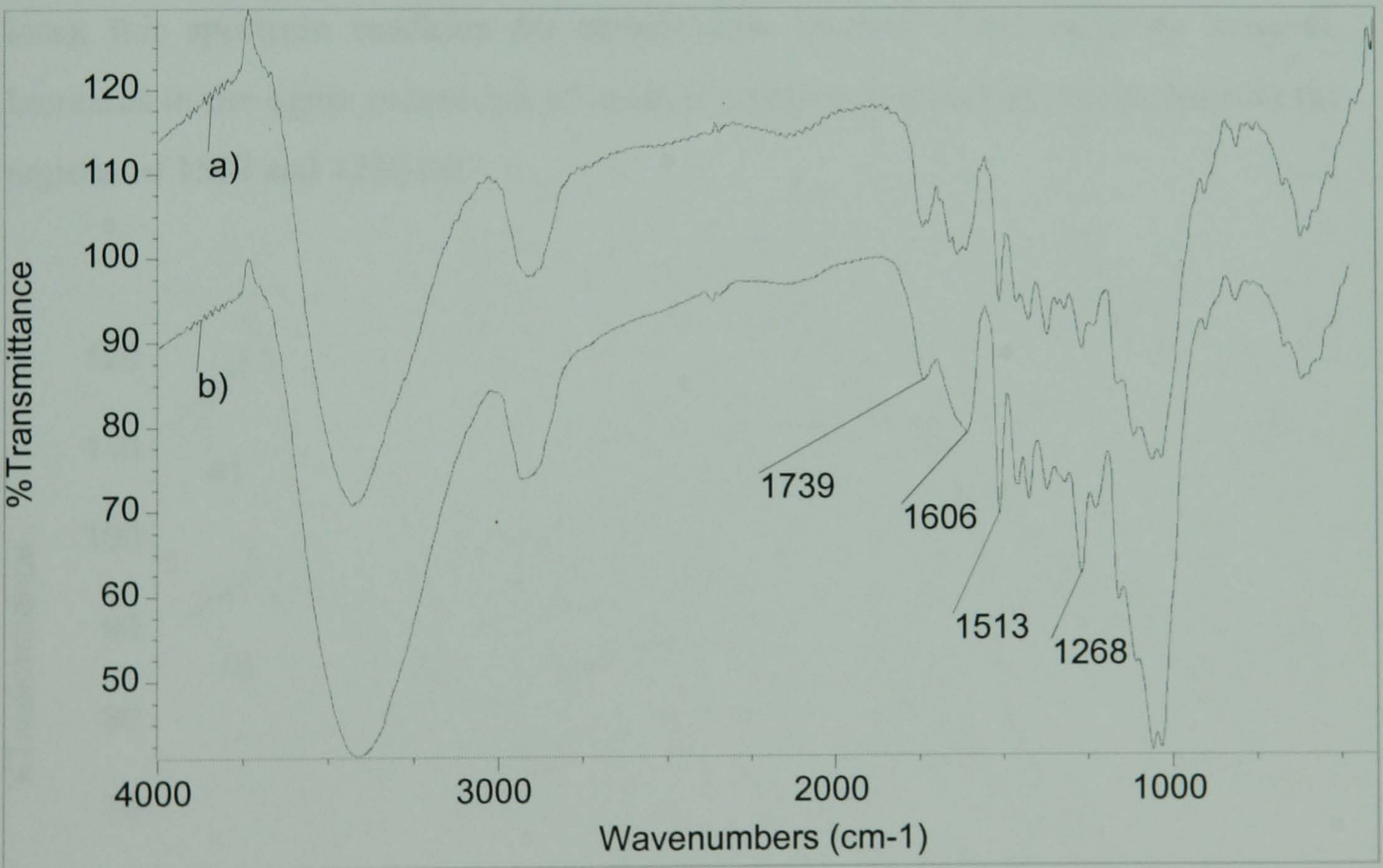


Figure 3.6 FT-IR Spectrum of sound (a) and decayed (24% weight loss) (b) spruce wood.

Figure 3.7 shows FT-IR spectra of sound (a) and brown rot decayed (b) pine samples. When the spectra of decayed pine sample was compared with the spectra of sound pine sample, the most significant difference is the slight increase in the regions of 1510 and 1275 cm^{-1} due to an increase in the proportional lignin content.

Figure 3.8 shows the FT-IR spectra of sound (a) and brown rot degraded (b) poplar samples. The band at 1740 cm^{-1}, which is known to be due to a carbonyl on xylan, is stronger in the spectra of hardwood than the spectra of softwood, which corresponds with the higher xylan content of the hardwoods. Differences in the region near 1230 cm^{-1} between the spectra of hardwood and softwood are also due to differences in xylan content. The relative intensities of the 1513 cm^{-1} band are different in the spectra of softwood and hardwood, but this may simply be a quantitative effect since the neighbouring band at 1463 cm^{-1} is due to the CH_2 group in xylan, which is more plentiful in hardwoods (Liang *et al.*, 1960). When the FT-IR spectra of the decayed poplar sample is compared with a sound poplar sample, there is significant reduction observed in the region of 1740 cm^{-1}, due to removal of holocellulose. As reported in Section 3.3.3, the highest degradation was obtained with poplar samples (34% weight loss), this spectrum confirms the considerable amount of holocellulose removal. Increases in the lignin proportion of decayed poplar are shown by the increase in the regions of 1507 and 1235 cm^{-1}.

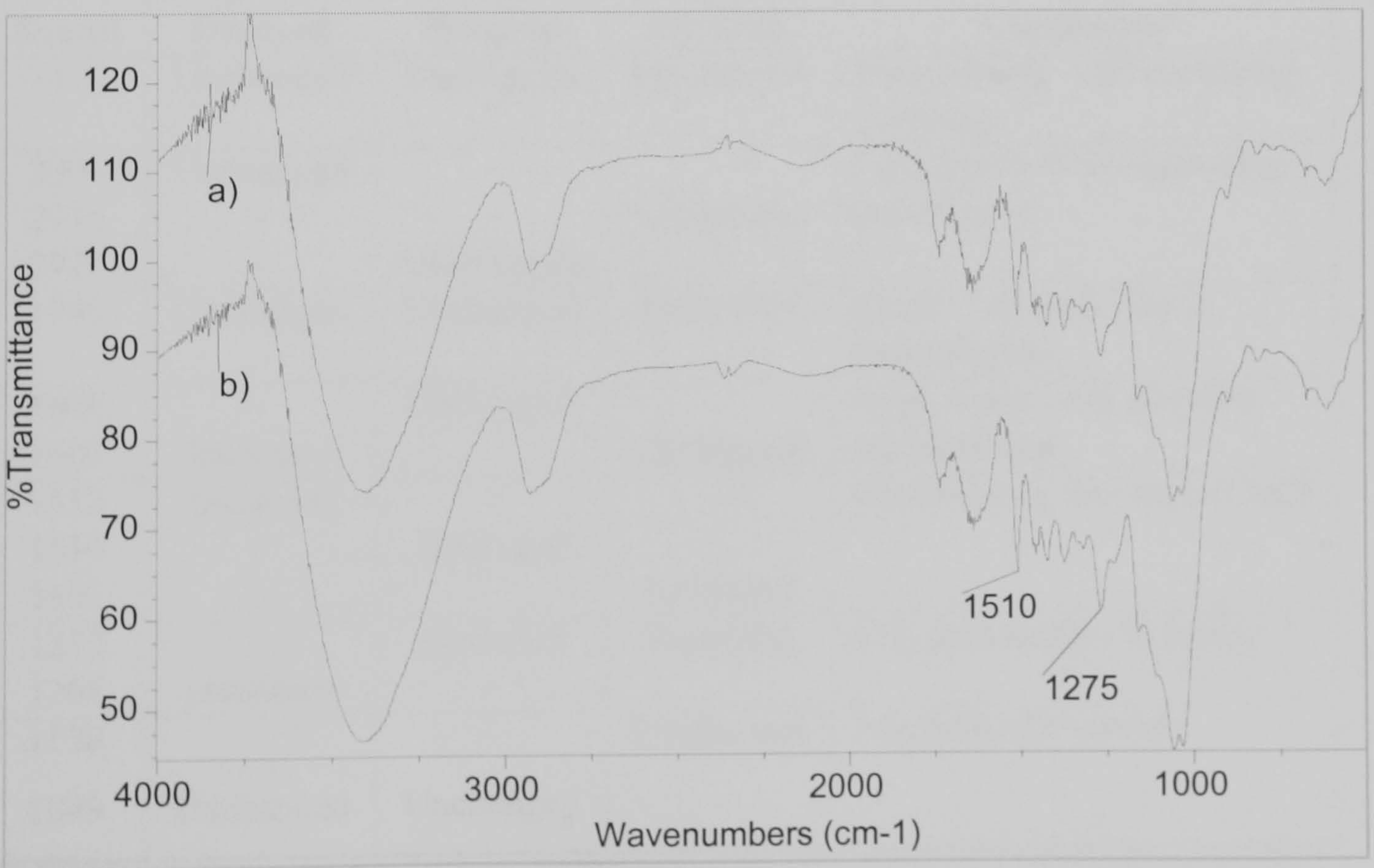


Figure 3.7 FT-IR Spectrum of sound (a) and decayed (25% weight loss) (b) Corsican pine wood.

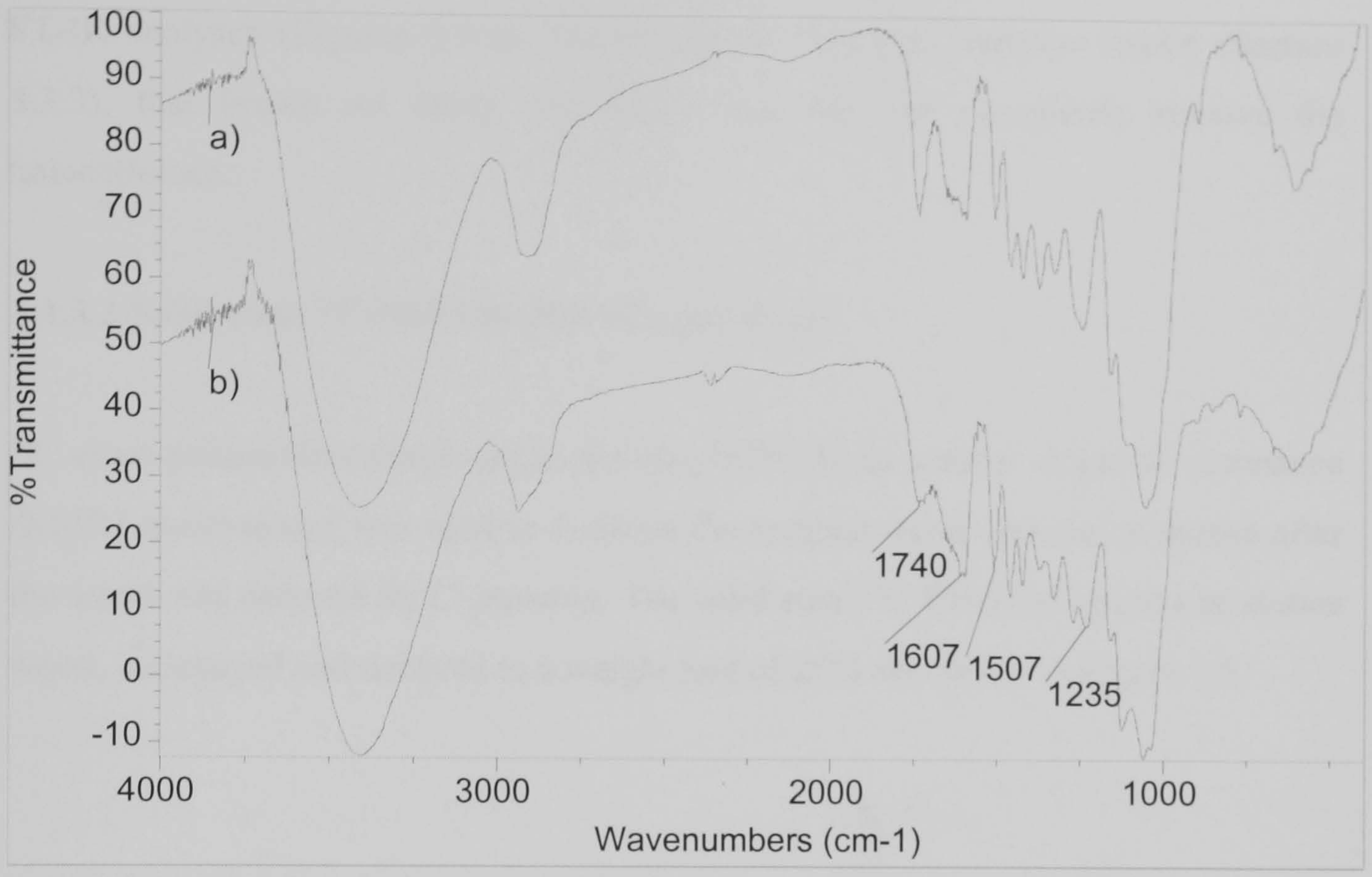


Figure 3.8 FT-IR Spectrum of sound (a) and decayed (34% weight loss) (b) poplar wood.

Table 3.4 The peak assignments of sound and brown rot decayed spruce, pine and poplar wood samples

Sound	Spruce Decayed	Pine Decayed	Poplar Decayed	Comments*
3416	Unchanged	Unchanged	Unchanged	Broad strong –OH stretching vibration
2906	Unchanged	-	-	C-H stretch in aromatic ring and alkanes
2916	-	-	Unchanged	
2925	-	Unchanged	-	
1740	Unchanged	Unchanged	Decreased	Small C=O peak due to holocellulose
1646	-	Unchanged	-	Weak broad peak possibly aromatic ring
1607	Increased	-	Unchanged	
1513	Increased	-	-	Benzene ring vibration (C=C)
1510	-	Increased	-	
1507	-	-	Increased	
1275	-	Increased	Increased	CH_3 deformation in lignin
1268	Increased	-	-	
1130	-	-	Unchanged	Alcoholic CH stretch
1049	Unchanged	Unchanged	-	

(* Liang *et al.*, 1960; Silverstein, 1991)

FT-IR analyses (Figures 3.6 to 3.8) confirmed chemical analysis results (Section 3.3.3), that brown rot decay was partial and did not completely remove the holocellulose.

3.3.3.2 Solid state ^{13}C-NMR studies of wood decay

^{13}C cross-polarisation magic-angle-spinning (CP-MAS) nuclear magnetic resonance (NMR) spectroscopy was used to examine the residual wood material of spruce after the wood was decayed by *C. puteana*. The solid state ^{13}C-CP-MAS spectra of spruce wood, undecayed and decayed to a weight loss of 25% are shown in Figure 3.9.

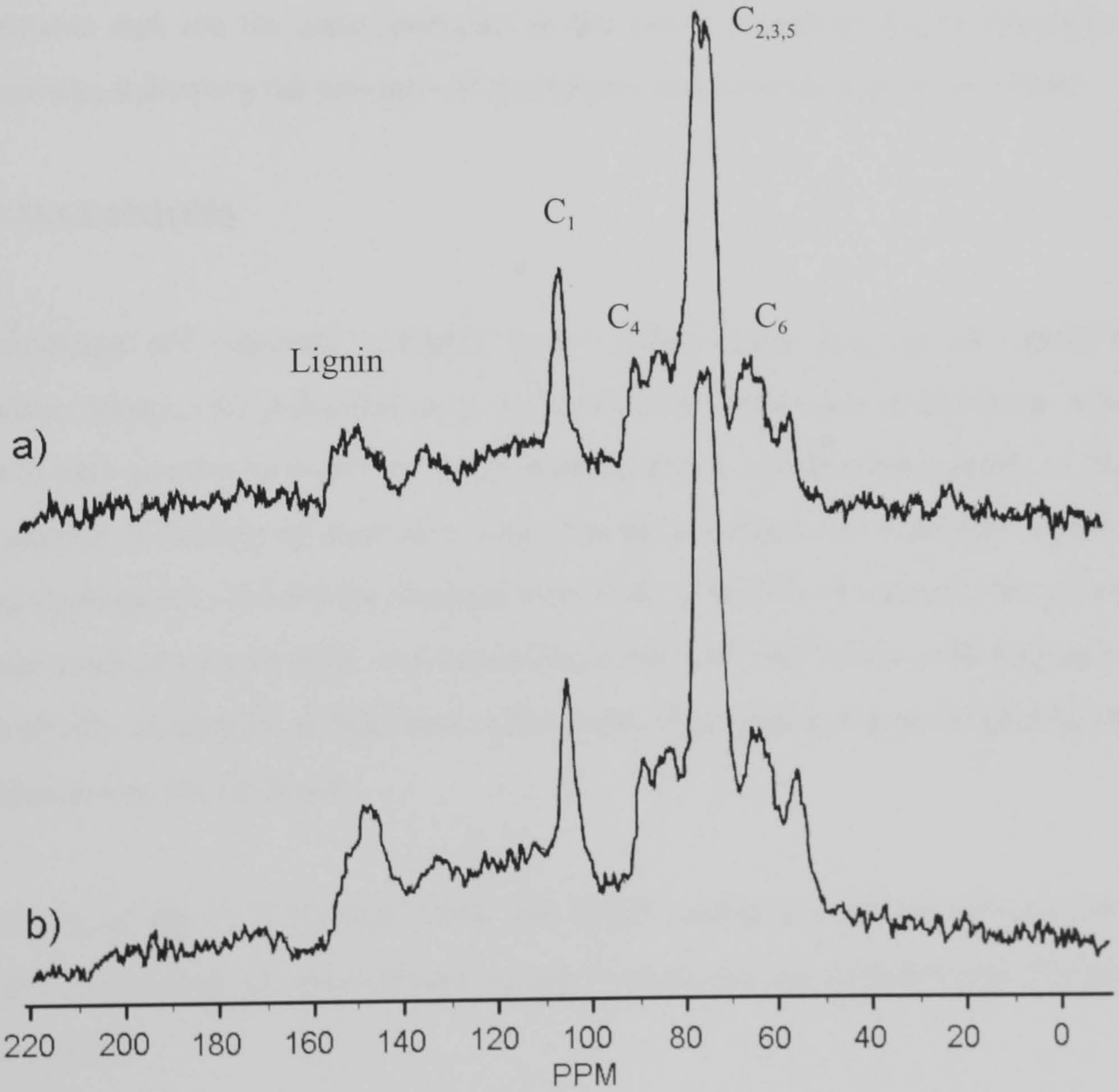


Figure 3.9 ^{13}C CP-MAS Spectra of the spruce decayed by *Coniophora puteana* a) undecayed spruce wood b) decayed spruce wood.

This shows an increase in the intensity of the aromatic region (110-160 ppm) relative to the carbohydrate C_1 peak (105 ppm), indicating a preferential removal of the carbohydrate fractions of the wood with respect to the lignin. A similar finding was reported by Davis *et al.* (1994). Lignin produces a broad peak at the region of 150 ppm, due to its heterogeneous nature (Silverstein, 1991). As can be seen from Figure 3.9, the lignin peak of brown rot degraded spruce showed an increase in the region of 150 ppm, compared to sound spruce.

In the carbohydrate region of the spectrum (Figure 3.9), there are peaks at 65, 74, 88 and 105 ppm, that can be assigned to crystalline cellulose. Peaks at 88 and 65 ppm correspond to C_4 and C_6 carbons, respectively, in the amorphous carbohydrate components and are the same intensity as the peaks corresponding to crystalline components, indicating the presence of amorphous components (Haw *et al.*, 1984).

3.4 CONCLUSIONS

The modified and naturally available brown rotted lignin may be an attractive polymeric resource for industrial uses. In this chapter, large-scale experiments were set up to treat wood with brown rot fungi to obtain lignin in sufficient quantity to use, in an attempt to develop an alternative source of the necessary raw materials required for wood adhesives. The results obtained from these preparations showed that a route to lignin using brown rot fungi was not readily achievable and would probably not be commercially acceptable at this time. The results show that complete holocellulose degradation was not obtained.

The results of the ^{13}C CP-MAS NMR and FTIR studies of decayed samples also indicated that brown rot fungi did not extensively remove the carbohydrate contents from the wood.

Since the results strongly suggest that holocellulose degradation was limited, and the product would need further purification, it was thus not readily usable for incorporation into of lignin phenol formaldehyde resin. Furthermore, this production method is not economical, as it is not currently a by-product of any industrial process. Work on this source of lignin was discontinued and attention was focussed on commercially available lignins instead.

CHAPTER 4

ISOLATION OF LIGNIN FROM BLACK LIQUOR AND CHARACTERISATION OF ALKALI SULPHITE AND ORGANOSOLV LIGNINS

4.1 INTRODUCTION

In Chapter 3, brown rot fungi were used in an attempt to isolate lignin by the degradation of wood. However, since the required quantity and quality of brown rot lignin was not obtained by this bioconversion technique, the work was not continued.

It was decided to investigate other potential lignin resources or isolation methods, using the criteria of cost effectiveness and purity. The objective of this chapter was therefore to investigate the isolation of lignin from black liquor produced as a waste from a standard process (i.e. alkali sulphite pulping of hemp and flax) and the potential of this lignin in the production of lignin-phenolic-resins.

Effluents from the pulping process of pulp and paper mills are dark brown or black in colour and hence are called black liquor. Black liquor (paper mill waste) causes severe pollution and cannot be discharged into a local sewer or river without some form of pre-treatment. Since these liquors can contain a considerable amount of lignin, the isolation for inclusion into a PF resin is very desirable for both economical and environmental reasons.

Black liquor mainly consists of both dissolved and suspended organic and inorganic substances, along with unreacted chemicals used during the pulping. The suspended matter is mostly cellulose containing fibrils (Rohella *et al.*, 1996). The lignin itself is a complete material that contains both aliphatic and aromatic hydroxyl groups, which are attractive sites for chemical modification.

Black liquors such as sulphite liquor (Pederson and Rasmmussen, 1963; Fross and Fuhrmann, 1979; Shen, 1974) and kraft black liquor from wood pulps (Dolenko and Clarke, 1978) have been studied previously in the production of LPF resins.

The aim of the work described in this chapter was:

1) To investigate the effectiveness of isolating lignin from black liquor produced by paper mills based on flax, or hemp pulping by the alkali sulphite process.

2) To elucidate and compare the properties of commercially available Alcell® (organosolv) lignin and alkali sulphite lignin, prior to production of lignin-based phenolic resins. The characteristics of the UV spectra, molecular weight distribution, ^{13}C-NMR spectra, FT-IR spectra, alkaline nitrobenzene oxidation and thermogravimetric analysis properties of organosolv lignin and alkali sulphite lignin are discussed.

3) To analyse the potential of these lignins for the production of lignin-phenolic resins concurrent with an assessment of whether the lignins could be used at an acceptable level of phenol replacement.

4.2 MATERIALS AND METHODS

4.2.1 Isolation of alkali sulphite lignin from black liquor

The black liquor used in this study was produced from an alkali sulphite pulping process of hemp and flax for cigarette tissue and was kindly supplied by Robert Fletcher, Greenfield, UK. Some important chemical characteristics of black liquor were that the pH was found to be 11.3 and the total solids content was only 10%.

Lignin was obtained by acidifying black liquor with 10N sulphuric acid (H_2SO_4) to pH 1.5-2. After allowing about 24 hours at 20°C for lignin particles to precipitate out, water from the top layer was decanted off. The lignin slurry was further concentrated by centrifuging at 4000 RPM for 10 minutes. Then the precipitated lignin was collected by filtration, washed thoroughly with acidic water (pH = 2) and dried at room temperature.

4.2.2 Analysis of Lignins

4.2.2.1 UV spectra

UV spectra were recorded on a Hewlett-Packard 8452A Diode Array spectrophotometer. Lignin samples (5 mg) were dissolved in 90% (v/v) dioxane-water (10 mL). A 1 mL aliquot was diluted to 10 mL with 50% (v/v) dioxane-water, and the absorbances between 200 and 400 nm were measured. Path length of cell was 1 cm.

4.2.2.2 Gel permeation chromatography (GPC)

The molecular average weight of lignins was determined by gel permeation chromatography on a PLgel 5μ Mixed-D column. The samples were dissolved with THF (tetrahydrofuran) with a concentration of 0.2% and a 200 μL sample in solution was injected. The columns were operated at 40°C and eluted with THF at a flow rate of 1 mL min^{-1}. The column was calibrated using polystyrene standards.

4.2.2.3 ^{13}C-NMR spectra

^{13}C-NMR spectra were recorded on a Brucker 250 AC operating in the FT mode at 62.4 MHz under total proton-decoupled conditions. They were recorded at 25°C from 250 mg samples dissolved in 1.0 mL DMSO-d$_6$ after 30000 scans. A 40° pulse flipping angle, a 3.0 μs pulse width, and 0.85 s acquisition time were used.

4.2.2.4 FT-IR spectra

IR spectra were obtained on a Mattson FTIR spectrometer (Nicolet 750, series II). The lignin was mixed with oven-dry potassium bromide (KBr) powder (the fibre flour/KBr ratio was 1:100) and placed in a vibrator ball mill capsule. The mixture was ground for about 2 minutes then pressed to form a window, prior to placing into the sample beam of the spectrometer.

4.2.2.5 Nitrobenzene oxidation

The method for determination of lignins was based on the procedure published by Scalbert *et al.* (1986) and Sun (1996). 1 M sodium hydroxide (7 mL) and nitrobenzene (0.4 mL) were added to lignins (20 mg) in stainless pressure vessels. The vessels were sealed tightly with a Teflon gasket and screw cap. The vessels were then heated in an oil bath for 3 hours at 175°C. After cooling the vessels, the reaction mixtures were filtered and the filtrates were extracted with chloroform (3x30 mL) to remove excess nitrobenzene and its reduction products. The solutions were acidified to pH 1 with 20% hydrochloric acid, and extracted again with chloroform (3x30 mL). These last chlorofom extracts were evaporated at 40°C to dryness and resolubilised in methanol (3 mL) containing 3', 5'-dimethoxy -4'-hydroxyacetophenone as an internal standard.

High performance liquid chromatography (HPLC)

Samples dissolved in methanol for measuring free phenolic acids and aldehyde content, were directly injected into a HPLC Kontron instrument, the samples in methanol were diluted in solvent A (water-methanol-acetic acid, 89:10:1) by addition of 9 mL solvent A to 1 mL methanol containing samples.

The redissolved samples were analysed by HPLC on a Spherisorb 5 0DS column of dimensions 250x4.6 mm. Separations were obtained using a linear gradient elution of solvent A (water-methanol-acetic acid, 89:10:1) solvent B (methanol-water-acetic acid, 90:9:1) from 0% to 40% B at a flow rate of 1 mL min^{-1} over 31 min. Products were detected at 280 and 320 nm using a HPLC 450 UV detector. Phenolic monomers in samples were identified by comparison of their retention times to those of known standards and quantified from peak areas (280 nm) which were calculated relative to the authentic phenolic acids and aldehyde standards using Kontron MT 450 software calibration.

4.2.2.6 Thermogravimetric analysis

Thermal analysis of organosolv lignin and alkali sulphite lignins was performed by Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) using a thermal analyser system (Model Stanton Redcroft TG-DSC, Simultaneous Thermal Anayser STA 625).

About 10 mg of powdered sample was placed in a tare pan for measurement of TGA and DSC and then a tare pan was put on the sample. The pan was placed on the support tube and was compressed by the probe with load under static air, then heated to 400°C at a ramp rate of 10°C per minute.

4.2.2.7 Reactivity of organosolv and alkali sulphite lignins with phenol

Before using organosolv lignin and alkali sulphite lignin as partial replacement of phenol in lignin-based resins, lignins were reacted with phenol by two methods in order to determine the reactivity of lignins with phenol. Firstly, either the precipitated sulphite lignin, or organosolv lignin was reacted with phenol. Lignin (100 g) was added to phenol (20, 60, 100 and 200 g) and 1-butanol (175 mL) to observe if the phenol would react with the lignin. 1-Butanol was chosen because its boiling point is higher than 100°C and some heat may have been required to ensure that the phenol-lignin reaction went to completion. A solvent was required since initial attempts to react phenol with lignin directly, gave anamalous results, which were attributed to poor mixing of the two components.

Oxalic acid (5 g) was added to the mixture to determine if the acid increased the phenol/lignin mole ratio. The use of oxalic acid in the experiments was thought desirable because it was thought (Kratzl *et al.*, 1962) to assist in the breakdown of the lignin molecule.

4.2.2.8 Reactivity of black liquor (alkali sulphite lignin) with phenol

In Section 4.2.2.7, the reactivity of alkali sulphite lignin (in powder condition) with phenol was determined. In this section, the reactivity of black liquor (in liquid condition) with phenol was determined. For that, phenol was added to the black liquor in two ways.

1) The black liquor (pH = 11.3) was adjusted to pH 4.2 by adding oxalic acid (14.5 g) to compare with organosolv lignin, the aqueous slurries of which are acidic (pH = 4.2). The viscosity of this mixture was determined before adding phenol (10 g) and heating to 100°C. The viscosity and free phenol content were determined as explained in Section 5.2.3.2 and Section 5.2.8.1. This procedure was repeated for 20, 40, 60 and 100 g of phenol and the mixture was heated to 100°C. The results are shown in Section 4.3.10.

2) The black liquor was adjusted to pH 4.5 by adding oxalic acid (14.5 g). Phenol (100 g) and 1-butanol (300 mL) were then added to the reaction flask containing the liquor and the mixture was heated to 100°C. 1-Butanol and water were distilled off using a Dean and Stark separator, which recycled the 1-butanol to the flask while the water was removed. The distillation was continued until all of the water was removed from the flask by condensation. Samples were then taken from the reaction vessel every hour to determine the phenol content. When the analysis of the samples showed that the free phenol content was constant, the flask was cooled and viscosity measurements taken.

4.3 RESULTS AND DISCUSSION

4.3.1 Black liquor results

Analytical results of the alkali sulphite black liquor are given in Table 4.1.

Table 4.1 Analysis of black liquor

Properties	Results
Non-volatile content %	10.0
pH of black liquor	11.3
Lignin % by weight of black liquor	3.8
Ash % of lignin	17.9

4.3.2.General properties of organosolv lignin

A good example of an organosolv lignin, known commercially as Alcell® lignin, is produced by Repap Enterprises. Inc., Newcastle, N.B. This material is produced from a mixture of hardwoods that included 50% maple (*Acer rubrum*), 35% *birch (Betula papyrifera*) and 15% poplar (*Populus tremuloides*).

Alcell® (organosolv) lignin powder has a dark brown colour and woody odour. The bulk and solubility properties of Alcell® lignin are shown in Table 4.2.

As indicated in Table 4.2, the lignin was spray-dried to about 4% moisture content with a resultant particle size of about 20-40 μm. This is similar to the particle size of powder phenolic resins. Since no sulphur-bearing chemicals are used in the process, no significant amounts of sulphur exist in the lignin. The ash of organosolv lignin is similar to wood and very low (<0.2% at 600°C), because there are no heavy chemical residues used in the pulping or recovery processes.

Table 4.2 Bulk and solubility properties of organosolv lignin

Analytical Test	Basis	Amount
Specific gravity	--	1.3
Median particle size	μm	20-40*
Moisture content	%	<4
Ash, 600°C	%	<0.2
Wood sugars	%	<0.5*
Combustion sulphur	%	<0.3*
pH (2% aqueous solution)	--	4.2
Volatiles	%	<5% H_20*
Solubility (25°C)		
Water	g/L	0.6
Ethanol	g/L	44.6
Methanol	g/L	73.5
N-Hexane	g/L	2.4
Acetone	g/L	320
Sodium Hydroxide, (0.5 N)	g/L	417

* (Sellers, 1993)

The sugar (carbohydrate) content is also very low (<0.5%). Sugars in lignins used for binders, can tie up the formaldehyde cross linker into non-durable exterior bonds; therefore, a low sugar content is a desirable characteristic. Like most wood based lignin, the organosolv lignin has low water solubility (<0.1 g/L), but is moderately soluble in organic solvents (44.6 g/L in ethanol and 73.5 g/L in methanol), but very soluble in sodium hydroxide (417 g/L). The lignin solubility in sodium hydroxide is important because sodium hydroxide is the catalyst/solvent of PF resol resins used as a binder in boards. pH of aqueous slurries is slightly acidic (pH = 4.2). Solubility of organosolv lignin in solvents is shown in Table 4.3. Organosolv lignin (≈0.005 g) was shaken at room temperature in 4-5 mL of solvent and observed for depth of colour of solvent and presence of undissolved material for solubility tests.

Table 4.3 Solubility of Alcell lignin in various solvents

Acetone	Highly soluble with a slight amount of residue remaining
Methanol	Somewhat soluble with a moderate amount of residue remaining
Butanone	Highly soluble with a slight amount of residue
Water	Insoluble
Chloroform	Highly soluble
Toluene	Virtually insoluble-solvent slightly coloured

4.3.3 UV spectra

Ultraviolet spectrophotometry is a useful technique for the determination and characterisation of analytical lignins, and lignin derivatives. In the UV determination of lignin, the absorptivity maximum at about 280 nm is normally used, and the absorbance is proportional to the lignin content of the sample (Fengel and Wegener, 1989).

The UV spectra of organosolv and alkali sulphite lignins are shown in Figure 4.1. As can be seen from the spectra, the organosolv lignin gave the maximum absorption, indicating the purest preparation at the same solubility/concentration. A lower absorption coefficient in alkali sulphite lignin might be due to non-lignin material such as protein, silica or polysaccharide sugars co-precipitated in the lignins.

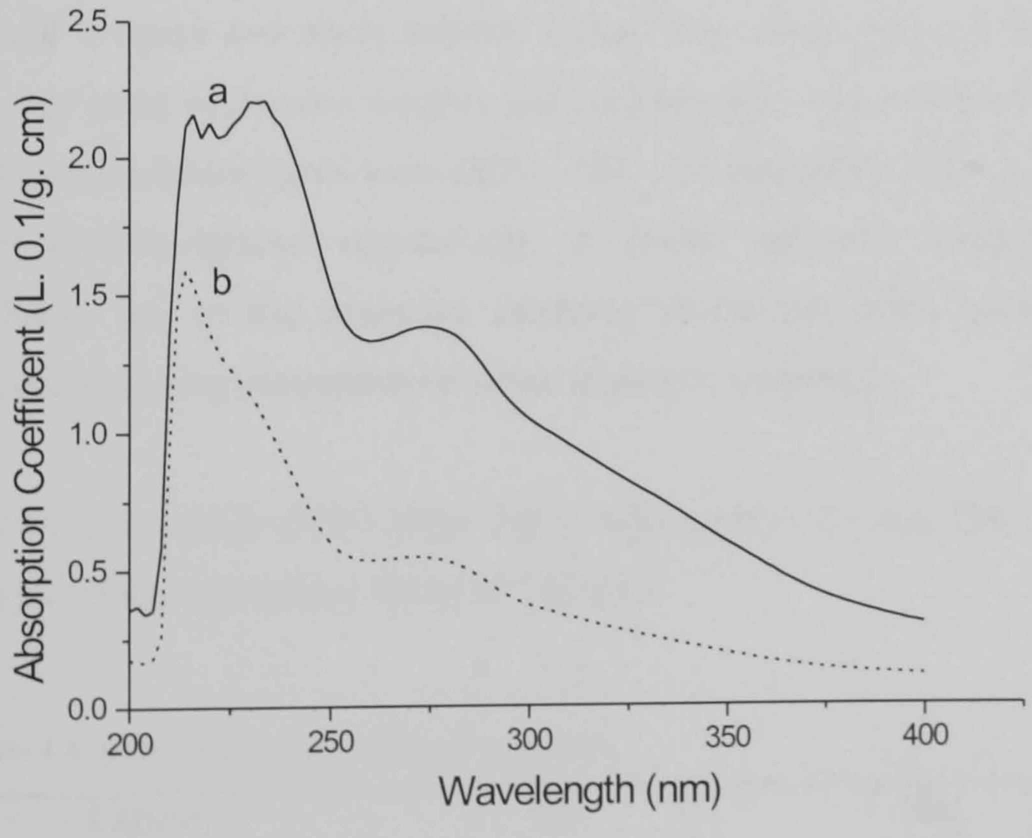


Figure 4.1 UV spectra of organosolv lignin (a), alkali sulphite lignin (b).

Maximum absorptivity appears in the range between 200-235 nm. The lignin spectra comprise a maximum at about 210 nm and 225 nm (for organosolv lignin), followed by a slope at lower wavelengths, with a pronounced peak in the region of 280 nm. The absorption maximum at about 280 nm originates from non-conjugated phenolic groups (aromatic ring) in lignin. The absorption coefficient of organosolv lignin at 280 nm was higher than that of alkali sulphite lignin, which indicates a higher content of non-conjugated phenolic groups in organosolv lignin than in alkali sulphite lignin (Sun, 1996).

The lignins appeared to have no absorption peaks at 314-316 nm, which would have originated from conjugated phenolic groups in *p*-coumaric and ferulic acids, the absence of these compounds was also confirmed by alkaline nitrobenzene oxidation.

4.3.4 Molecular weight distribution

Figures 4.2 and 4.3 show the molecular weight distribution patterns of organosolv (Alcell®) lignin and alkali sulphite lignin. The weight-average (Mw) and number-average (Mn) molecular weights and polydispersity (Mw/Mn) of organosolv lignin and alkali sulphite lignin were 1824, 1158, 1.57 and 2060, 1603, 1.28 computed from their chromatograms, respectively. A lower molecular weight of lignins was probably due to the extensive breaking of the inter-unit linkages in the lignin molecules during concentration in the treatment processes.

The weight average (Mw) molecular weight, number average (Mn) molecular weight and polydispersity (d) are listed in Table 4.4.

Table 4.4 Molecular weight averages of lignins

Lignins	Mw	Mn	d
Organosolv Lignin	1824	1158	1.57
Alkali sulphite lignin	2060	1603	1.28

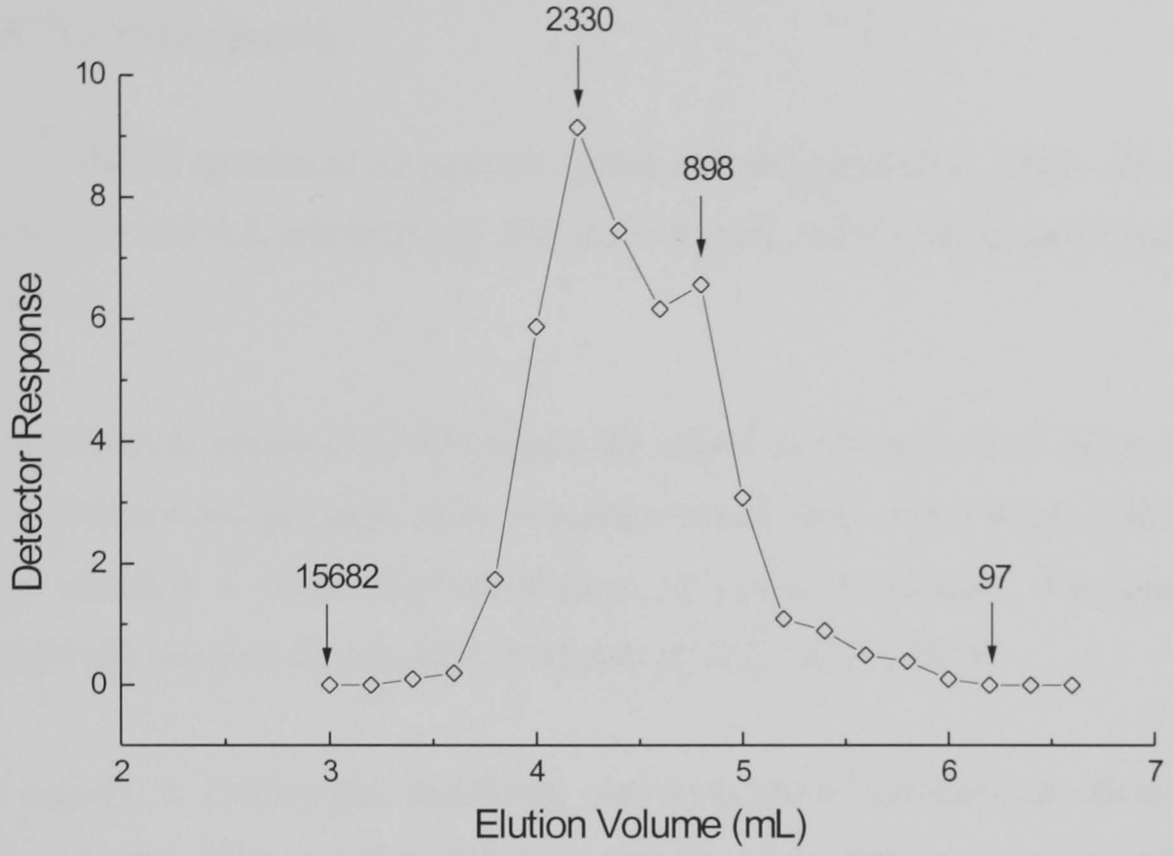


Figure 4.2 The GPC range of molecular weight of organosolv lignin (molecular weights from polystyrene standards).

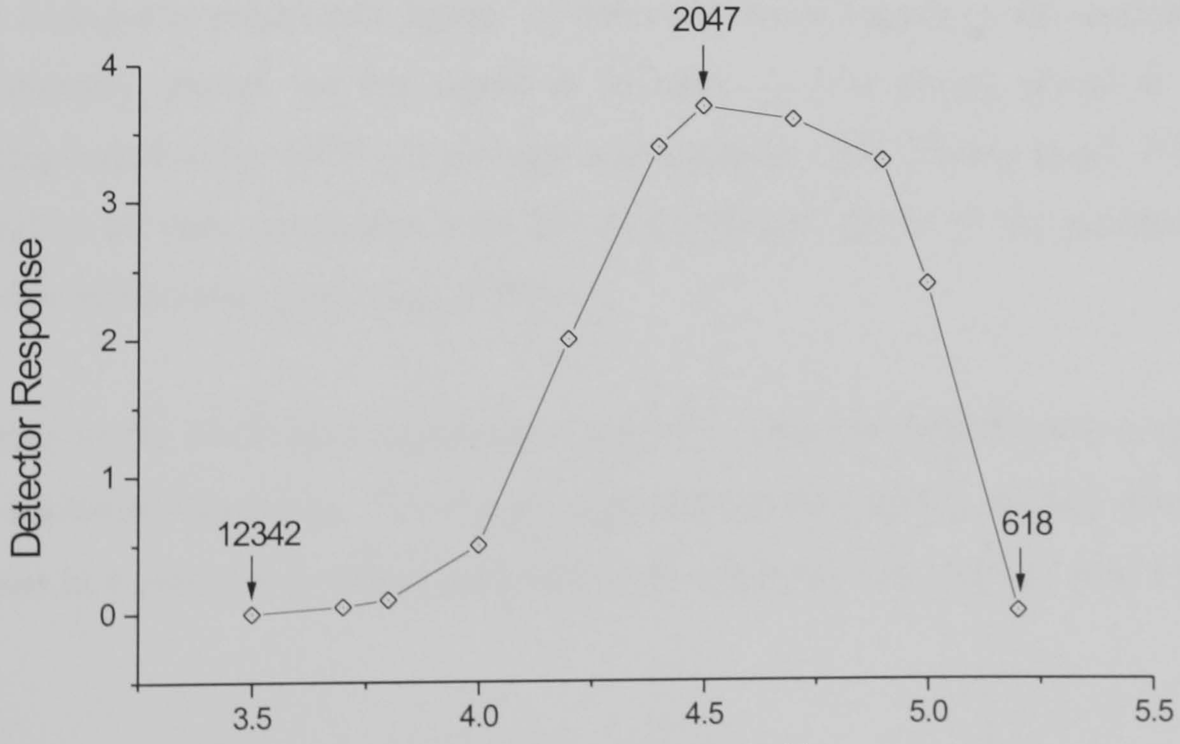


Figure 4.3 The GPC range of molecular weight of alkali sulphite lignin.

4.3.5 ^{13}C-NMR spectra

The ^{13}C-NMR spectra of organosolv lignin and alkali sulphite lignin are shown in Figures 4.4 and 4.5, respectively. The main signals and the assignments are listed in Table 4.5.

In the aromatic region (153-104 ppm), the signal at 148 and 149.2 ppm, due to C-3/C-4 in etherified guaiacyl units, is highest in intensity, demonstrating that Alcell® lignin contains a rather high proportion of guaiacyl moieties. The presence of syringyl (S) residues as indicated by signals at 152.2 (C-3/C-5, S).

The signals at 129.6 ppm, indicating *p*-hydroxyphenol residues for alkali sulphite lignin, are the main signal in the grass lignins. Grass lignins may be distinguished from other angiosperm (GS) lignins as GSH lignins. This signal was absent in the organosolv lignin and a weak signal in the alkali sulphite lignin.

Signals in 86-50 ppm region, are attributed to oxygenated and non-oxygenated inter-unit linkages in organosolv lignin. As observed, those signals in the spectra are low in intensity, except for the signal at 56 ppm. A very strong signal at 56 ppm corresponded to the OCH_3 in syringyl and guaiacyl units (Thring *et al.*, 1996). The signal at 60 ppm, originates from the 4-*O*-methoxyl group of the glucuronic acid residue in the xylan (Sun *et al.*, 1996).

Signals in the 34-12 ppm region are assigned to saturated hydrocarbon structures in the aliphatic side-chains. The signals representing the γ-methyl, α-and β-methylene groups in n-propyl side chains appeared in the spectrum between 14.1 and 33.8 ppm.

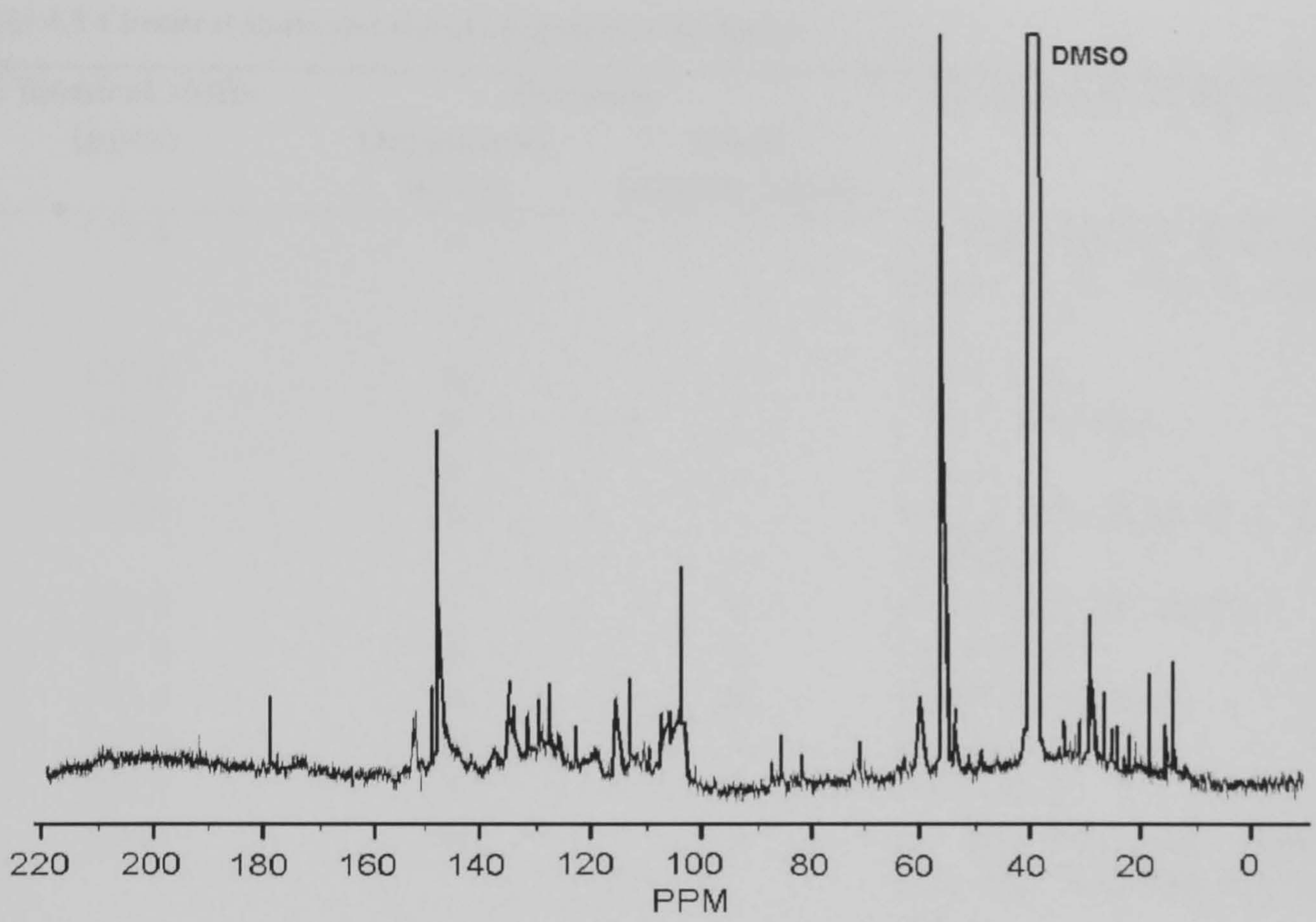


Figure 4.4 ^{13}C-NMR spectrum of organosolv lignin.

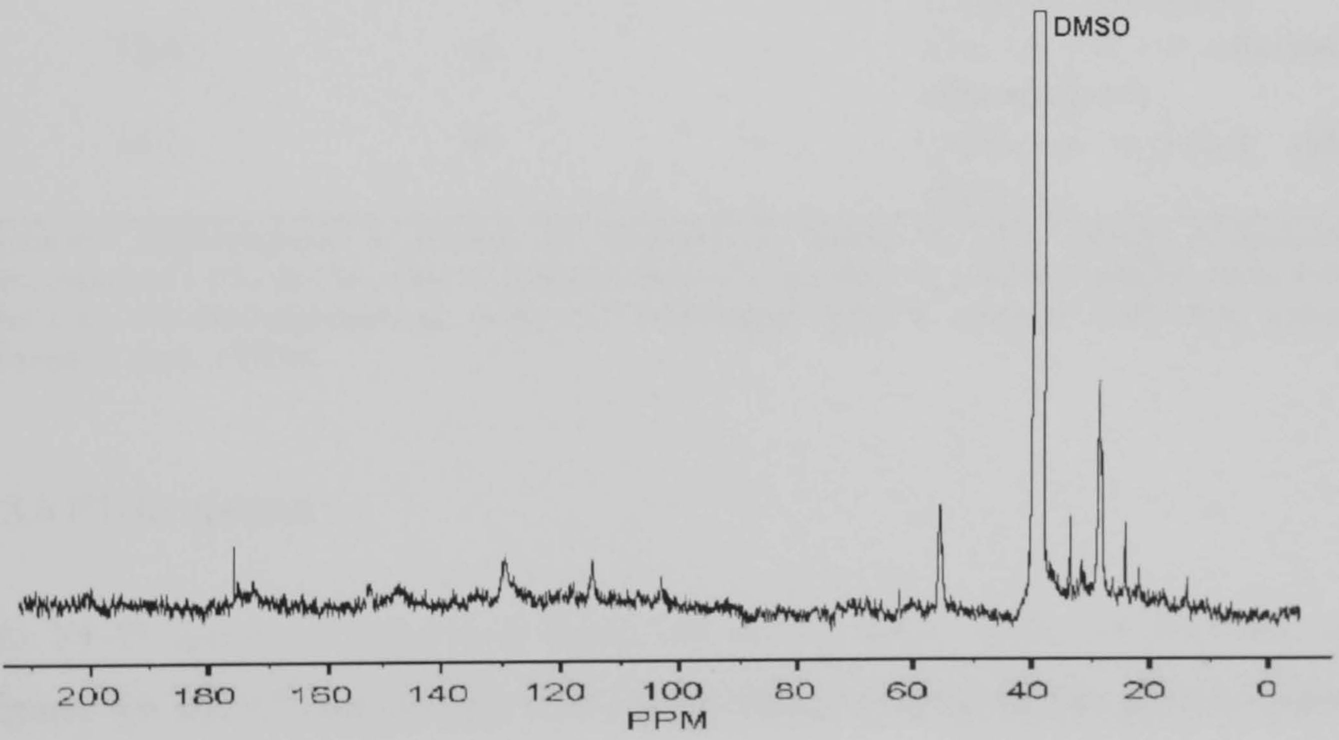


Figure 4.5 ^{13}C-NMR spectrum of alkali sulphite lignin.

Table 4.5 Chemical shifts and signal assignments for lignins

Chemical shifts (ppm)	Intensity[1]		Assignment[2] of signals
	Organosolv lignin	Alkali sulphite lignin	
178.4	w	-	-COOH, aliphatic acids or esters; C-G, Glc A and ester
152.2	w	-	C-3/C-5, S
149.2	w	-	C-4, G etherifed
148.0	s	-	C-3, G
134.9	w	-	C-1, S etherified; C-1, G etherified
129.6	-	w	C-2/C-6, H (PC ester)
127.8	w	-	C-2/C-6, H
115.4	w	w	C-3/C-5, PC ester
112.9	w	-	C-2, G
103.6	m	-	C-2/C-6, S
60.0	w	s	C-γ in β-O-4; β-aryl ether; C-6, Glc; 4-O-MeGlcA in xylan
56	vs	s	OCH$_3$, G S
33.8	v	m	*γ*-methyl, *α*-and *β*-methylene groups
29.1	s	vs	CH$_2$ in aliphatic side chain
26.7	m	m	CH$_3$ or CH$_2$ groups in saturated side chains
18.6	m	-	CH$_3$ or CH$_2$ in saturated aliphatic chain
14.1	m	v	γ-CH$_3$ in n-propyl side chain

Intensity[1] abbreviations: s, strong; m, medium; w, weak; vs, very strong. Assignment abbreviations[2]: FE, ferulic acid; G, guaiacyl unit; Glc, glucose; H, *p*-hydroxyphenyl unit; 4-O-MeClcA, 4-O-Methylglucuronic acid; PC, *p*-coumaric acid; S, syringyl unit; Xyl, xylose (Vazquez *et al.*, 1997b).

4.3.6 FT-IR spectra

The FT-IR spectra of organosolv lignin and alkali sulphite lignin are illustrated in Figures 4.6 and 4.7, respectively. The corresponding assignments are given in Table 4.6.

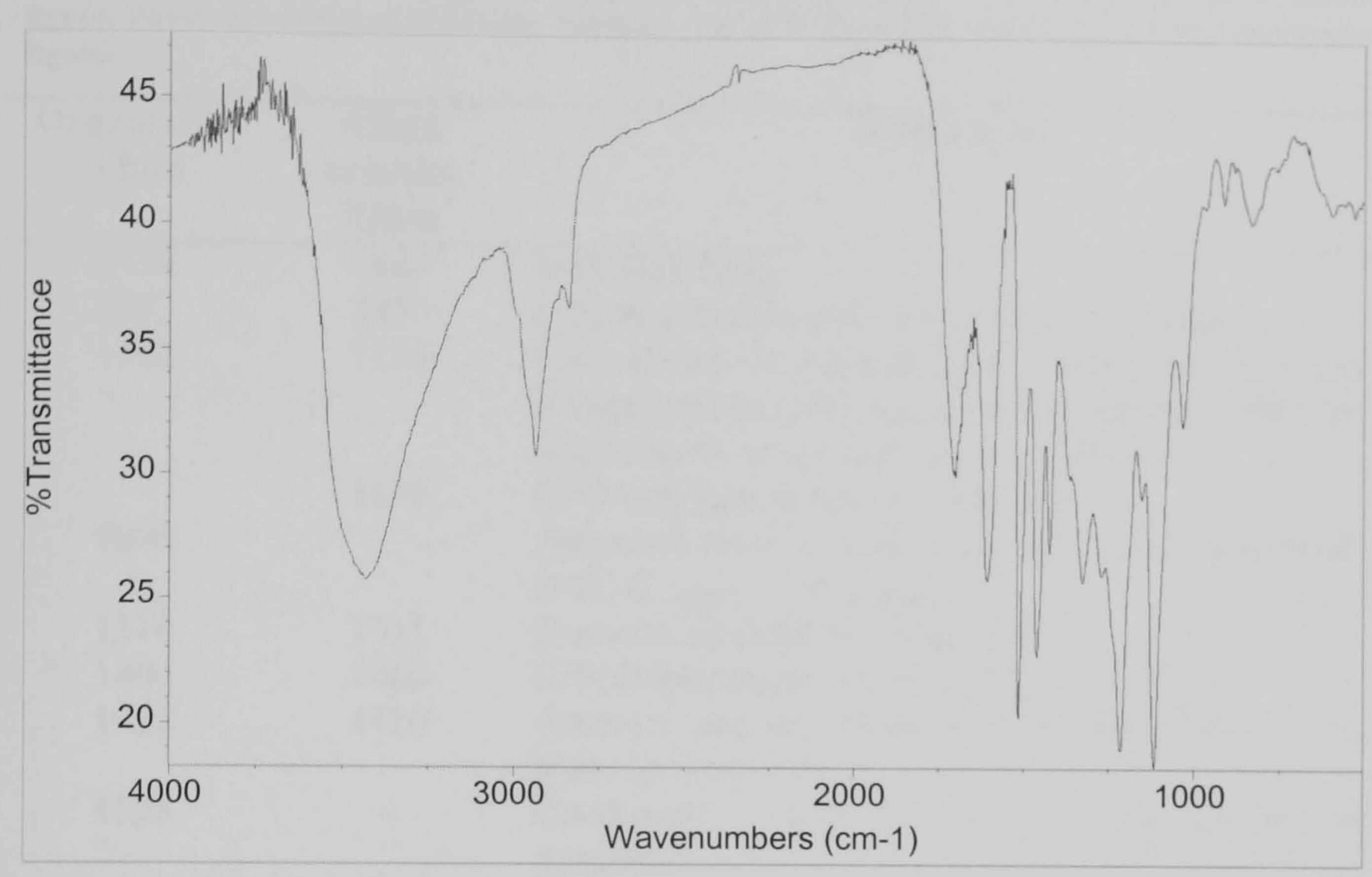


Figure 4.6 FT-IR spectra of organosolv lignin.

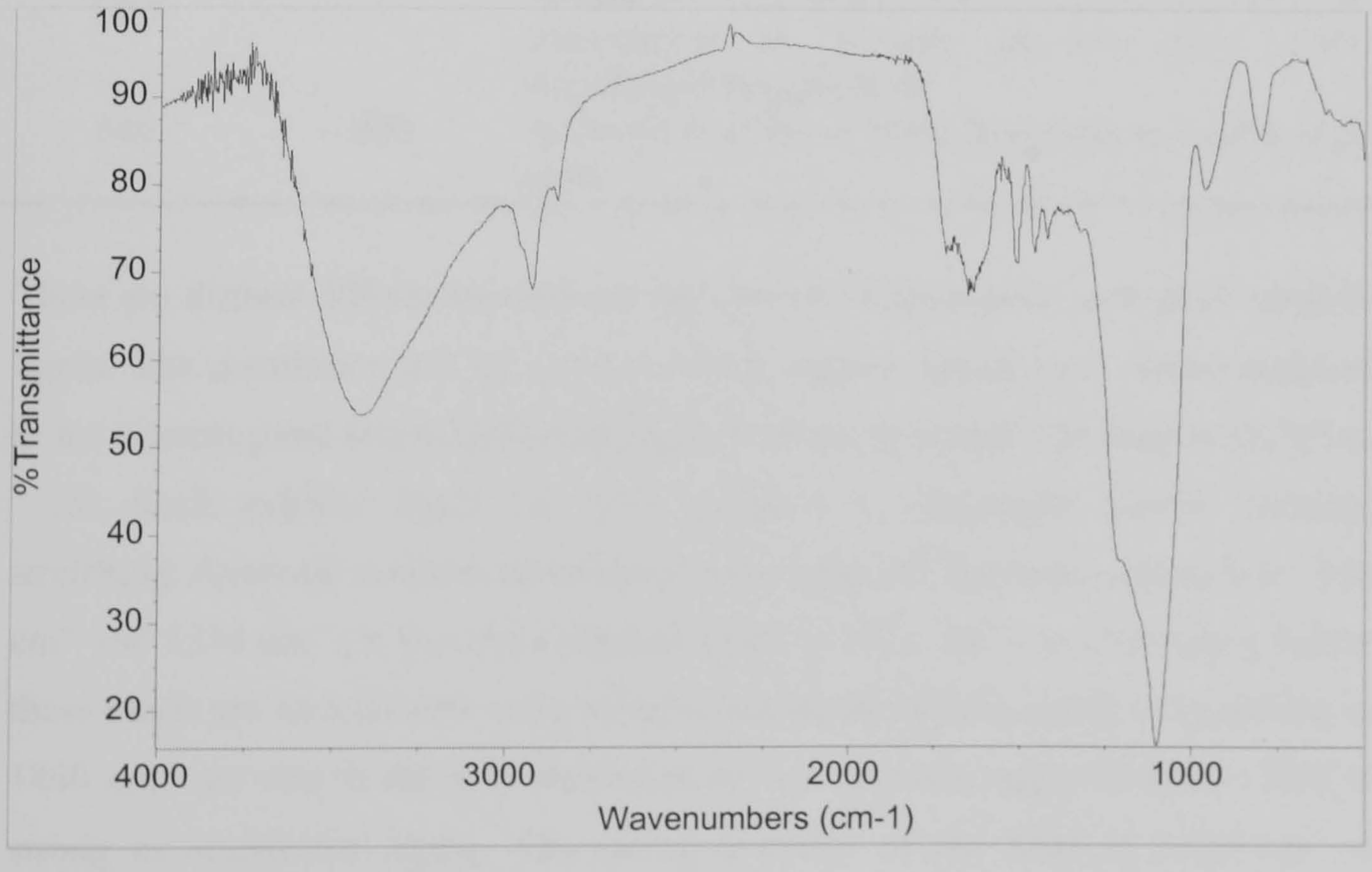


Figure 4.7 FT-IR spectra of alkali sulphite lignin.

Table 4.6 Assignments of FT-IR absorption bands (cm^{-1}) of organosolv lignin and alkali sulphite lignin. Bands are assigned following Vazquez *et al.* (1997b) assignments for pine and eucalyptus lignins

Organosolv lignin	Alkali sulphite lignin	Assignment
3434	3426	O-H stretching
2937	2950	C-H stretch in methyl and methylene groups
1702	1716	C=O stretch in unconjugated ketone, carbonyl and in ester groups (conjugated aldehydes and carboxilic acids absorb around and below 1700 cm^{-1}.
	1659	C=O conjugated ketone stretching
1608		Aromatic skeletal vibrations plus C=O stretching; S>G; G$_{\text{condensed}}$ >G$_{\text{etherifed}}$
1514	1511	Aromatic skeletal vibrations (G>S)
1460	1460	C-H deformations (asym. in-CH_3 and CH_2-)
1425	1420	Aromatic skeletal vibrations combined with C-H in-plane deformations
1328	-	Condensed S and G rings (G ring bound via positions)
1215	-	C-C plus C-O plus C=O stretching (G$_{\text{condensed}}$>G$_{\text{etherifed}}$)
1115	1112	Typical of S units; also secondary alcohols and C=O stretching
1032	-	Aromatic C-H in-plane deformation (G>S) plus C-O deformation in primary alcohols plus C=O stretching (unconjugated)
840	820	Aromatic C-H out of plane in positions 2 and 6 of S units

There are distinct differences between the spectra of organosolv and alkali sulphite lignin. The absorbance at 1702 (1716 in alkali sulphite lignin) cm^{-1} can be assigned to the unconjugated ketone and unconjugated carbonyl groups. The band at 1659 cm^{-1} for alkali sulphite lignin has been assigned to conjugated ketone carbonyl stretching. Aromatic skeleton vibrations in the organosolv lignin are assigned at 1608 cm^{-1} and 1514 cm^{-1} (in the alkali sulphite lignin at 1511 cm^{-1}). In organosolv lignin, these bands are considerably more intense than alkali sulphite lignin. Absorptions at 1460 cm^{-1} are due to the C-H deformations and aromatic ring vibrations. This is strong in organosolv lignin. The strong intensity of the band at 1328 cm^{-1} is associated with syringyl structures in organosolv lignin, while the relative intensities of the bands at 1215 and 1032 cm^{-1} are associated with guaiacyl units in organosolv lignin.

The sulfonic acid groups in technical lignin sulfonates appear at about 1200 cm^{-1}. The acid lignins show generally broader bands, probably due to condensation reactions during lignin preparation (Fengel and Wegener, 1989). The width and intensity of the bands between 1000 and 1100 cm^{-1} indicate the presence of sugar or polysaccharide moieties. In the organosolv lignin, absorption is high near 1330 cm^{-1} and absent at 1265 cm^{-1}. Further evidence of the syringyl content of organosolv lignin is afforded by its having a band near 840 cm^{-1}. Aromatic C-H out of plane bending appears at 840 cm^{-1} and 820 cm^{-1}, respectively for organosolv lignin and alkali sulphite lignin.

4.3.7 Nitrobenzene oxidation

The separation and elucidation of lignin-related phenolic monomers, post oxidation, has been accomplished by high performance liquid chromatography using an ultraviolet detector. Peaks of the components in alkaline nitrobenzene oxidation products of lignins were identified according to the standards as follows: *p*-hydroxybenzoic acid, *p*-hyroxybenzaldehyde, vanillin, vanillic acid, syringic acid, syringaldehyde, *p*-coumaric acid, ferulic acid.

Yield of phenolic acids and aldehydes obtained by alkaline nitrobenzene oxidation of the organosolv and alkali sulphite lignins is given in Table 4.7. These products, acids and aldehydes, result from the degradation of non-condensed lignin monomers.

As seen in Table 4.7, the main degradation products of alkaline nitrobenzene oxidation for organosolv lignin were found to be syringaldehyde, syringic acid and vanillin. The predominant degradation product, syringaldehyde, results from the degradation of non-condensed syringyl (S) units. The presence of small quantities of vanillin is due to the degradation of non-condensed guaiacyl (G) units.

Table 4.7 Yields of phenolic acids and aldehydes in alkaline nitrobenzene oxidation products of lignins (% lignin samples w/w)

Phenolic acids and aldehydes	Organosolv lignin	Alkali sulphite lignin
p-hyroxybenzoic acid (HA)	ND[d]	0.20
p-hyroxybenzaldehyde (H)	ND[d]	0.38
Vanillin (V)	2.01	1.65
Vanillic acid (VA)	Trace	0.32
Syringic acid (SA)	2.41	1.50
Syringaldehyde (S)	5.62	3.76
p-coumaric acid (CA)	ND[d]	Trace
Ferulic acid (FA)	ND[d]	ND[d]
Total (HA+H+V+VA+SA+S+CA+FA)	10.04	7.81

[d]ND Not detectable

When comparing the corresponding yields of alkaline oxidation products of organosolv lignin (Table 4.7), with the lower yields of alkaline nitrobenzene oxidation of alkali sulphite lignin, a higher degree of condensation of this lignin was indicated. Organosolv lignin gave a relatively high yield of alkaline nitrobenzene oxidation products, suggesting that more contents of non-lignin material might be co-precipitated on alkali sulphite lignin.

4.3.8 Thermogravimetric analysis

Phenolic compounds when curing, reach a glassy solid state followed by a liquid state (melt-flow) and then progress to a chemical curing reaction of rigid cross-linking. Some resols may have a Tg (glass transition) near room temperature (25°C) and highly cross-linked phenolics as high as 150-225°C.

The thermal properties of the two lignins were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA and DSC spectra for organosolv lignin and alkali sulphite lignin are shown in Figures 4.8 and 4.9, respectively. In Figure 4.8, the TGA curve shows that organosolv lignin decomposition begins at *ca.* 200°C and rapid deterioration continues until a temperature of 400°C, showing 35% weight loss.

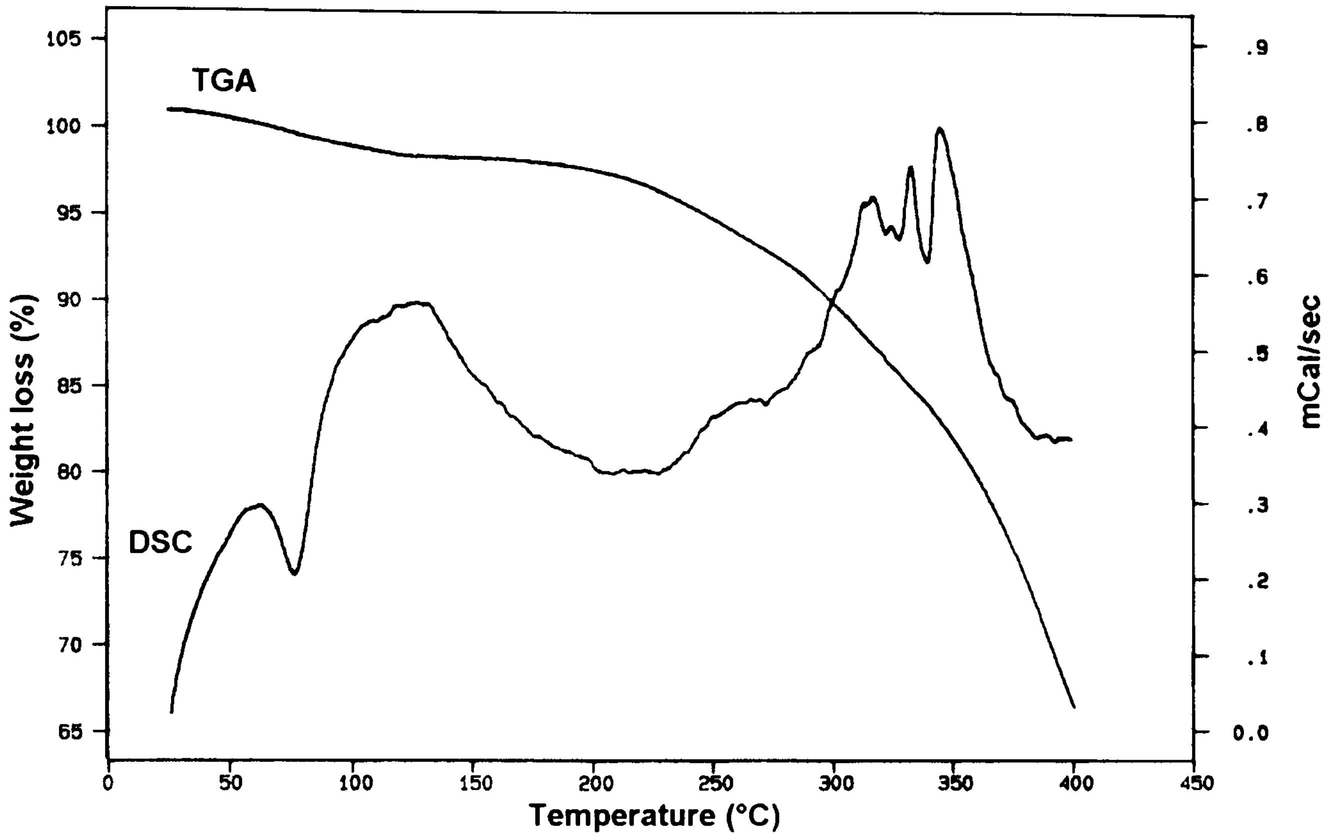


Figure 4.8 TGA/DSC curves of organosolv lignin.

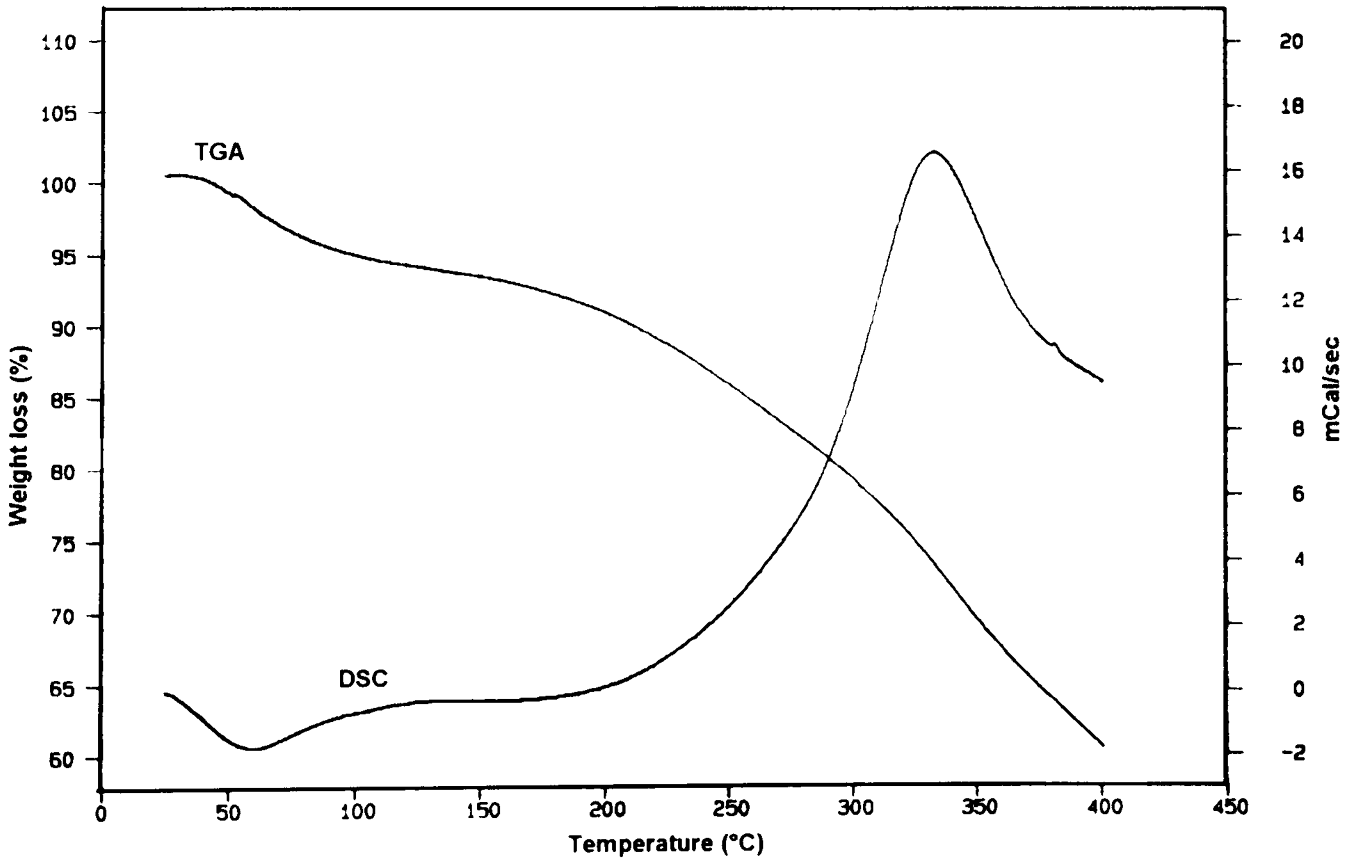


Figure 4.9 TGA/DSC curves of alkali sulphite lignin.

A combination of DSC and TGA confirms an endothermic phase transition at 78°C.

In Figure 4.9, the thermogram of alkali sulphite lignin, shows at first an endothermal maximum in the range of 50-100°C, which is attributed to the evaporation of strongly bound water. The exothermal peaks at 150-300°C and those higher than 400°C are due to a degradation of the lignin. The TGA curve shows 40% weight loss.

4.3.9 The reactivity of organosolv and alkali sulphite lignins with phenol

The results of the alkali sulphite lignin powder phenolation in the presence of 1-butanol, are shown in Table 4.8 and compared with those obtained with the organosolv lignin.

Table 4.8 The phenolation reaction results for organosolv lignin and alkali sulphite lignin

Wt% of phenol in initial lignin/phenol mixture	Wt% free phenol	Alkali sulphite reacted lignin P/L mole ratio	Organosolv reacted lignin P/L mole ratio
16.7	10.65	1.5	1.5
37.5	24.42	3.0	4.5
50.0	34.52	6.1	6.6
66.7	46.42	12.6	12.9

The free phenol content was determined according to the method described in Section (5.2.8.1, page 111). The results tabled above were combined with the results obtained from reactions involving the addition of oxalic acid to the initial mixture to produce Figure 4.10 below. Despite one anomalous result with oxalic acid at high weight % phenol levels, the results indicate that the lignin obtained from the simple treatment of the black liquor, compare similarly to the commercially purified organosolv lignin.

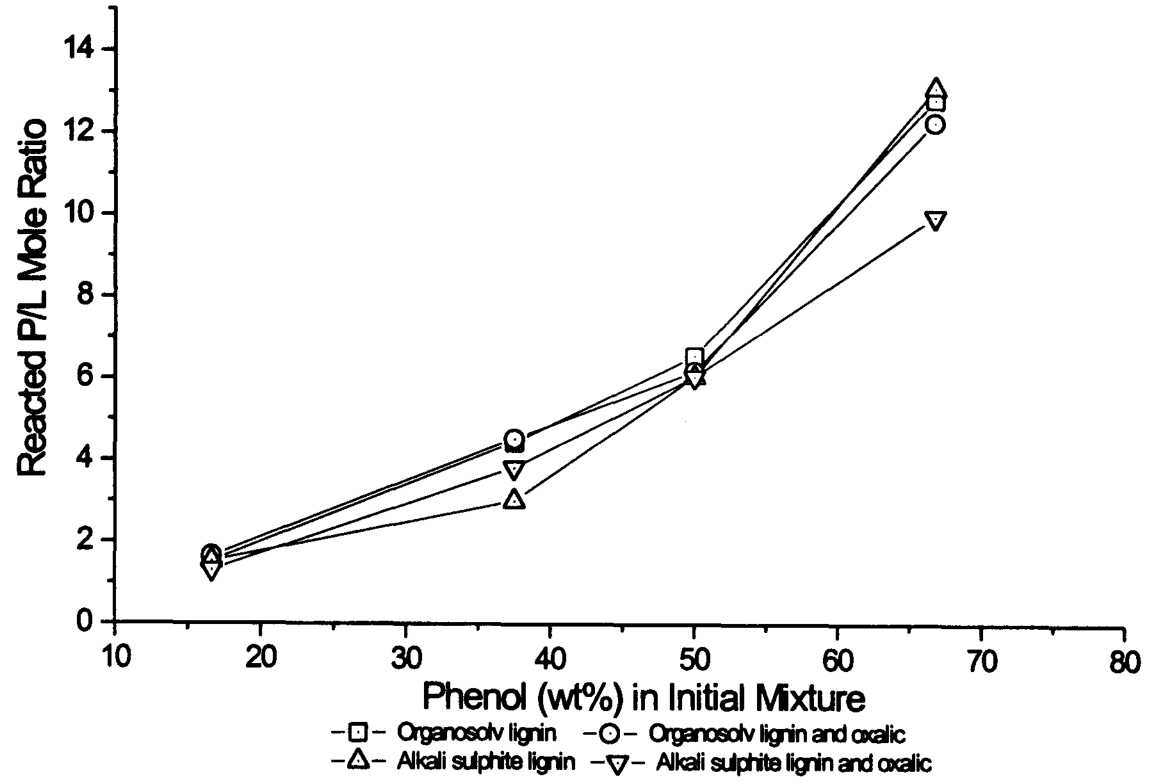


Figure 4.10 Comparison of P/L mole ratios of lignins with and without oxalic acid.

4.3.10 The reactivity of black liquor (alkali sulphite lignin) with phenol

As explained in section 4.2.2.8, phenol was reacted with black liquor in two ways.

1) In the first experiment where the black liquor of alkali sulphite lignin pH was adjusted to 4.5 by adding oxalic acid and viscosity was determined, the addition of phenol did not affect the viscosity, which remained at approximately 9 cP. Because of the high percentage of water in the mixture, the free phenol results were not consistent and no conclusions could be drawn on whether there was any reaction taking place between phenol and lignin in the black liquor.

2) In the second experiment, where the Dean and Stark separator was used to isolate the water from the black liquor, the addition of phenol also did not affect the viscosity, which remained also at approximately 9 cP, in this experiment. Because of the high percentage of water in the mixture (even if water was removed during

reaction) the free phenol results were not consistent and no conclusions could be drawn in this condition.

4.4 CONCLUSIONS

The lignin was obtained from alkali sulphite black liquor, which since it is a waste product from the pulping industry, would be a cost effective source. The reaction of this lignin with phenol, was (within experimental error) identical to the commercially purified organosolv lignin.

Even though large quantities of black liquor lignin could be obtained, this black liquor lignin was not used in the bulk of this thesis. Commercially available organosolv lignin was preferred for production of LPF resins for following reasons:

- As the use of small-scale laboratory equipment, precipitation and filtration of the black liquor is very labour intensive, requiring a long time to produce sufficient quantities for a phenolic-lignin resin trial, where commercial organosolv lignin could be obtained in kg quantities.
- High ash content and low purity of alkali sulphite lignin compared to organosolv lignin.
- Utilisation of black liquor lignin would possibly result in inorganic salts being present in the resin, which could affect the wood composite properties. This complication was not deemed desirable in this work but should be studied as a separate topic. Because the isolation of the lignin material from paper mill wastes is liable to remove all the acid insoluble organics, there would be a considerable improvement in the quality of water being discharged.

In the light of these observations, it was decided to use readily available organosolv lignin for production of lignin-based resins. The production of resins and formulations are explained in Chapter 5.

CHAPTER 5

USE OF ORGANOSOLV LIGNIN IN PREPARATION OF PHENOLIC RESINS

5.1 INTRODUCTION

The use of lignin as a filler or extender in combination with PF resins is well known. Many attempts have also been made to utilise lignin as a phenolic substitute in PF resins. Unfortunately, the structure of lignin restricts its reactivity and thus limits the industrial usefulness of lignin-based resins. The priority is to obtain an adhesive based on lignin that maintains the performance of any given wood-based product.

The aim of the work described in this chapter was to find a formulation for lignin-based resins to replace as much phenol as possible with lignin. However, any resin that is formulated should be industrially viable, i.e. having short press times and produce strong bonds in the composite. Work already reviewed (in Chapter 2) indicated that the successful replacement of phenol with lignin was likely to be at no more than 30% by weight.

The resins in this study included a commercial PF resin (PF_com) (DynoChem DPL 5681) as a reference, a laboratory made PF resin (PF_made), and resins containing organosolv lignin (Alcell® lignin) substituted for phenol. In order to prepare the lignin resins, lignin was introduced in two ways. Firstly, lignin was used directly as a replacement for phenol. In the second method, lignin was modified by phenolation and then incorporated into the resin formulations.

Before making phenolated-lignin-formaldehyde resins, the reaction between the lignin and phenol was studied. Lignin was reacted with phenol with and without oxalic acid at various temperatures and times. In addition to that, the effect of alkali, solvent, and water was determined for lignin-phenol reaction. The maximum possible

P/L mole ratio and the effect of adding additional phenol to the reaction mixture after the initial reaction had taken place was also established. The different resin formulations were prepared according to the data obtained from the results of these reactions.

Three batches of a PF_made resin, lignin-phenol-formaldehyde (LPF) resins, and phenolated-lignin-formaldehyde resins were made. All the lignin-based resins were characterised and comparisons were made with both the PF_com resin and PF_made resins.

The production of the PF_made and all lignin-based resins were produced to give an end product that was similar to the characteristics of the reference PF_com resin; 200-300 cP viscosity, 50-55% nonvolatile solids content, pH 10.2.

5.2 MATERIALS AND METHODS

5.2.1 Reagents and solvents

The essential raw materials used in the preparation of phenolic resins were:

- A commercial powder organosolv lignin (trade name ALCELL® lignin, from Alcell Technologies, Ltd.)
- Commercial grade phenol of 99% purity
- Formaldehyde solution (35 weight % aqueous solution)
- Sodium hydroxide solution (NaOH, 40 weight % aqueous solution)
- 1-Butanol (99%)
- Industrial methylated spirit (IMS). These two solvents were used to reduce the viscosity of the reaction mixture and, it was initially assumed, to facilitate the mobility of the reacting species.

- Commercial resol type liquid PF resin (code DPL 5681, which is a particleboard binder resin) supplied by DynoChem Ltd. PF_made resin was also prepared as explained in Section 5.2.2.1.

All the chemicals (except lignin and PF_com resin) used were supplied by Aldrich and used without further purification.

5.2.2 Phenolic resol resin preparation

In order to characterise the lignin-based resins produced, it was necessary to compare their properties with other similar resins. Therefore a sample of PF_com resin (DPL 5681) was obtained and this material was used as a standard with which to compare all other resins that would be produced in the laboratory. On receipt, it was analysed for chemical and physical properties, which are described in Section 5.3.2 (page 115).

Comparisons were made with the following resins produced in the laboratory:

1) A phenol-formaldehyde resin.
2) Lignin-based phenol-formaldehyde resins.

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

1) By substituting phenol with lignin at different percentages.
2) By substituting phenol with phenolated-lignin compounds at different percentages. The preparation of these resins is explained in Sections 5.2.2.2 and 5.2.6.2.

5.2.2.1 PF resol resin synthesis

A reaction vessel equipped with an electric stirrer, thermometer, reflux condenser and heating mantle was used for preparing all the resins (Figure 5.1).

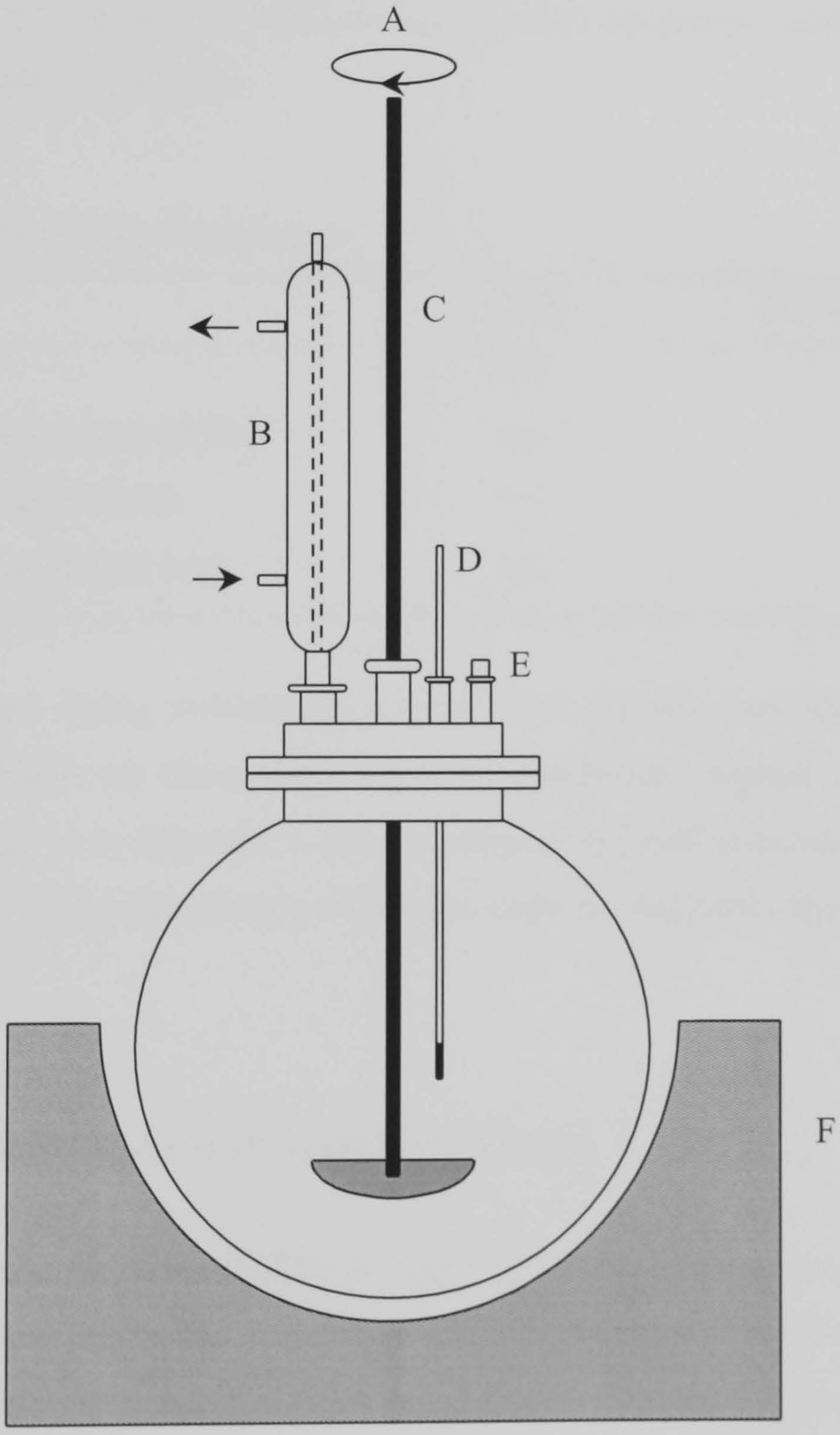


Figure 5.1 Reaction equipment for resin synthesis: A) Stirrer speed motor B) Condenser C) Stirrer guide and seal D) Thermometer E) Sample tube F) Heater.

In order to compare any new lignin resins with a PF resin, it was decided to produce three identical PF resins and test them for conformity.

A standard PF base was prepared using a recipe considered being typical of a commercially available PF resin. A quantity of base product (6 kg, 3x2 kg) was prepared by mixing phenol, formaldehyde and caustic soda and heating this blend to 50°C. Table 5.1 shows the formulation for the laboratory produced phenol-formaldehyde (PF_made) resin.

Table 5.1 Phenolic resol for PF application

Ingredients	Parts	Batch Weight (g)
Phenol	100	483.0
Formaldehyde solution (35%)	140	707.6
Sodium hydroxide (10N)	3.5	16.9
Para toluene sulphonic acid	4.6	22.2

At critical stages during manufacture of each resin, samples were taken to confirm conformity. Details of these tests, and the manufacture method used for each PF_made, are given in Appendix 1. pH was adjusted to 7 with para toluene sulphonic acid in the end of the manufacture of resin in order to maximises the pot life of the resin.

5.2.2.2 Organosolv lignin in PF resins (LPF Resins)

The addition of a PF precondensate to lignin has been used as a way to introduce phenolic reactivity into lignin. 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 was incorporated into the PF base combination that was produced as described in Appendix 1. At stage 5, in the procedure, the PF batches were modified. By adding organosolv lignin at 5, 10, 20, 30 and 40% of the original phenol content, then continuing the production of the resins from step 6 in the PF procedure, different resins were produced and examined.

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). An adjustment had to be made to bring the solids content to 50-55% and NaOH added to increase the pH to bring the specification in line with the commercial reference.

5.2.3 Lignin-phenol derivative reactions

Lignins have -CH_2OH type groups. But, what is not well documented is how many of the -CH_2OH groups on the lignin molecule are potentially reactive to phenol. Further, one should suspect that this will vary depending on source of lignin used.

When lignin is added to the base PF resin, these groups should react with unreacted sites on the phenol molecule. With the lignin molecule being high in molecular weight, and a complex molecule with anticipated high steric hindrance, the rate of reaction might be expected to be lower than for simple mono-, di- or tri- methoylated phenols reacting with each other. It is no surprise, therefore, to find the LPF resins having longer hardening times, as a consequence of the higher lignin contents.

From the lignin skeleton (Figure 2.4), it can be seen where there are potential reactive centres. Some of these are -CH_2OH groups, which may be active toward phenol groups, others are phenolic sites in the *ortho* or *para* positions, which will react with formaldehyde. From the literature survey (Kratzl *et al.*, 1962), most of the work seems to have concentrated on using the phenolic sites, but little work appears to have been done on the -CH_2OH sites. There also appeared to be evidence that weak bonds may break down on acid hydrolysis to give more -CH_2OH sites.

Although some of these sites may not be capable of reacting with phenol, due to steric hindrance it was decided:

- To investigate this area of the lignin molecule, with the aim of producing a lignin-phenol compound.
- To determine the number of moles of phenol that could be added to on a lignin molecule.
- To determine the stability of the lignin-phenol compound produced.
- To base the amount of formaldehyde to be added to produce a resin, on the number of theoretical additive sites in the lignin-phenol compound.

5.2.3.1 Organosolv lignin in 1-butanol

Before producing phenolated-lignin-formaldehyde resins, some preliminary investigations were carried out, in order to find an optimum pathway to produce a satisfactory lignin-phenol reaction.

Initial work used only lignin plus phenol, but subsequent analysis of the material after various reaction times, gave anomalous results that were initially attributed to poor mixing of lignin in the phenol.

Since the organosolv lignin is a dry solid, it was therefore decided to dissolve the lignin (100 g) in 1-butanol (175 mL). 1-butanol was chosen because its boiling point is higher than 100°C and it was considered that some heating may be required to push the phenol lignin reaction to completion. Before using phenol in the reaction, some simple data was collected, and this is shown in the results Section 5.3.3.1 (page 118).

5.2.3.2 Addition of phenol to lignin

According to the results that obtained in Section 5.3.3.1 (page 118) it was decided to study the viscosity of the lignin/1-butanol solutions when phenol was added to the solution. It was hoped that the active groups on the lignin molecule (the methoylated groups reported to be on the structure) would preferentially react with phenol instead of active groups on other lignin molecules. If this happened, then the resultant product might stay liquid and the viscosity would fall, if the reaction were lignin-phenol rather than lignin-lignin.

In order to monitor the change in the viscosity caused by the addition of varying amounts of phenol added to the lignin/1-butanol mixture, viscosity measurements were taken throughout the experiments.

Organosolv lignin (100 g) was dissolved in 1-butanol (175 mL) at room temperature with rapid stirring. Increasing amounts of phenol (from 5 g to 200 g) were added immediately to the lignin/1-butanol mixture. This mixture was heated to 100°C and kept at that temperature for 30 minutes to observe the viscosity changes. The experiment was repeated with and without oxalic acid to determine whether or not the observations on acid hydrolysis (see 5.2.3, page 97) were valid. Viscosity of the resin samples was measured using a low-shear rotating apparatus Brookfield LVF viscometer (Model DV-II + Viscometer), spindle 2 and speed 100 rpm. Viscosity was estimated as centipoise (cP) at a constant temperature (25°C).

The results for this part of experiment are shown in Section 5.3.3.2 (page 119).

5.2.4 The study of the lignin-phenol reaction

The concept of phenolation was explored. In order to determine how many moles of phenol were reacting with the lignin, a number of experiments were carried out where the weight of lignin (100 g) and 1-butanol (175 mL) were held constant and varying amounts of phenol with and without oxalic acid, were added.

Commercially produced organosolv lignin (100 g) was mixed with various amounts of commercial grade phenol (20 g to 200 g) and with and without oxalic acid. The mixtures were heated in an oil bath at various temperatures (25°C, 50°C, 75°C, 100°C). Since time in contact with phenol may be important, the reaction mixture was allowed to stand for periods of time (10, 20, 30, 45, 60, 90, 120, 150, 180, 210, 240 minutes) before sampling. After a period of time, the mixture was withdrawn and analysed immediately by GC (Section 5.2.8.1, page 111).

5.2.5 The determination of potential variables in lignin-phenol reactions

Before making resins, all potential variables were investigated to determine the possible influences that these might have during the resin preparation (e.g. speed of reaction, which would effect viscosity) and in the final properties of the resin (e.g. setting/hardening times). Knowing this would allow changes to be made to optimise resin properties. Therefore in this part of the work, the aim was:

- To determine the effect of pH.
- To determine the effect of solvent.
- To determine the maximum possible P/L mole ratio.
- To determine if the addition of extra phenol to the mixture of lignin-phenol increased the P/L mole ratio.
- To establish the effect of water.

5.2.5.1 Use of alkali as catalyst (or effect of pH on the reaction mechanism)

The initial work reported above was carried out with oxalic acid. Because there was some evidence in the literature (see 5.2.3, page 97) that the lignin might dissociate more effectively in acid conditions and as hypothesised by Kratzl *et al.* (1962) might expose more -CH_2OH groups that would be capable of reaction with phenol.

Some of the tests were repeated using an alkali, instead of oxalic acid, in order to determine the effect that a change in pH would have on the reaction mechanism. In these tests, sodium hydroxide was added to the phenol to increase the pH to 10.2 (as used in the formation of the phenol formaldehyde resin), before adding this to the lignin. Results are shown in Section 5.3.5.1 (page 132).

5.2.5.2 Effect of solvent on P/L mole ratio

As explained in Section 5.2.3.2 (page 98) 1-butanol (175 mL) was added to 100 g of lignin then phenol was added immediately. To assess the effect of the solvent, and determine the need for a solvent in the work, further work was carried out with no 1-butanol and 350 mL of 1-butanol. All the work was carried out at 100°C, and the P/L mole ratio determined. Results are shown in Section 5.3.5.2 (page 134).

5.2.5.3 The determination of maximum possible P/L mole ratio

The maximum possible P/L mole ratio was determined using the data generated from more than twenty lignin-phenol experiments and allowed the creation of an equation (from regression analysis) to link phenol concentration, catalyst concentration and reaction temperature. Results are shown in Section 5.3.5.3 (page 137).

5.2.5.4 Effect on P/L mole ratio on the addition of extra phenol to lignin-phenol mixture

To determine what happens to the P/L mole ratio if more phenol is added to a phenol/lignin mixture, the P/L mole ratio was determined for a mixture before extra phenol was added. The P/L mole ratio was determined after each of two additions. Results are shown in Section 5.3.5.4 (page 140).

5.2.5.5 Effect of the water on the P/L mole ratio

To determine if the P/L mole ratio is affected by the presence of water in the phenol/lignin mixture, phenol (210 g) was added to the organosolv lignin (100 g) in 1-butanol. The experiment was repeated, but water was added to the lignin prior to the addition of phenol. Results are shown in Section 5.3.5.5 (page 141).

5.2.6 Preparation of phenolic resins using phenolated-organosolv lignin

In this second approach to producing a resin, the lignin was allowed to react with the phenol first to form a phenolated lignin, in the hope of creating more active sites on the "new molecule". The phenolated lignin was then reacted with formaldehyde to produce a resin.

The phenolysis reaction was used as a means of modifying the structure and reactivity of the organosolv lignin for these reasons:

- First, because lignins and carbohydrates are known to react with phenols under acidic conditions.

- Second, because unreacted phenol could be removed easily from the phenolated product after reaction if required, before conversion to the adhesive resin.

It was a reasonable assumption that because of the excess of phenol in the reaction mixture, the combination of phenol with lignin is most likely to involve only one of the three reactive positions on the aromatic ring of the phenol. Consequently, the reactivity of the modified lignins to formaldehyde ought to be enhanced, relative to the pre-phenolysed material because, for every reactive position lost by combination, two new reactive positions, would be created by the added phenol moiety (Allan *et al.*, 1989).

Chemical modification by phenolation, in which lignin is treated with phenol to form a lignin-phenol derivative, was selected and evaluated for the manufacture of resins. Phenolated resins were prepared by a two-step reaction, involving phenolysis of the lignin to form lignin-phenol (LP), followed by a polymerisation stage using formaldehyde (LPF). In stage one (lignin-phenol), the lignin is treated with phenol and this leads to condensation of phenol into the lignin ring and side chain. In stage two, the formaldehyde solution was added to the L-P product and resol type lignin-based PF resins were made.

5.2.6.1 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 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. The lignin was treated this way in order to produce a lignin-base combination. IMS was evaporated off under 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 GC (as described in Section 5.2.8.1 (page 111) to ensure that the reaction had gone to the expected completion.

5.2.6.2 Preparation of phenolated-lignin-formaldehyde resins

The base combinations were prepared as explained above in Section 5.2.6.1. The base combination (lignin-phenol product), a black viscous resin, (which was stable in free phenol) and was placed in a flask. The amount of formaldehyde solution that was to be added to the LP product to produce a resin, was calculated by determining the available *ortho* and *para* positions capable of reacting with the formaldehyde. This was done, by determining the free phenol content in the LP base product, and hence the amount of phenol reacted with the lignin assuming mono addition of the lignin to the phenol. The same proportion of aldehyde / free *ortho*, *para* phenol positions was used as used in the preparation of the initial PF resins. The calculated amount of formaldehyde solution (35%) was added into the phenolated-lignin product and the pH of the mixture was adjusted by adding 10N NaOH solution to raise the pH to 10.2. After the formaldehyde solution was mixed, the mixture was then heated up to 50°C and held 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 product was soluble in water at this point.

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 was reached and the product was used for further study.

It was found that care had to be taken throughout the polymerisation stage. The viscosity measurements of the reaction mixture were taken frequently during the reaction, because the condensation of methoylated compounds into larger molecules proceeded more rapidly during the reaction stage at 80°C than with the normal PF resins.

5.2.7 Resin formulation methods

All the phenolated-lignin-formaldehyde resins (LPF 10A, LPF 10B, LPF 20A, LPF 20B, LPF 30A, LPF 30B, LPF 40A, LPF 50A, LPF 60A, LPF 70A) were prepared using the same methods as described in Sections 5.2.6.1 and 5.2.6.2, respectively. The formulation methods were designed to prepare modified lignin resins at different P/L ratios. Firstly, some preliminary experiments were performed. Initially, lignin (200 g) and phenol (400 g) was mixed to prepare the base combination (LP), as explained in Section 5.2.6.1. After IMS removal, the lignin-phenol product was divided into two equal parts. In order to establish the formaldehyde addition level to be used, the resulting mixture was analysed to determine the free phenol content. Two formaldehyde solution (35%) addition levels were applied to the two bases of the lignin-phenol (base LP) product, in order to produce two resins (LPF 10A, LPF 10B) with different PL/F molar ratios. The addition levels can be seen in Table 5.2 (see Appendix 2 for more details). With these being the first resins produced using the P/L combinations, it was thought that if the original phenol/formaldehyde ratio (that was used in the preparation of the PF resins, Section 5.2.2.1) was used, any unreacted methylol groupings on the lignin might take part in the polymerisation reaction and the rate of reaction might be uncontrollable. Therefore, the amount of formaldehyde added to the LP mixture was reduced by ≈15% (Resin LPF 10A) and by ≈40% (Resin LPF 10B). The resin preparation was then continued, as detailed in Section 5.2.6.2.

Table 5.2 Typical lignin-phenol co-polymer formulations using organosolv lignin

	Ingredients	Weights (g)
	Phenolated-Lignin Condensation Step	
Base LP 10	Lignin	100
	Phenol (99%)	200
	Phenolated-Lignin-Formaldehyde Co-Condensation Step	
Resin LPF 10A	Base LP 10 + Formaldehyde (35%)	300 + 179.2
Resin LPF 10B	Base LP 10 + Formaldehyde (35%)	300 + 125.4

5.2.7.1 Synthesis of resins

Although the effort to produce resins for evaluation in the wood composite industry is not high, the production of the wood composite and the testing of the resultant product do require time and resources that were both limited in this work. Therefore, an attempt was made to follow the "Taguchi method" (i.e. using orthogonal arrays) in the planning of an experiment to find the best formulation of P/L mole ratio, free phenol and formaldehyde. These three are the primary variables in the process. From the data generated using the equation (from regression analysis), several resins were produced and their use as wood glues were assessed.

It can be seen from Figure 5.2 (which was drawn from the study of the lignin-phenol reaction), that if the initial phenol content in the mixture was 36.6% then after the reaction with the lignin, it would be expected that 27% free phenol would be present. Similarly, if the initial phenol content in the mixture was 60% then after the reaction with lignin, it would be expected that 41% free phenol would be present.

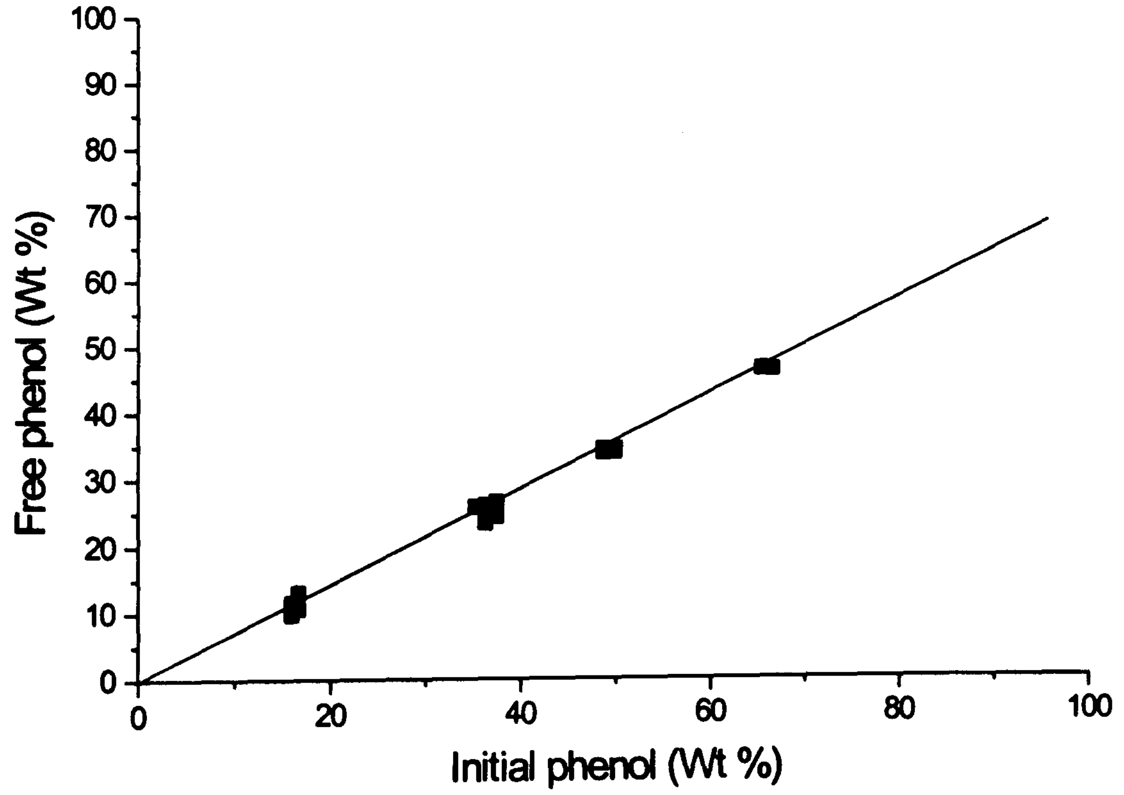


Figure 5.2 The effect of initial phenol content (wt%) on free phenol content (wt%).

Furthermore, it can be seen from Figure 5.22 (page 138) if the initial phenol content in the mixture was 36.6% then after the reaction with the lignin, it would be expected that a compound with a P/L mole ratio of 5 would be present. Similarly, if the initial phenol in the mixture was 60% then after the reaction with the lignin, it would be expected that a compound with a P/L mole ratio of 10 would be present. Following Taguchi's recommendation (Caulcutt, 1991) three primary variables were assigned to three columns as shown in Table 5.3.

As can be seen from Table 5.3, the resin LPF 20A had 27 weight % free phenol for its base combination but in LPF 20B, phenol was added to increase the free phenol weight % to 41%. The resin LPF 30B (to achieve an initial P/L mole ratio of 10) had a free phenol content of 41%, but to achieve 27 weight % free phenol in resin LPF 30A, phenol had to be removed from the mixture.

The last column refers to the percentage of the formaldehyde solution added to the LP base combinations to produce the phenolated-lignin-formaldehyde resins. Formaldehyde was calculated by determining the available *ortho* and *para* positions capable of reacting with the formaldehyde. This was done, using the free phenol content in the liquid, and the amount of phenol reacted with the lignin assuming *mono* addition of the lignin to the phenol. The same proportion of aldehyde / free *ortho*, *para* phenol positions was used as used in the preparation of the initial PF resins (see Appendix 3 for more details).

Table 5.3 Experimental array for phenolated-lignin phenolic resin formulations

Resins	P/L Mole Ratio	Free Phenol (wt%)	Formaldehyde Solution (wt%)
LPF 20A	5	27	32.8
LPF 20B	5	41	38.1
LPF 30A	10	27	38.1
LPF 30B	10	41	32.8

In order to produce the lignin-phenol base combinations for LP 20 and LP 30; and from them, the resins LPF 20A, LPF 20B, LPF 30A, and LPF 30B, the same procedure was used, as explained in Sections 5.2.6.1 and 5.2.6.2, respectively. Table 5.4 below shows the formulations of these resins.

Table 5.4 Typical lignin-phenol co-polymer formulations using organosolv lignin

	Ingredients	Weights (g)
	Phenolated-Lignin-Formaldehyde Resins	
Base LP 20	Lignin	100
	Phenol (99%)	71.6
Resin LPF 20A	Base LP 20 + Formaldehyde (35%)	171.6 + 83.8
Resin LPF 20B	Base LP 20 + Formaldehyde (35%)	171.6 + 121.6
Base LP 30	Lignin	100
	Phenol (99%)	150
Resin LPF 30A	Base LP 30 + Formaldehyde (35%)	250 + 122
Resin LPF 30B	Base LP 30 + Formaldehyde (35%)	250 + 121.6

5.2.7.2 Resins using different P/L mole ratio

A series of phenolated-lignin-formaldehyde resins were prepared as explained above. It was hoped that the results from these resins (as can be seen from Table 5.13, page 142) and subsequent bonding testing (in Chapter 6) would indicate the direction to change the primary variables (P/L mole ratio, free phenol and formaldehyde content) to produce the best results. This appeared to suggest that better wood bonding strength would occur if:

- The reacted P/L mole ratio was increased.
- The formaldehyde usage is increased.

As can be seen from the results (Table 5.13, page 142), the array resins, had a high free formaldehyde content and a long curing time. The aim of this work, therefore, was to reduce the curing time, and improve the degree of the cure of the resins produced via the lignin-phenol route, based on different P/L mole ratio. Since all the comparisons were made against the PF_com resin, it seemed from the data, that 50% free phenol in the base combination was a good starting point. An attempt was also made to reduce the free phenol content below 50% (LPF 70A) as can be seen from Table 5.5.

Therefore, with the target of 50% free phenol content in the base combinations, new resin formulations were prepared. Table 5.5 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. The base combinations were prepared as explained in Section 5.2.6.1 (page 103).

Table 5.5 Parameters for phenolated-lignin resin formulations

Resins	P/L Mole Ratio	Free Phenol Content (Wt %)	Formaldehyde Solution Added (Wt %)
LPF 40A	19	50	70
LPF 50A	14	50	70
LPF 60A	9	50	70
LPF 70A	19	45	50

In the LP 40, LP 50 and LP 60 base combinations, the free phenol contents were less than the desired 50%. Therefore, extra phenol (320 g, 275 g and 542 g) was added to the LP 40, LP 50 and LP 60, 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 to catalyse the reaction. Then, the resin cook method was carried out using the same method as described in Section 5.2.6.2 (page 103). As can be seen from the Table 5.5, only the base of the resin LPF 70A included less free phenol (45%) and formaldehyde contents (50%) in its base combination. Table 5.6 shows the formulations of these resins.

Table 5.6 Typical lignin-phenol co-polymer formulations using organosolv lignin

	Ingredients	Weights (g)
	Phenolated-Lignin-Formaldehyde Resins	
Base LP 40	Lignin	250
	Phenol (99%)	700 + 320
Resin LPF 40A	Base LP 40 + Formaldehyde (35%)	1270 + 890
Base LP 50	Lignin	250
	Phenol (99%)	550 + 275
Resins LPF 50A	Base LP 50 + Formaldehyde (35%)	1075 + 752.5
Base LP 60	Lignin	500
	Phenol (99%)	550 + 542
Resin LPF 60A	Base LP 60 + Formaldehyde (35%)	1592 + 1114.4
Base LP 70	Lignin	200
	Phenol (99%)	560
Resin LPF 70A	Base LP 70 + Formaldehyde (35%)	760 + 380

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.

5.2.8 Testing and characterisation of the resins

The previous section details the formulation of lignin-based resins. This section details the testing and characterisation of the resulting resins for their free phenol, free formaldehyde, solid content, viscosity, specific gravity, pH and hardening time on heating.

The determination of the properties of phenolic resins is important and these properties affect the performance of the wood composite product. Good process control of the resin during manufacture and quality testing at critical stages of the preparation are essential to ensure that the phenolic resins are made to a specification.

5.2.8.1 The quantitative determination of phenol content in resins by gas chromatography (GC)

Gas chromatography is one of the analysis methods by which phenol can be separated and quantitatively determined. The free phenol content for all the resin types was measured by gas chromatography (GC) using a flame ionisation detector (FID) on a glass column RTX-1 (7.5 m x 0.53 mm). The FID (flame ionisation detector) oven and injector oven temperatures were 350°C and 320°C, respectively and oven temperature programmed from 100 to 190°C at 2°C per minute with a 10 minute hold at 190°C. Helium was used as a carrier gas at a flow rate of 36 mL/min.

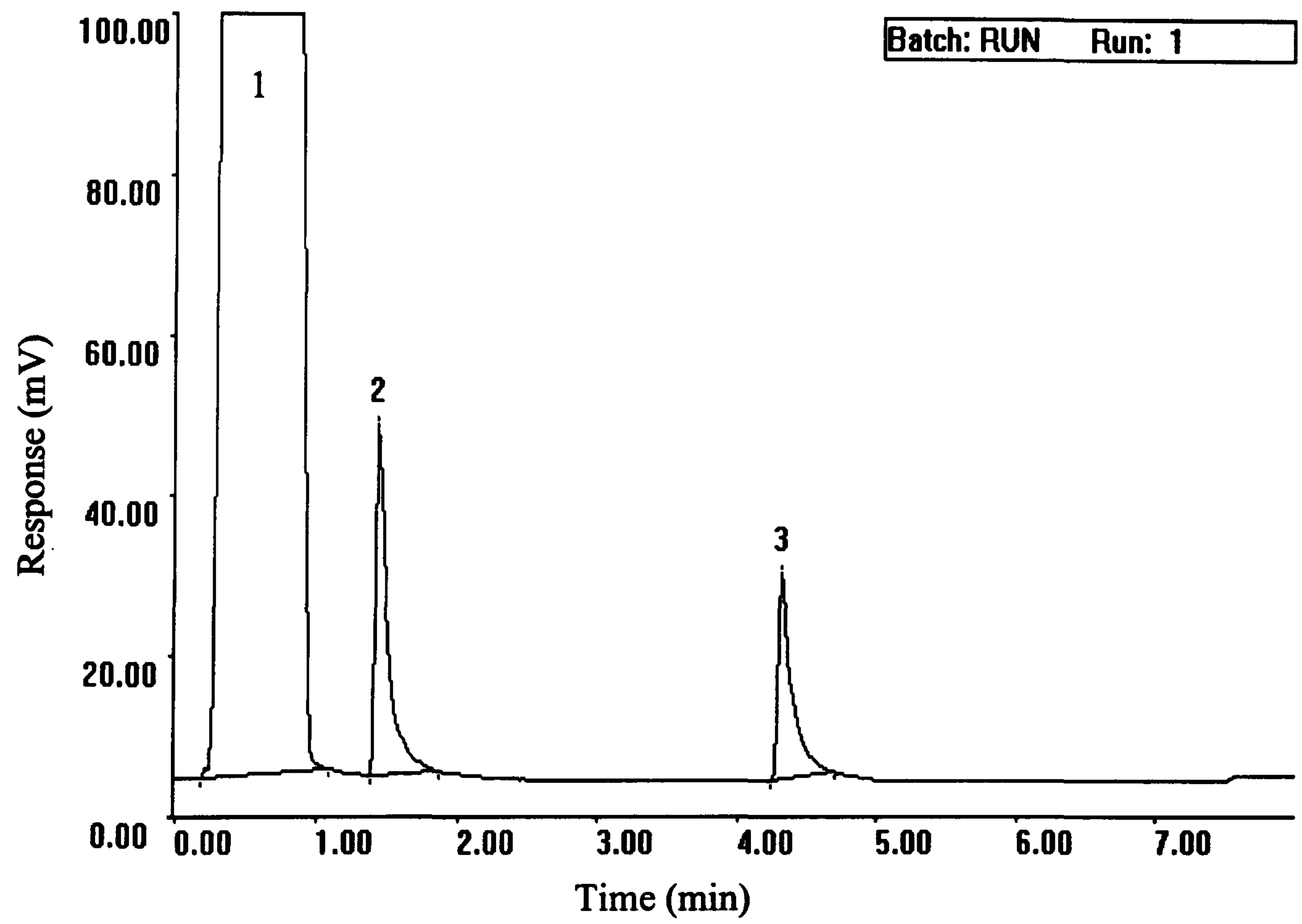
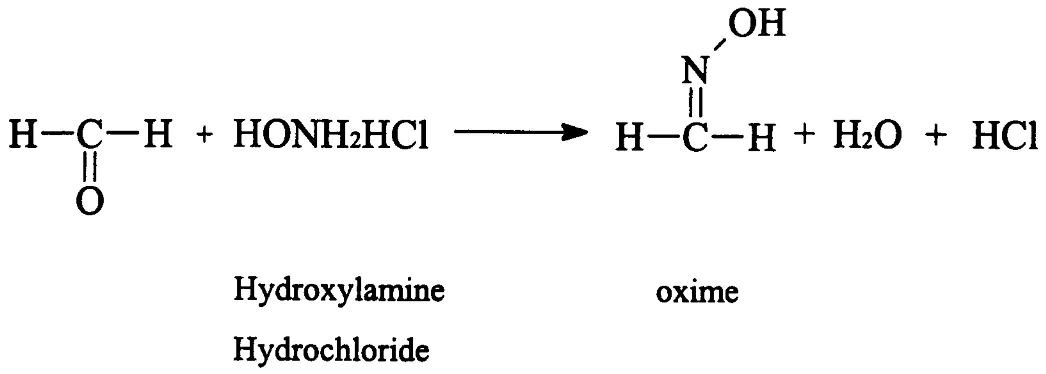


Figure 5.3 Gas chromatogram of phenolic resins (1: solvent acetone, 2: phenol, 3: naphthalene internal standard).

A sample of resin (about 0.1 g) and known quantity of naphthalene (acting as internal standard, 500 ppm) was dissolved in 10 mL acetone. A sample of this mixture was injected into a GC column, then analysed by GC. A typical gas chromatogram is shown in Figure 5.3.

5.2.8.2 The determination of free formaldehyde using hydroxylamine hydrochloride

The reaction product resins were analysed for free formaldehyde content. The method used was applicable to phenolic resins. The appropriate weight of sample was taken. 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.



$$H_2C{=}O + HONH_2HCl \longrightarrow H_2C{=}N{-}OH + H_2O + HCl$$

If the specification mid-point was in the range 0-5%, 2 g of sample was taken.
If the specification mid-point was in the range 5-10%, 1 g of sample was taken.
If the specification mid-point was above 10%, then 0.5 g of sample was taken.

25 mL of industrial methylated spirit (IMS) was added to the resin samples and stirred until dissolved. 2-3 drops of 0.1% bromo phenol blue was added and the solution was then carefully neutralised with 0.5N sodium hydroxide, or 0.5N hydrochloric acid, as required. 10 mL of 10% hydroxylamine hydrochloride aqueous solution was added and the mixture was then heated to 50-55°C in the water bath for 5 minutes. The mixture was cooled to room temperature and titrated with 0.5N sodium hydroxide solution. A blank was carried out on 25 mL of neutralised industrial methylated spirit (IMS) and 10 mL of hydroxylamine hydrochloride, under the same conditions. The calculation and the expression of the results were formulated as follows:

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

where:

V1 = Volume of 0.5 N sodium hydroxide required for sample
V2 = Volume of 0.5 N sodium hydroxide required for blank
f = Factor of normal (N) sodium hydroxide = 0.5
W = Weight of sample

5.2.8.3 Solid content

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

$$Solid\ Content\ (\%) = \frac{Dry\ weight}{Initial weight}\ x\,100$$

5.2.8.4 Viscosity

One of the most important physical properties to be controlled for adhesives is viscosity. The measured viscosity of an adhesive is an important measure of the uniformity of the product. Viscosity is also a measure of the degree of polymerisation or condensation of the resin. In addition to this, the viscosity of an adhesive describes to a large degree the character and can be related to storage life of the adhesive (Tappi, 1996).

Viscosity of the resin samples was measured using a low-shear rotating apparatus Brookfield LVF viscometer (Model DV-II+ Viscometer). Viscosity was estimated as centipoise (cP) at a constant temperature (25°C) as detailed previously in Section 5.2.3.2 (page 98).

5.2.8.5 Specific gravity (S.G.)

Specific gravity is a measure of the resin content and is related to the solids content. A uniform temperature (25°C) is desirable for the resin solution being checked for specific gravity (Sellers, 1985).

A specific gravity bottle was used for the resins. 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.

5.2.8.6 pH

The alkalinity or acidity of solutions has a major effect on many adhesive 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. In this work, a pH meter (Kent Eil 7020) with silver-silver chloride glass inverted sleeve reference electrode was used.

5.2.8.7 Heat hardening time

The hardening time is of great importance in phenolic resin technology. For some applications, very fast curing resins are necessary, whereas in other cases a long curing time is essential (Lightbody, 1999).

The test was carried out in a small tube placed in an oil bath thermostatically controlled to the test temperature of 150°C. A known weight of the resin (0.3 g) was charged to the tube, which contained a glass rod as a stirrer. The resin was stirred at frequent intervals until the resin passed from a liquid to a rubbery state and then broke away from the stirrer rod. The time that elapsed from the initial charging of the resin to the end point was recorded.

5.3 RESULTS AND DISCUSSION

5.3.1 Phenol formaldehyde resin

PF resol resin was made in the laboratory as explained in Section 5.2.2.1 (page 95). In industrial production, large batches of resin are produced only after experiments are made to determine the optimum conditions for the process. The heating of phenol and formaldehyde with NaOH results in an exothermic reaction and there can be potential problems with the temperature control of the reaction mixture. Loss of control can lead to runaway reactions, vapourisation of water and formaldehyde, and pressurisation of the reaction system. The product viscosity would rise exponentially leading to the reactor contents solidifying.

The small-scale laboratory reaction work carried the same risks, however because of the smaller batch size, the process time was shorter, making speed of analysis when approaching end points, critical.

The measurement of water content is an important factor in making PF and LPF resins. However, in this work, water content could not be measured. The lack of equipment did not permit this. Considering that water is one of the important factors in resin making, water determination by titration using the Karl-Fischer method was attempted, but the dark colour of the lignin resins prevented consistent results by this method. A potentiometric method was also tried without success.

5.3.2 Lignin-phenol-formaldehyde-resins

Five types of lignin resins were prepared (i.e., 5-40% lignin addition) as explained in Section 5.2.2.2. PF_com, PF_made and LPF (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 5.7. All the resins had 200-250 cP viscosity and 50-55% solid content.

Table 5.7 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
PF_made	12.9	1.75	3.29	1.2
LPF1 (5%)	14.1	2.40	3.30	1.2
LPF2 (10%)	14	3.40	3.36	1.19
LPF3 (20%)	16.8	3.87	3.49	1.17
LPF4 (30%)	21	5.21	4.53	1.18
LPF5 (40%)	22	5.76	6.45	1.19

The hardening times of lignin-based phenolic resins at 150°C is explained in Section 5.2.8.7 (page 114). 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 the resins in particleboard production. Figure 5.4 shows the relationship between hardening time at 150°C and lignin content. The cured films were almost insoluble in acetone.

The hardening times of the PF resins (PF_com and PF_made) were found to be 3.29 minutes. It was noted that the hardening time increased, as the lignin content in the PF resin was increased. An increase of lignin content increased the hardening time from 3.30 minutes to 4.53 minutes, the hardening times of the resin LPF5 increased to 6.45 minutes with 40% added lignin. The fastest gelation rate occurred at 5% lignin content. The hardening time increased sharply after 20% lignin addition.

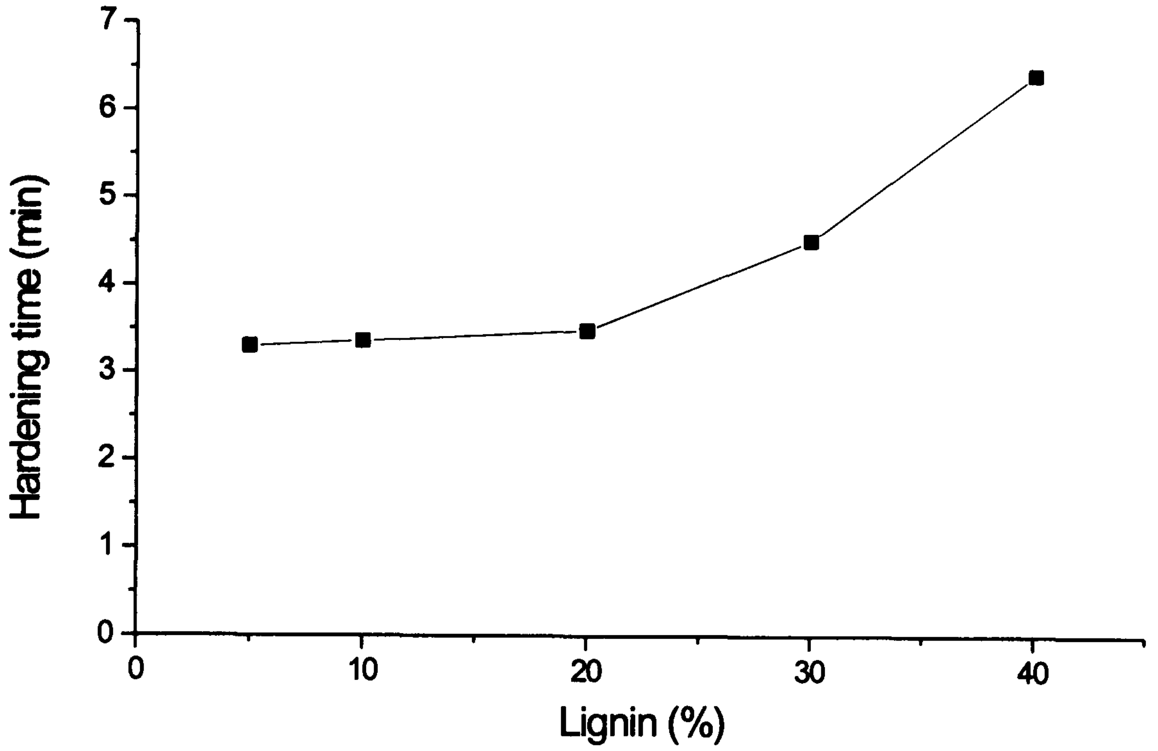


Figure 5.4 Hardening time versus lignin (%) for lignin-phenol-formaldehyde resins.

It was also noted that as lignin addition increased, so free phenol content of the final resin increased from ≈14 to 22% for the lignin resins LPF1 to LPF5, respectively (Figure 5.5).

This implies that the lignin addition competes with the phenol when reacting with the active methylol groups on the PF polymers. The methylol groups produced when phenol reacts with formaldehyde in alkaline conditions are very reactive and would react with themselves in preference to phenol. The object of this work was to use the methylol groups on the lignin to react with phenol first and then use the combination formed to react with formaldehyde/phenol. It is not surprising, therefore, that the PF resol reacts more quickly or preferentially with a compound containing methylol groups rather than phenol. Because this is the case the free phenol content is not used up in a resol where lignin has been added, as completely as it was in a simple PF resins. Figure 5.5 shows the relationship between free phenol (%) and lignin %.

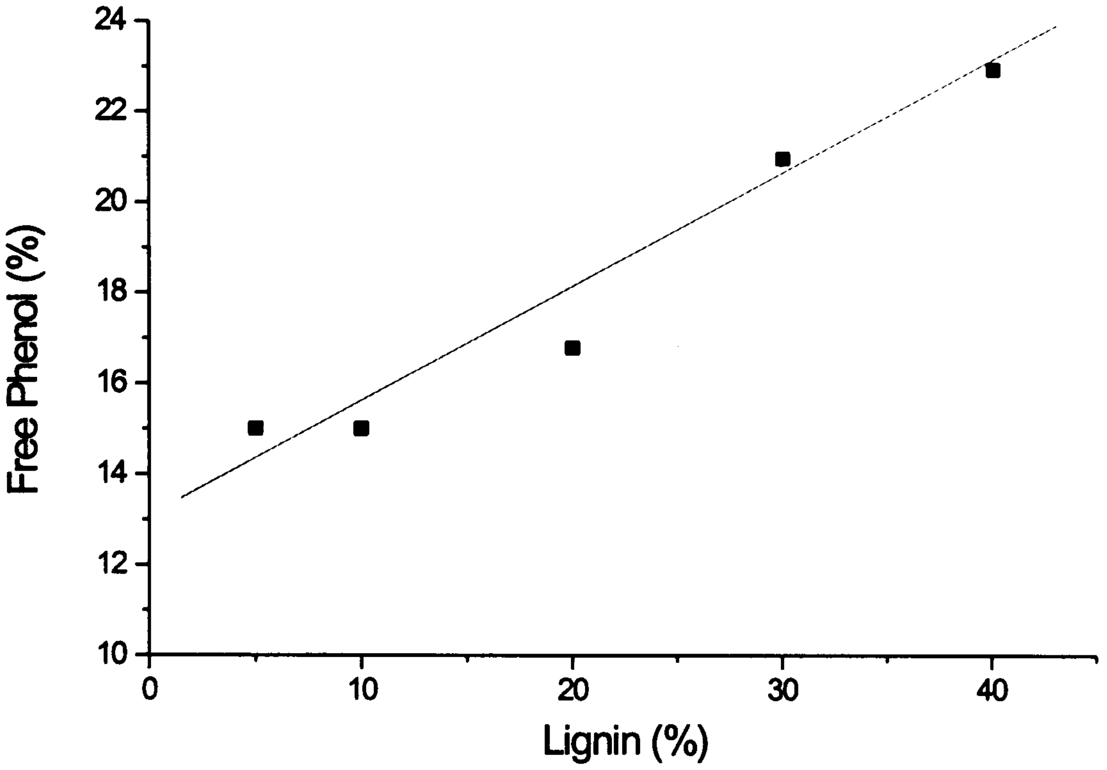


Figure 5.5 Effect of lignin % on free phenol contents of the lignin-phenol-formaldehyde resins.

5.3.3 Lignin-phenol derivative reactions

Before trying new resin formulations by modification methods, some experiments were made.

5.3.3.1 Organosolv lignin in 1-butanol

Before using phenol in the reaction, some simple data was collected.

1. Organosolv lignin (100 g) was taken and dissolved in 175 mL 1-butanol. The pH of the mixture was measured and found to be 4.2.

2. The viscosity of the lignin/1-butanol mixture was measured. As this was being determined, it was noted that the viscosity was changing. The viscosity was found to increase from ≈100 cP toward 8000 cP, on standing at room temperature.

Although the lignin initially dissolved at ambient temperature, as the solution stood, a solid started to precipitate out. When the mixture was heated to 100°C, then cooled to 25°C (to measure the viscosity), a precipitate rapidly fell out of solution.

It was hypothesised that there was a rearrangement-taking place within the molecule, and given some mobility (in solvent) either hydrogen bonding or weak chemical bonds were breaking down and re-forming. Reactive groups were then reacting with other groups on the lignin molecules to form higher molecular weight polymers.

5.3.3.2 Effect of adding phenol on the viscosity

The change in the viscosity caused by the addition of varying amounts of phenol added to the lignin/1-butanol mixture, was monitored throughout the experiments as explained in Section 5.2.3.2.

The graph of weight of added phenol versus viscosity, both with and without added oxalic acid, is shown in Figure 5.6. The lignin/1-butanol weight ratio was kept constant at 1:1.43. The phenol content was increased, as explained above in Section 5.2.3.2 (page 98).

An attempt was made to determine the maximum viscosity of the lignin in 1-butanol, without phenol being added (as explained in Section 5.3.3.1); since the viscosity appeared to increase then decrease as a solid precipitated. This was difficult to obtain, but from the results it was deduced as being ≈8000 cP but might well be much higher before precipitation of the solid.

It was noted from Figure 5.6 that the viscosity varied with differing amounts of phenol added to the lignin/1-butanol mixture. Figure 5.6 also shows that when oxalic acid (5% of the lignin weight) was added to the reaction mixture, the viscosity was lower than without oxalic acid.

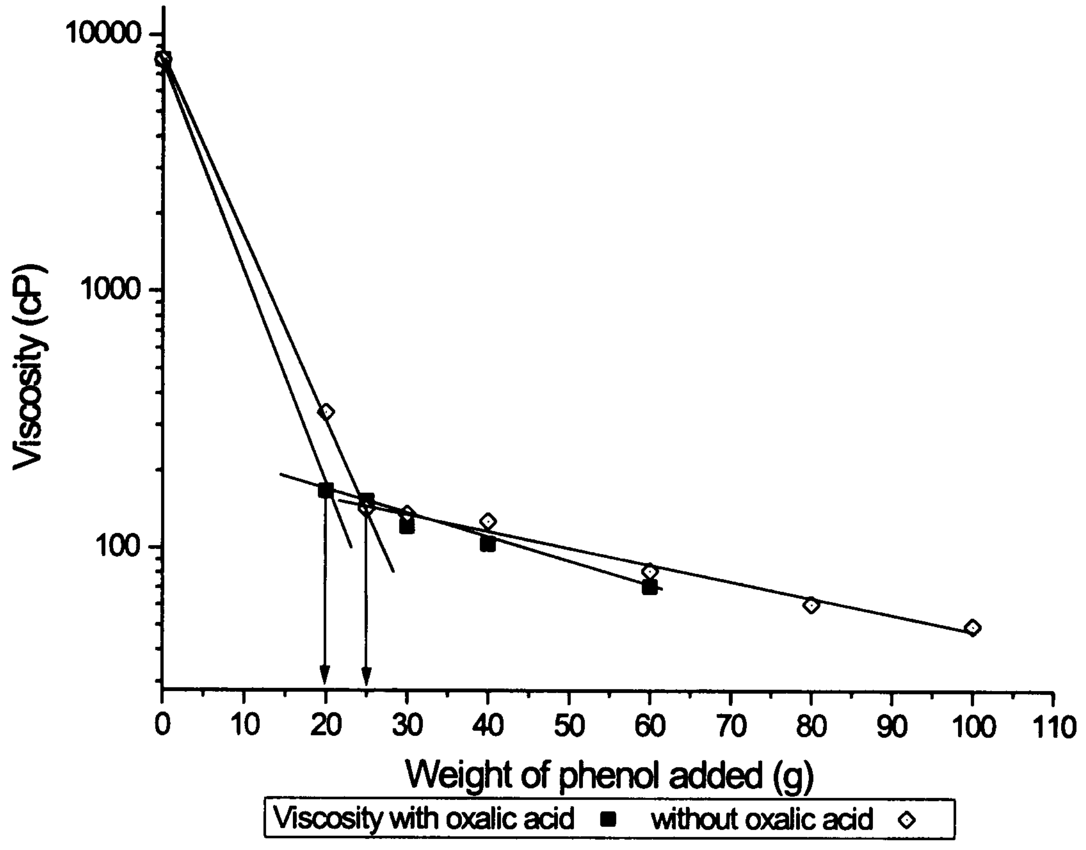


Figure 5.6 Viscosity versus weight of phenol (g) added to lignin (100 g) in 1-butanol.

The reaction between the phenol and the lignin is fast, so oxalic acid is playing an important role at low concentrations by either:

- Altering the rate of rearrangement of the lignin or,
- Altering the rate of the phenol/lignin reaction or,
- Reacting with the lignin itself.

If oxalic acid caused faster rearrangement and polymerisation of the lignin to a solid, then the viscosity of the mixture would fall. If it slowed the rate of the lignin/phenol reaction, then there would be more free phenol in the mixture, which would cause the viscosity to fall. All other scenarios would cause the viscosity to potentially rise.

A point of inflection can be seen in Figure 5.6 where, after the addition of >25 g phenol, the rate of change of the viscosity is markedly different. The percentage of the phenol between 5% to 20% gave a highly viscous product, but the product was a workable liquid after ≈20% phenol.

These results, plotted in Figure 5.6, illustrate that the phenol content has a profound effect on viscosity. It was found that if there is no phenol present in the lignin/1-butanol mixture, a solid precipitates quickly, but with phenol the material stays in solution with the viscosity falling rapidly to an inflection point (20 g phenol:100 g lignin).

The addition of oxalic acid to catalyse more reaction with phenol appeared to fail. It can be hypothesised that given some mobility in the solvent, the reactive groups on the lignin have rearranged, then slowly reacted with themselves to form higher molecular weight polymers at ambient temperatures, and faster at higher temperatures.

Since no precipitation of polymer occurs after the nodal point, it can be further hypothesised that phenol (more ionic than 1-butanol) must not merely be acting as a solvent, but must be taking part in a reaction at a faster rate than the alternative lignin intra-molecular reaction.

The reason why precipitation occurs at low concentrations of phenol may be due to the fact that there was not enough phenol present to convert all of the lignin to the L-P compound and as that a result lignin polymer is formed.

5.3.4 The reaction of lignin and phenol

Studies of the kinetics of phenol and of the first polycondensates toward formaldehyde in solution show that these methylol phenolic groups react faster with themselves or phenol than with formaldehyde (Loustalot *et al.*, 1994). In this work, the lignin (which contains an unknown number of methylol phenolic groups) was reacted with phenol. The unknown factor in the work was the rate of formation of lignin polymerisation versus lignin-phenol reaction, which would be influenced by steric hindrance, mobility of the lignin molecule (temperature and solvation might influence this) and availability of phenol.

The experimental study of the lignin-phenol reaction was explained in Section 5.2.4 (page 99). It seemed from this work, that the reaction between phenol and the organosolv lignin was fast and that the drop in free phenol content from 16% at initial addition to 10% after mixing and heating, was dramatic enough for further work to be justified done. Efforts to establish the structure of the lignin-phenol compound were unsuccessful due to the lack of equipment and financial resources.

Figure 5.7 shows the weight of phenol added to the mixture versus weight of phenol reacted with the lignin after reaction. The reaction was carried out at 100°C. It can be seen from Figure 5.7 that, for example, when 20 g of phenol (16%) was initially added into the mixture, after reaction 7.75 g (6%) was reacted with lignin. The weight of phenol reacted in the lignin/phenol/1-butanol mixture, increases with the increase in the amount of phenol added at a constant weight of lignin.

This implies that the lignin is highly reactive. Addition of 50 g of phenol affords around 30% (15 g) uptake of phenol by the lignin molecule, increasing the phenol content to 100 and 200 g still yields around a 30% uptake. This was surprising as all initial thought had been for the addition amount to plateau out as the total number of available sites on lignin were used up. This plateau was not evident within the range of this initial experimental work, which allowed Figure 5.7 to be drawn.

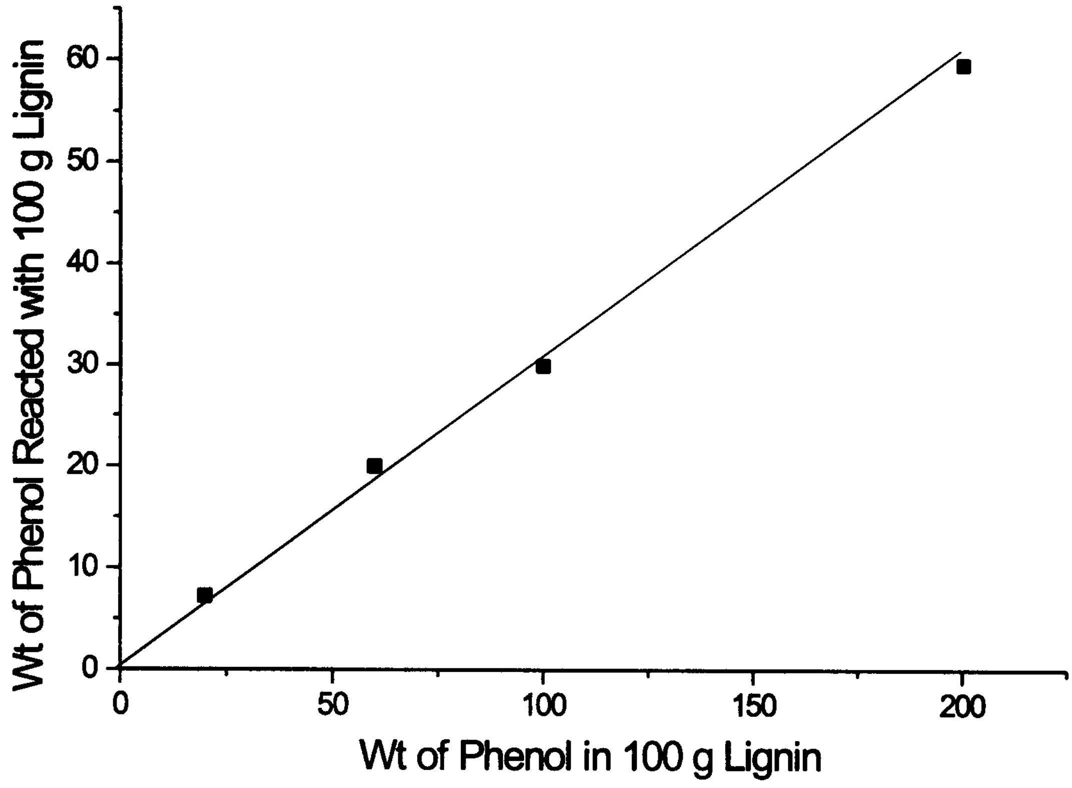


Figure 5.7 Reaction of lignin and phenol.

Initially, the consistency of the GC results was disappointingly poor, with the same sample being analysed with ±20% difference. The sample appeared to be affecting the sensitivity of the equipment, particularly where the viscosity of the sample was high. Since the samples containing <20% phenol (>80% lignin) were not in the area where resins were liable to be required, these were avoided. Where phenol rich samples were analysed, the introduction of a standard sample in the analysis procedure gave confidence in results and helped to determine when the GC required cleaning/flushing. In this way, good consistency of analysis was achieved during the investigative work with 1-butanol.

5.3.4.1 Regression analysis of data

A series of experiments were carried out at temperatures between 25°C and 100°C, where, in each case, the amount of free phenol in the reaction was determined by GC, after extraction from the reaction mixture during the reaction. The difference between the free phenol percentage and the initial percentage of phenol in the reaction vessel at time zero gave an amount of phenol that was assumed to have been added on to the lignin. The decrease in the free phenol content clearly demonstrated that reaction with lignin occurs, as the reaction proceeds.

The data generated from more than twenty experiments allowed the creation of an equation (from regression analysis) to link phenol concentration, catalyst concentration and reaction temperature. More data was produced and analysed using a regression analysis tool (LINEST, see Appendix 4 for more details).

Each result was determined at various time intervals (i.e. 30 seconds, 60 seconds, 120 seconds etc.). However, results showed only variability around an average and were deemed not related to time (after 30 seconds).

The results from the regression analysis of the data gave the series of equations shown below.

P/L mole ratio =

-0.00482 x Phenol (Weight %) content at time zero
+0.24900 x Catalyst (Weight %)
-0.00457 x Temperature (°C)
+0.00345 x (Phenol content)^2
+0.00312 x (Phenol content * Catalyst content)
-0.0006 x (Phenol content * Temperature)
-0.0278 x (Catalyst content)^2
+0.00018 x (Catalyst content * Temperature)
+0.00021 x (Temperature)^2

The P/L mole ratio was calculated using this equation by putting in the phenol content, catalyst content and temperature back into the equation and comparing it with the actual value determined by experiment.

Figure 5.8 shows the relationship between actual P/L mole ratio and calculated P/L mole ratio and gave the user confidence that the equations could be useable within the range of the experimental work. It should be remembered at this point that since the P/L mole ratio was calculated from the free phenol results, if the P/L mole ratio equation is good then the equation relating "free phenol" with the reaction parameters must also be good. Accepting this obvious fact, the equation was worked out, in case further work was required.

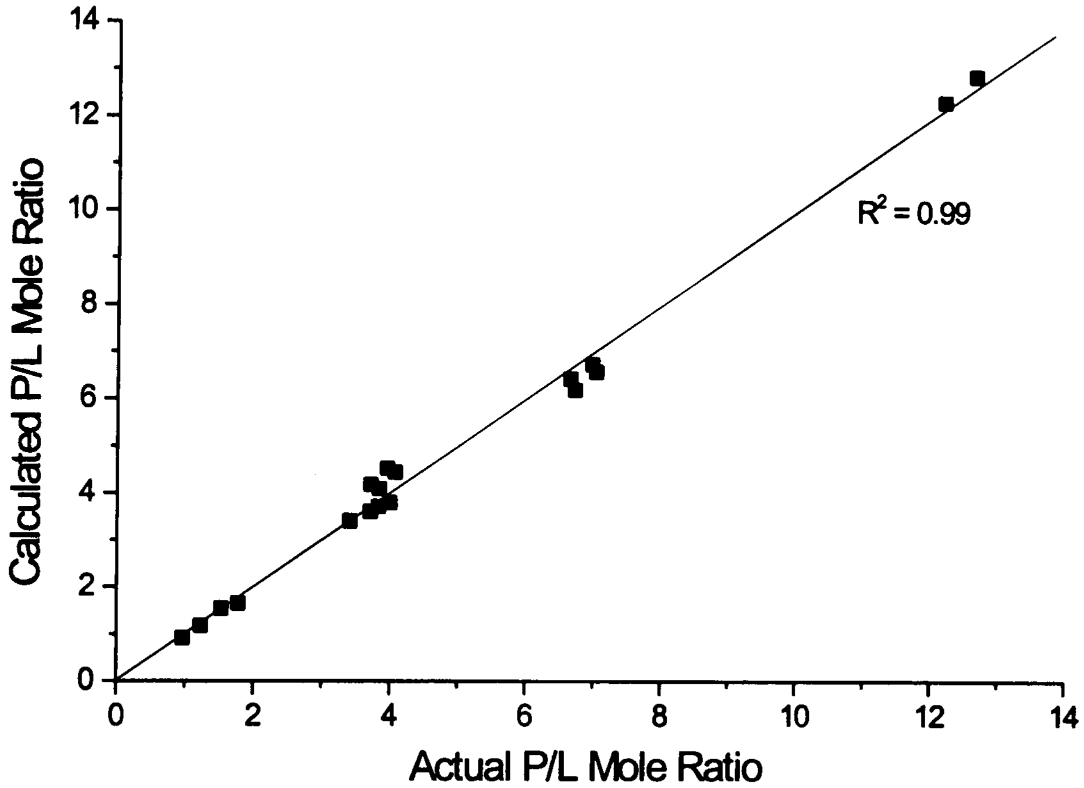


Figure 5.8 Calculated P/L mole ratio versus actual P/L mole ratio ($R^2 = 0.99$).

The regression analysis gave formulae that described the best fit of all the data. If the calculated P/L mole ratio (from the formulae) when plotted against the actual experimental results gave a scatter of results around a line drawn at 45° then the formulae would not have described the reaction variable accurately. It can be seen from Figure 5.8 that the relationship between calculated P/L mole ratio and actual P/L mole ratio appeared to be good. This implies that the formulae derived from the regression analysis describe the relationship between the variables within the range of the experimental work.

Linear regression models were found to strongly represent the observations of actual data. Regression analysis of the experimental data allows quantitative comparison of the functional relationship between the calculated free phenol and actual free phenol content. Plotting this data for calculated free phenol against the actual free phenol can be seen in Figure 5.9.

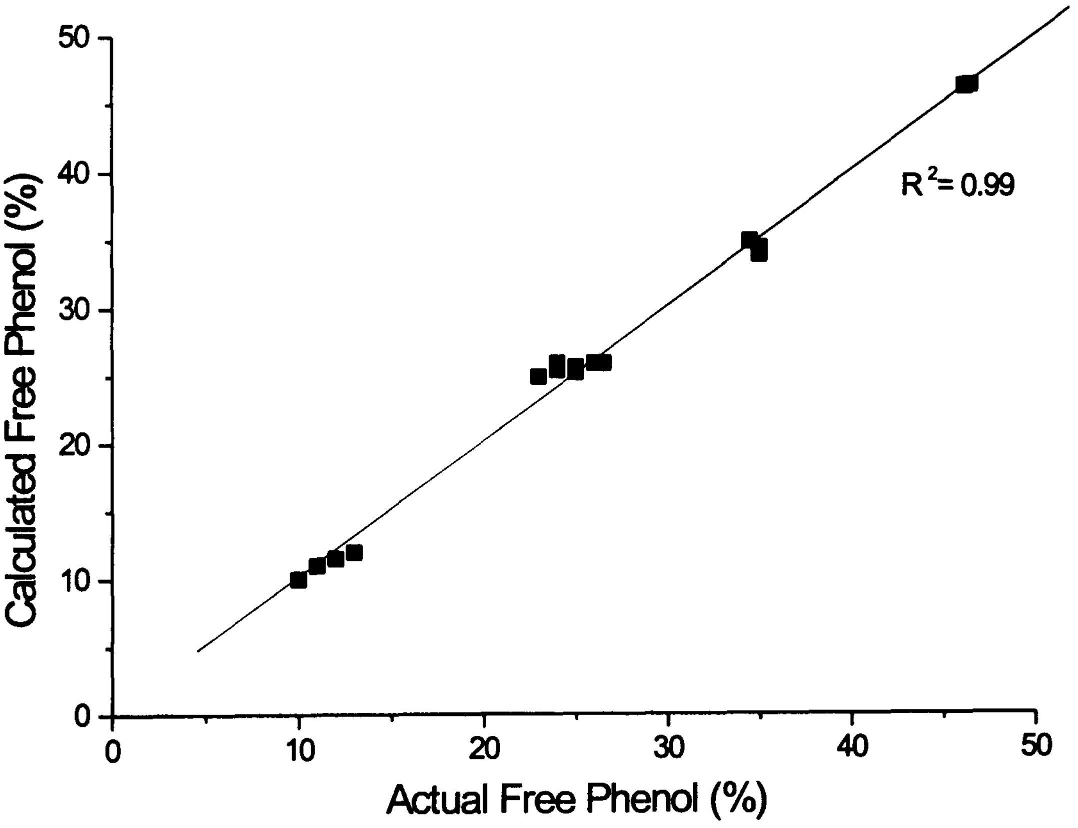


Figure 5.9 Free phenol contents calculated versus actual (R^2 = 0.99).

The regression equation, shown below, was used to determine the effect of temperature and catalyst on the reaction of phenol and the lignin as a P/L mole ratio at the various weight percentages of phenol in the combinations.

P/L mole ratio =

-0.49584 x Phenol (Weight %) content at time zero
-0.54474 x Catalyst (Weight %)
+0.113653 x Temperature (°C)
+0.001114 x (Phenol content)^2
+0.02461 x (Phenol content * Catalyst content)
+0.00124 x (Phenol content * Temperature)
+0.174072 x (Catalyst content)^2
-0.009597 x (Catalyst content * Temperature)
-0.001104 x (Temperature)^2

The regression equation was used to determine the effect of catalyst and temperature on the reaction of lignin with phenol at low concentrations of phenol (20%, 30% and 40 weight %). The results are shown in Figures 5.10 to 5.14.

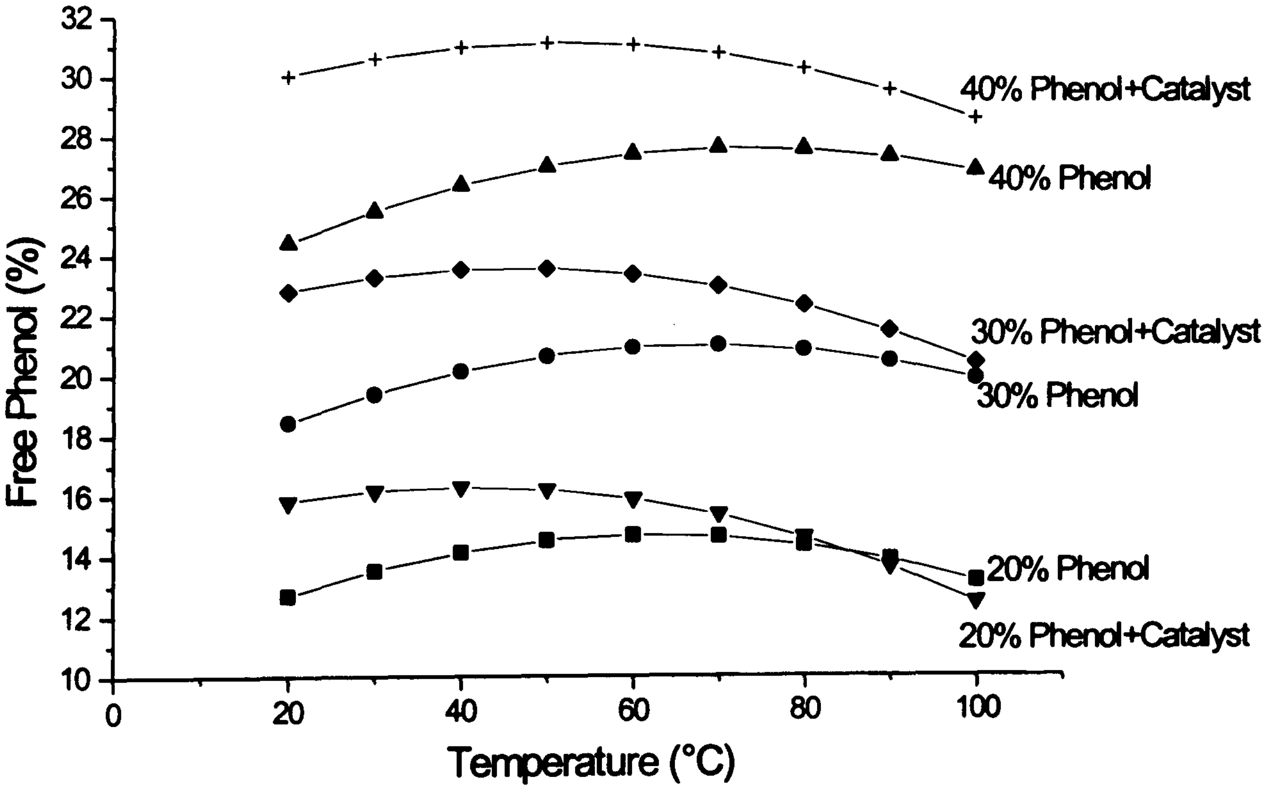


Figure 5.10 Free phenol versus temperature.

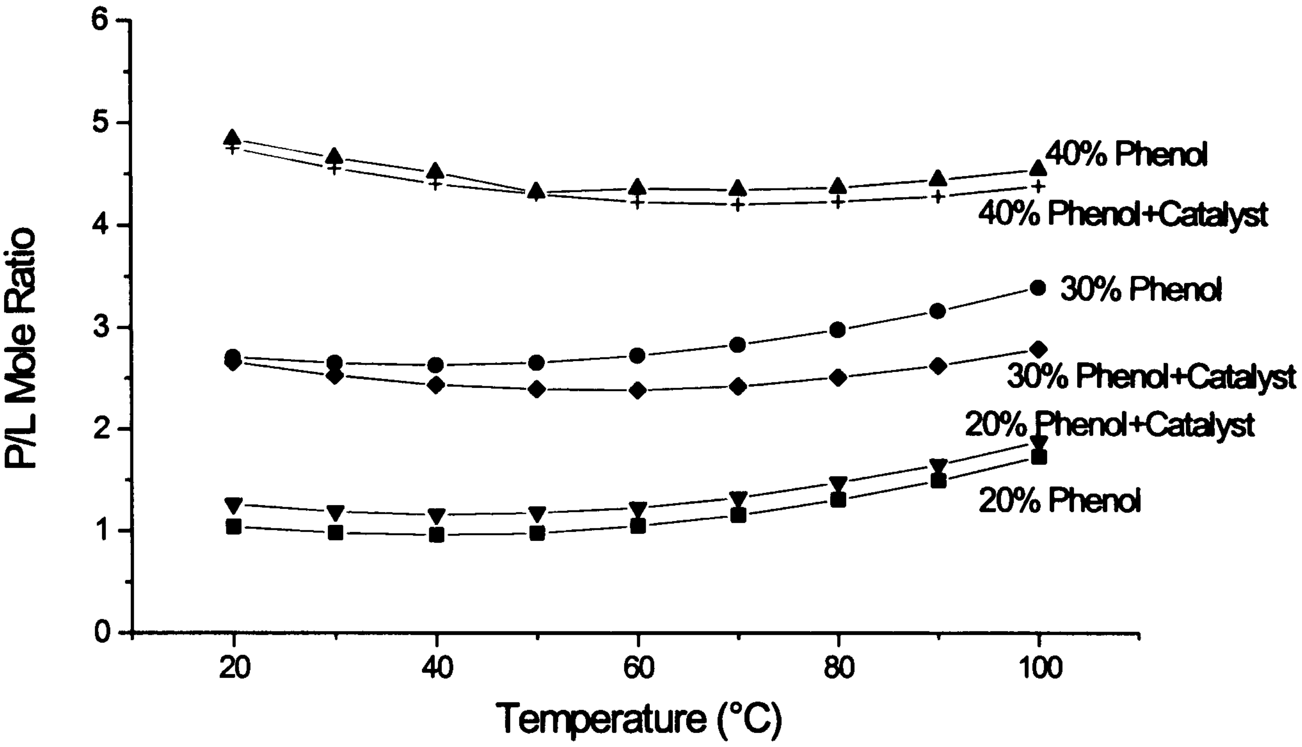


Figure 5.11 P/L mole ratio versus temperature.

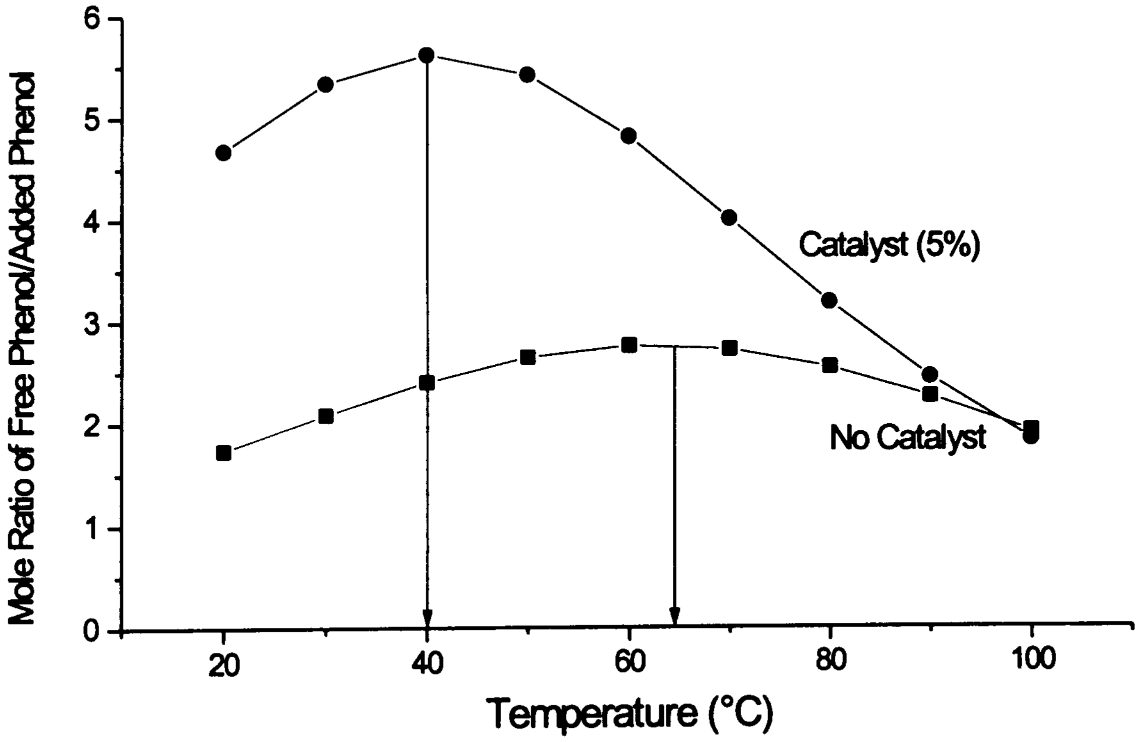


Figure 5.12 Change in ratio of free phenol:added phenol with temperature at 20 weight % phenol in mixture.

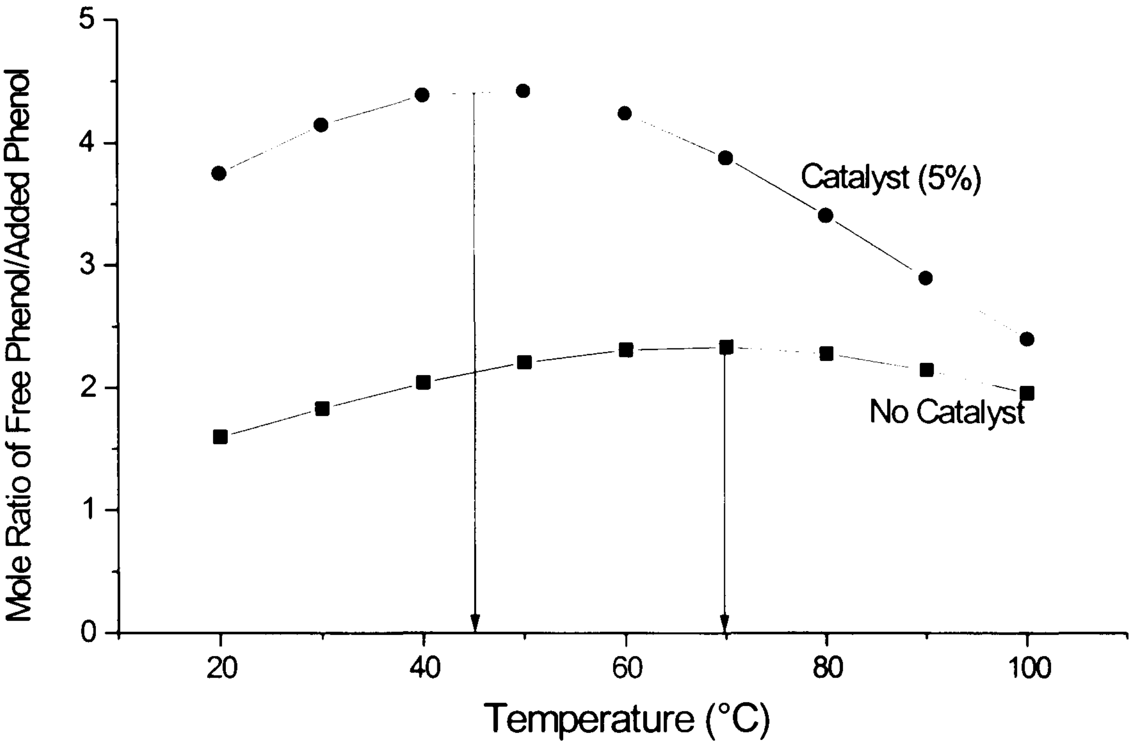


Figure 5.13 Change in ratio of free phenol:added phenol with temperature at 30 weight % phenol in mixture.

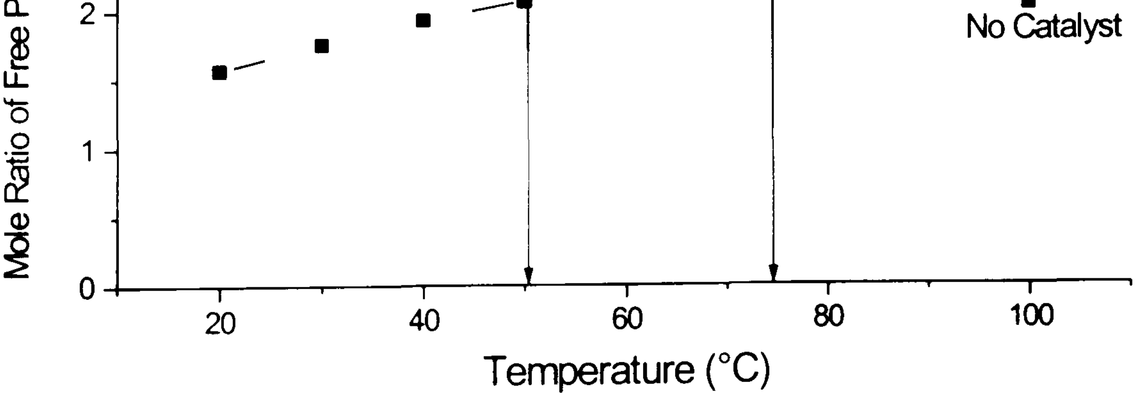


Figure 5.14 Change in ratio of free phenol:added phenol with temperature at 40 weight % phenol in mixture.

In Figures 5.12 to 5.14, the amount of free phenol was calculated from the regression analysis at temperatures between 20-100°C, using initial phenol additions to the lignin of 20, 30 and 40 wt %, respectively with and without the addition of oxalic acid. If the free phenol content is high, the phenol combined with the lignin would be small, therefore the ratio of free phenol to added phenol would increase dramatically. The Figures 5.12 to 5.14 were drawn this way to accentuate changes at these low initial phenol additions to the reaction vessel.

Increasing the temperature did not affect the mole ratio of free phenol/added phenol significantly, when oxalic acid was absent (1.5 to 2.5), but when oxalic acid was present, the ratio appeared to decrease as the temperature was increased toward 100°C (approximately 4.5 to 2). Both lines passed through a maximum (approximately 40°C with catalyst and 65°C without catalyst) and converged around 90°C.

Figures 5.12 to 5.14 illustrate the followings:

a) That the oxalic acid had a detrimental effect on the P/L mole ratio at all temperatures but more at low temperatures.

b) That temperature has little effect on the reaction over the range studied if no oxalic acid is present, although lower temperatures appear to favour the reaction (<40°C).

5.3.4.2 Determining the ratio of free phenol to phenol added to lignin

The ratio of free phenol : phenol added to the lignin was calculated for each weight percentage phenol in the initial mixture. As can be seen from Figure 5.15, the ratio is moving toward a constant 2.3:1 (2.3 free phenol to 1 added on the lignin). The temperature ranged from 25°C to 100°C.

There are four points at the 16 weight % phenol in the initial mixture and these have a wider scatter, probably due to the difficulty of analysis at low phenol levels and as shown in Figure 5.15, the effect of catalyst and temperature is more pronounced at low weight % phenol additions.

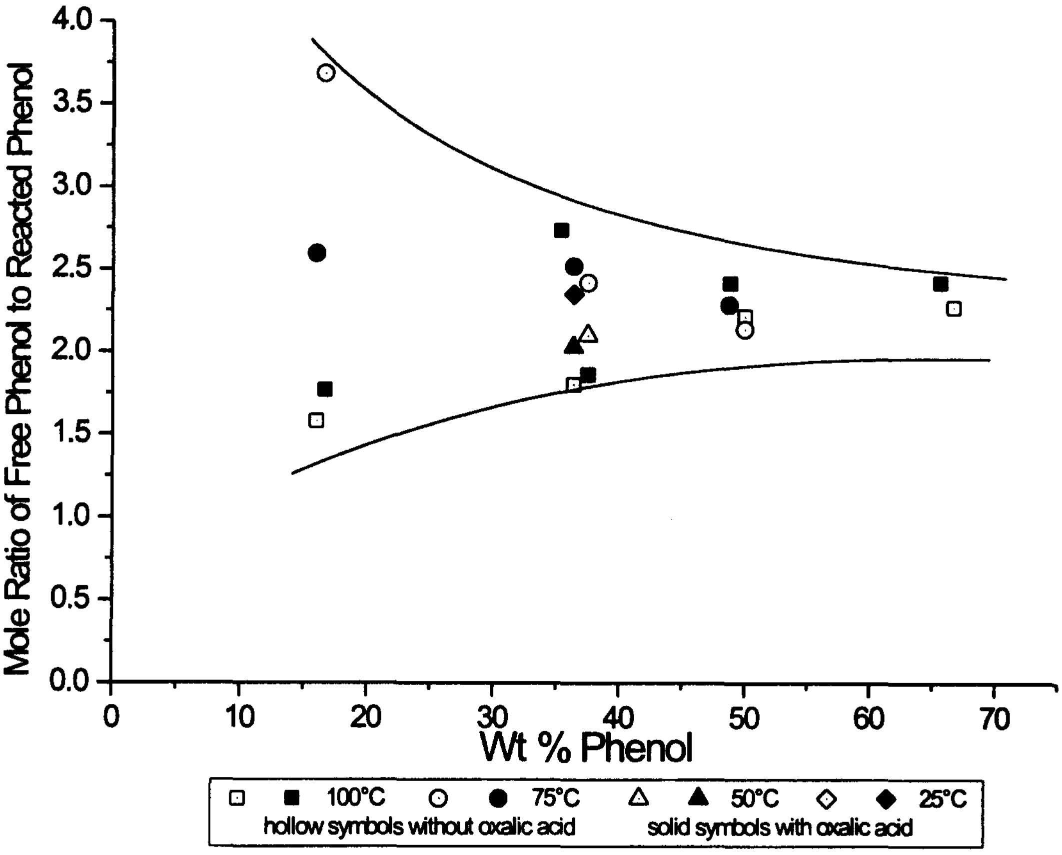


Figure 5.15 Ratio of free phenol:reacted phenol versus weight % phenol in initial mixture.

Where oxalic acid was used, results indicate again that a catalyst level above *ca.* 30% its use does not play a significant role. It would also suggest that, in the range measured, temperature does not have much effect above 30 weight % phenol.

It was assumed that as zero % phenol is approached, the lignin sites reacted with one another, because the dissolved lignin is seen to fall out of solution. As the phenol concentration increases, the formation of the P/L compound will compete with the lignin to lignin reaction. Because the lignin breakdown will occur at the same rate, it was concluded at this point that the ratio of free to added on phenol becomes constant regardless of temperature and catalyst concentration.

It might be expected that there also would be more chance of errors in the 16% experiments because of the lower numbers involved, and because of this when data was entered for the regression analysis the average results of the timed experiments were used.

The conclusion of this would be that to get the maximum addition of phenol to lignin, low temperatures and no oxalic acid should be used. The best ratio of free phenol to added on phenol is *ca.* 2.3:1.

If lignin is dissociating very slowly at low temperature, and if the addition of oxalic acid speeds up the formation of P/L bonds, then the solvent penetration of the lignin molecule may be slower. This would cause less effective dissociation of the L-L bonds and as a result fewer P/L bonds will be produced.

It can be concluded from Figure 5.15 above, that more lignin-phenol compound is produced if the breakdown of the lignin is slower (i.e. no oxalic, low temperature). It might be that as lignin breaks down, it disperses in the solvent, and creates active sites (or exposes active sites) before these sites can react with one another. This is contrary to the literature view (Ono and Sudo, 1989; Van der Klashorst, 1989) that the use of acid in the experiments was thought desirable, because it was supposed to assist in the breakdown of the lignin molecule.

5.3.5 The determinations of potential variables in lignin-phenol reactions

5.3.5.1 Use of alkali as catalyst (or the effect of pH on the reaction mechanism)

As before (Section 5.3.4.1) the P/L mole ratio and free phenol in the mixture after reaction was determined and compared with the data used for the regression analysis.

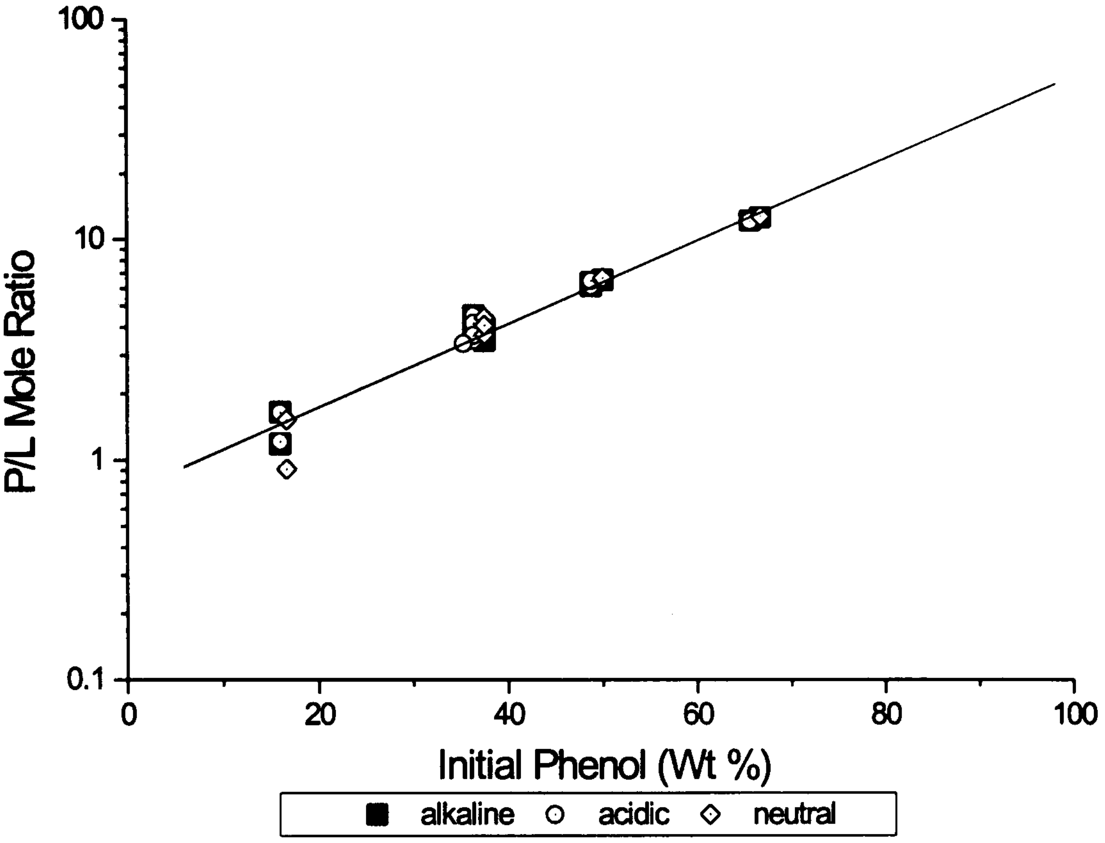


Figure 5.16 Regression analysis data plus P/L mole ratio of alkali, acidic and neutral tests.

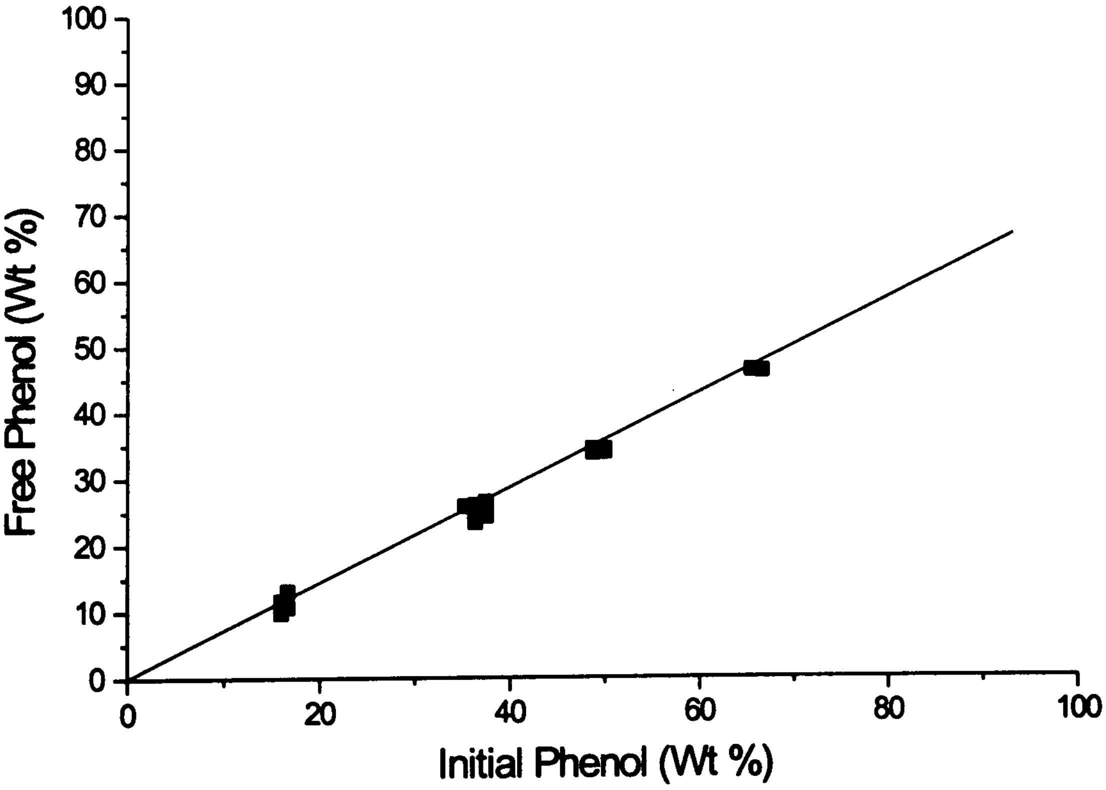


Figure 5.17 Regression analysis data plus free phenol under alkali condition.

Figures 5.16 shows the regression graphs of the alkali, acidic and neutral tests. Clearly, therefore, the addition of phenol to the lignin can occur to the same extent under neutral, acid or alkaline conditions. Figure 5.17 shows the regression analysis data for free phenol under alkali tests conditions.

5.3.5.2 Effect of solvent on P/L mole ratio

A regression analysis of this data was carried out in the same manner, as before i.e. the phenol and lignin weight % was solvent free. This data fit was not as good as those derived previously in Figure 5.8 but the scatter of points in the Figure 5.18 have been overlaid with

a) boxes (results from 350 mL 1-butanol in lignin at 100°C)
b) triangles (results from 175 mL 1-butanol in lignin at 100°C)
c) diamonds (results from no addition of 1-butanol).

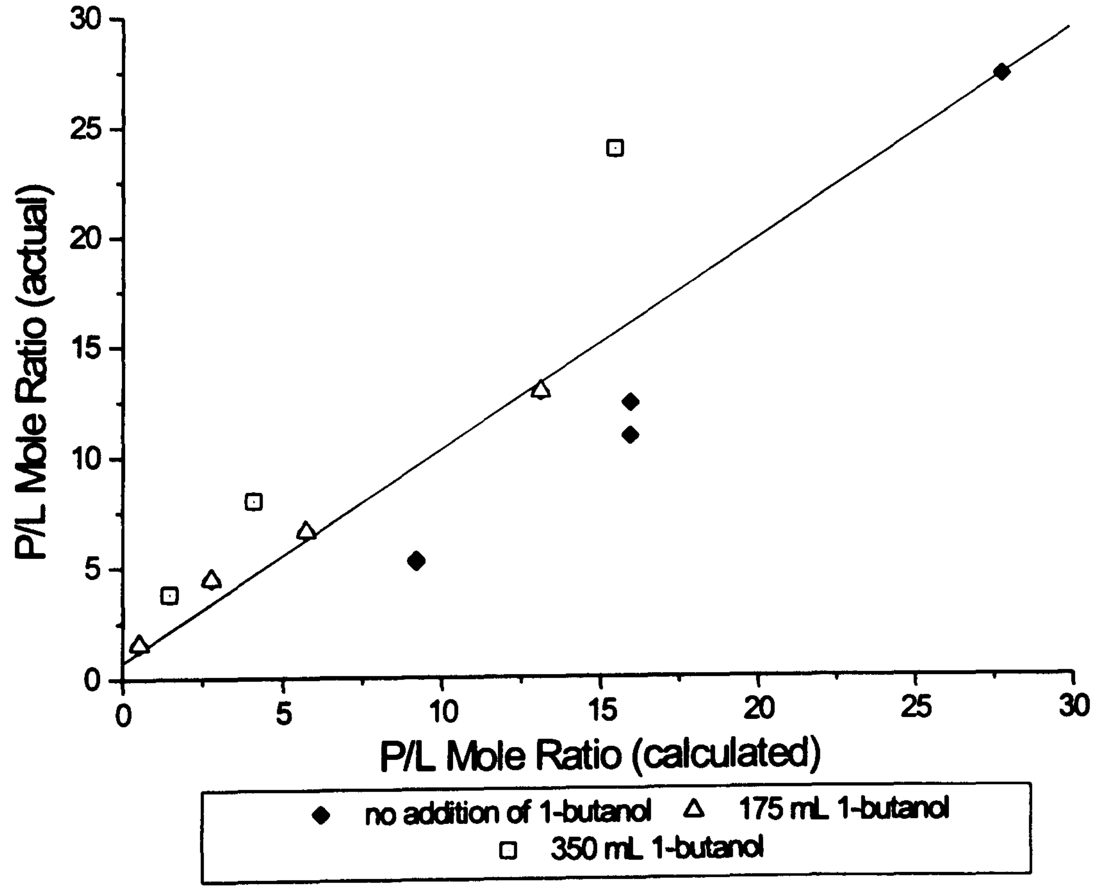


Figure 5.18 Regression analysis of solvent/ no solvent experiments ($R^2 = 0.84$).

There is an indication that there is an increase in P/L mole ratio, as the solvent addition is increased. The regression analysis was rerun with solvent added to the list of variables. The plot derived is shown in Figure 5.19. This gave a better correlation than that achieved in Figure 5.18.

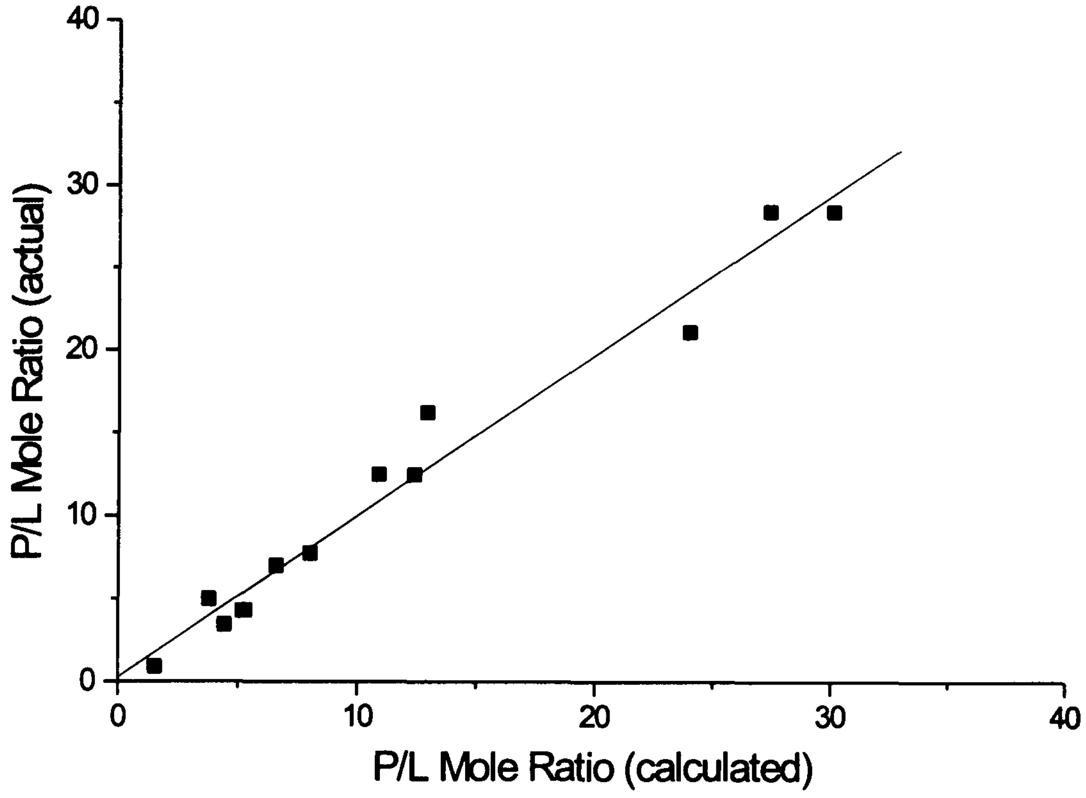


Figure 5.19 Regression analysis where solvent is included as a variable ($R^2 = 0.97$).

To determine the effect of solvent, the P/L mole ratios were derived from the regression analysis for solvent/lignin ratios from 0 to 3:1 at different weight % phenol and the data was plotted in Figure 5.20.

As expected, all the lines converge as 100% phenol is approached. One reason that ties in with the earlier work might be the solvation of the lignin. Figure 5.20 shows that the lignin precipitates out, when the P/L mole ratio is at 30% phenol and no solvent. It was seen from (Figure 5.6, page 120) that the viscosity was high until 20% phenol added. But 1-butanol was added to the lignin. So the above clearly justifies the use of a solvent in the mixture.

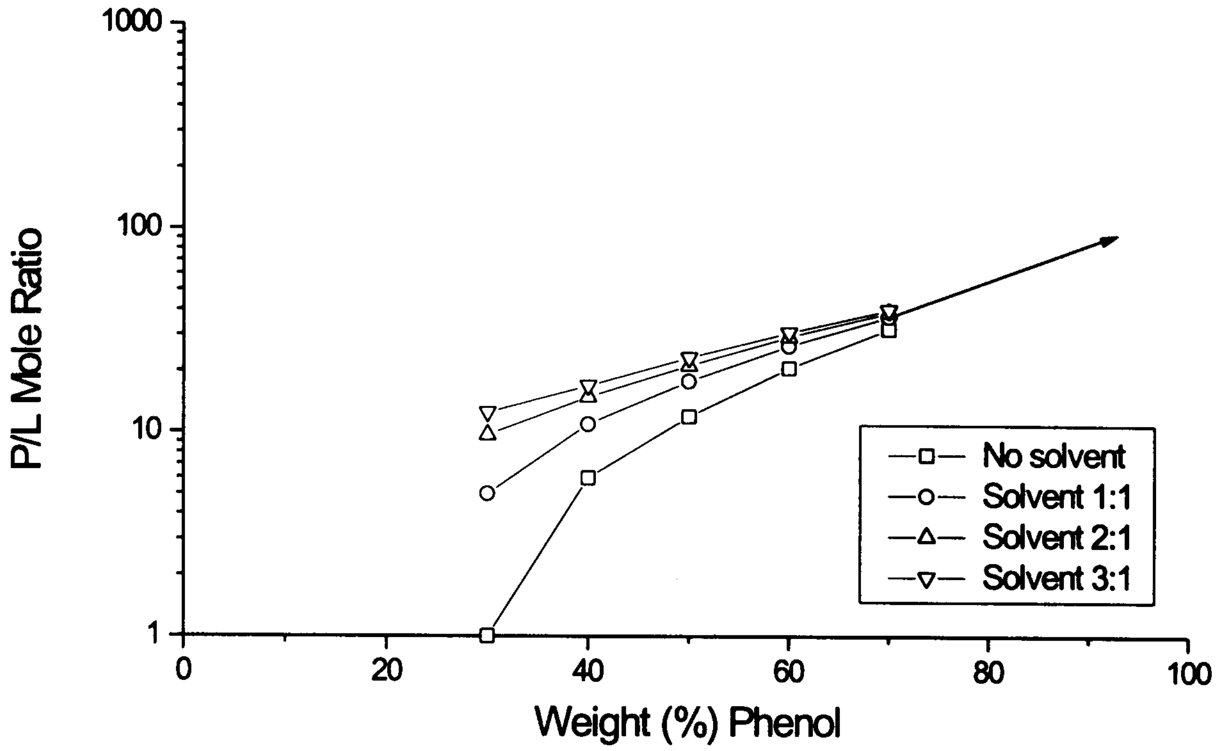


Figure 5.20 Effect of solvent:lignin weight ratio on P/L mole ratio.

If, for example, the 50 weight % phenol line is considered, and assuming 100 g of lignin then, Table 5.8 can be constructed for different solvent : lignin weight ratios.

Table 5.8 Effect of solvent:lignin weight ratio on P/L mole ratio.

P/L Mole Ratio	Solvent weight (g)	Phenol weight (g)	Phenol weight % in mixture
12	Nil	100	50
18	100 (i.e. 1S:1L)	200	50
22	200 (i.e. 2S:1L)	300	50
24	300 (i.e. 3S:1L)	400	50

By repeating the above Table 5.8 with 30 and 70 weight % phenol and plotting the results, Figure 5.21 was constructed.

Figure 5.21 shows that the addition of solvent helps to increase the P/L mole ratio at all levels of phenol concentrations. However, if there is no requirement for high P/L mole ratios then 1-butanol need not be used to solvate the lignin. Phenol will act as the solvent for the lignin.

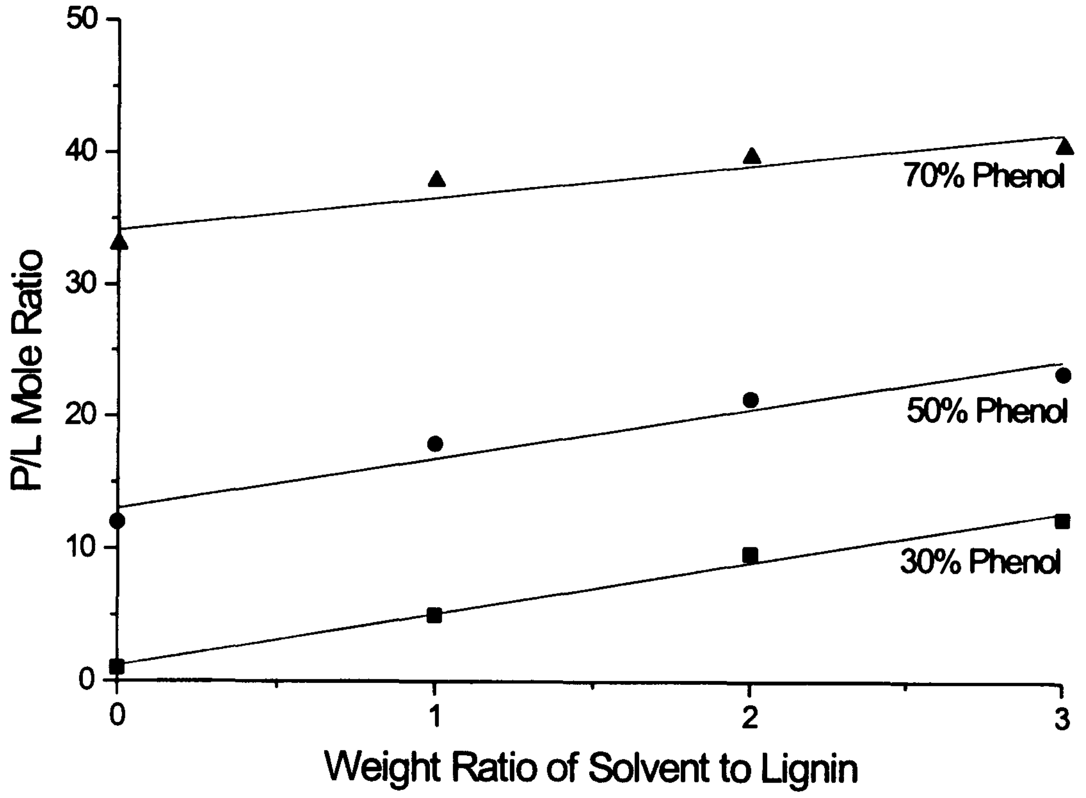


Figure 5.21 Effect of solvent on P/L mole ratio.

5.3.5.3 The maximum possible P/L mole ratio

The maximum possible P/L mole ratio was determined. From the early data produced and used in the regression analysis of P/L mole ratio versus phenol (weight %) added, Figure 5.22 was constructed. To check the validity of the graph, two further points were determined which were not included in the regression analysis data and added after the construction of the graph. These points are given in Table 5.9.

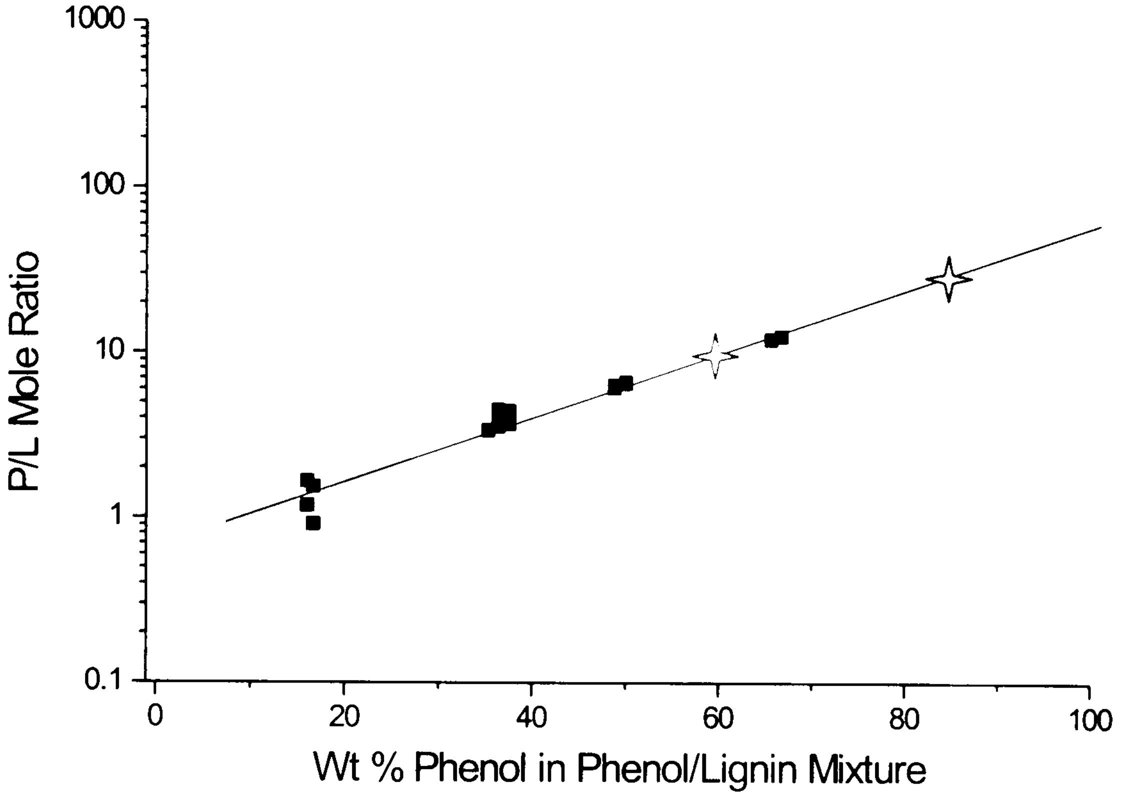


Figure 5.22 Maximum potential P/L mole ratio for lignin – stars showing the "check on validity".

Table 5.9 Additional determinations of P/L ratio to check validity of data

Weight % Phenol Added to lignin	P/L Mole Ratio
56	8
82	27

Figure 5.22 shows that the maximum potential P/L mole ratio, in the used of 1-butanol was ≈70 for this lignin. A number of trials were conducted with no solvent, which gave the results shown in Table 5.10.

Table 5.10 Experimental results using no solvent

Phenol Weight %	P/L Mole Ratio
37.5	5.2
50	12.4
66.6	30.1
37.5	5.3
50	10.9
66.6	27.4

From this data, Figure 5.23 was constructed showing that the maximum P/L mole ratio would approach 200 for this lignin, if solvent were not used. Reducing the molar concentration of phenol in the mixture by using solvent therefore reduces the maximum potential P/L mole ratio.

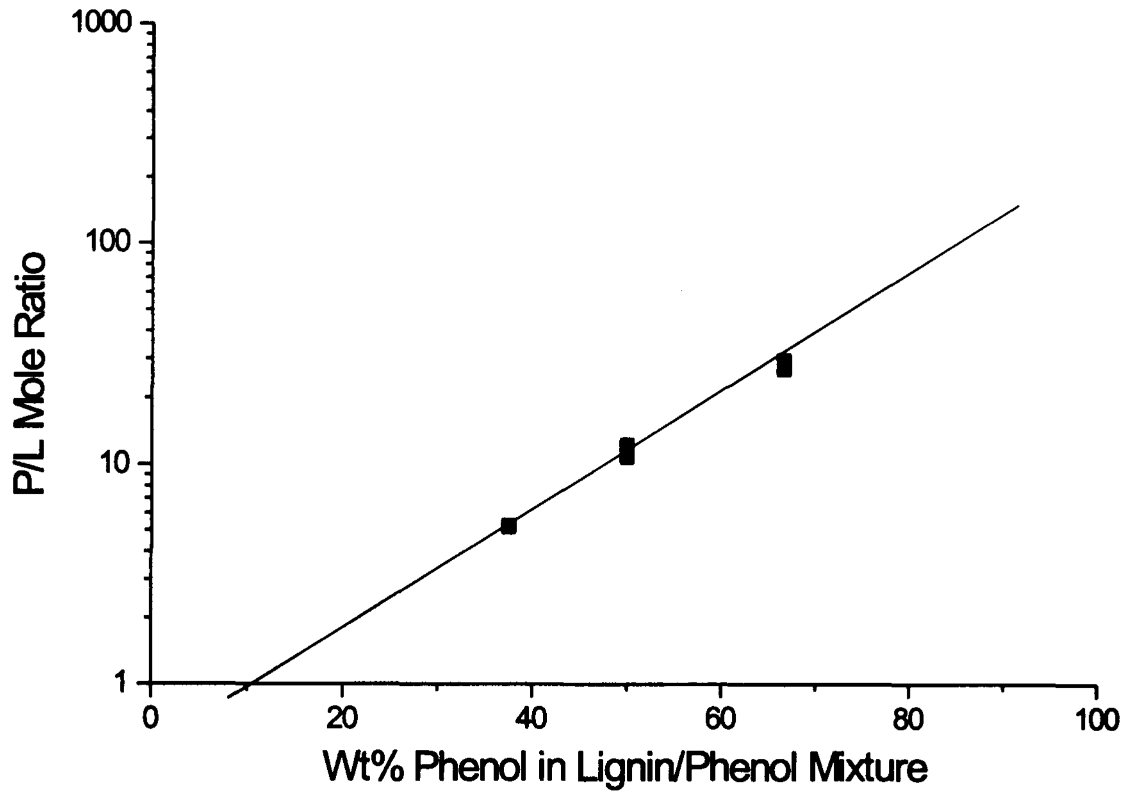


Figure 5.23 The maximum potential P/L ratio without solvent.

Figure 5.23 shows the P/L mole ratio falling to ≈1 at 10% phenol and no solvent. When the viscosity versus the amount of phenol added, was plotted (Figure 5.6, Section 5.3.3.2, page 119), the viscosity was high until ≈20% phenol but in this case 1-butanol was added to the lignin. Clearly there was not enough solvation of the lignin from 1-butanol and phenol at these low concentrations, which caused the errors in the analysis at the beginning of the work and led to the constant use of solvent in the work subsequent to it.

5.3.5.4 Effect on P/L mole ratio on the addition of extra phenol to lignin-phenol mixture

The results, for the effect on P/L mole ratio on the addition of extra phenol to lignin-phenol mixture, are shown in Table 5.11 and illustrated as stars in Figure 5.24.

Table 5.11 Effect on P/L mole ratio on the addition of extra phenol to lignin-phenol mixture

Weight % Phenol	P/L Mole Ratio
38	5
38 increased to 55	22
55 increased to 64	36

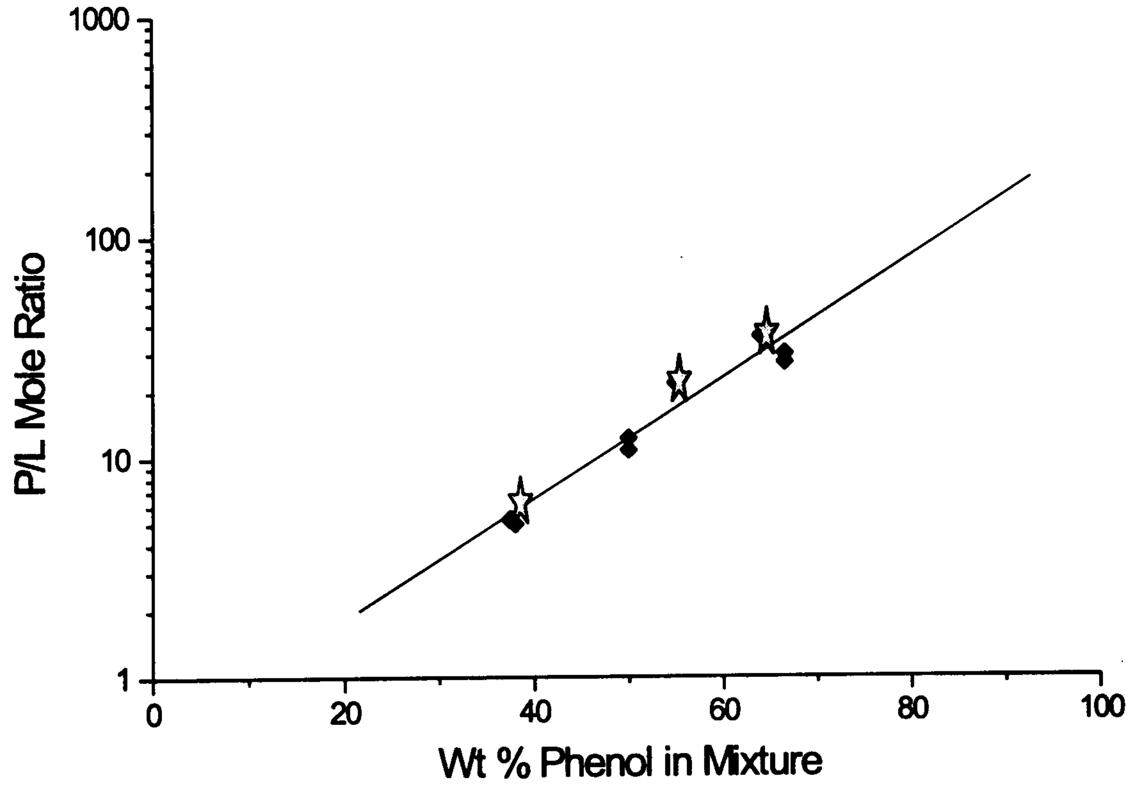


Figure 5.24 Effect on P/L mole ratio on the addition of extra phenol to lignin/phenol mixture.

The results show that if more phenol is added to a phenol/lignin mixture the P/L mole ratio will increase and the increase appears to agree with the P/L mole ratio that would have been obtained if the total phenol added had been added initially.

This gives a problem with the competing reaction argument (i.e. lignin reacting with lignin) which was put forward to account for the observation that when lignin was dissolved in 1-butanol, then it precipitated out of solution on standing. It should also be remembered that on addition of phenol to the lignin/1-butanol mixture the viscosity fell quickly until at >20 wt % addition of phenol and it remained <150 cP without signs of any precipitation. It is also true to say that it is not known if removal of phenol from the mixture decreased the phenol/lignin mole ratio since when conducting that experiment the viscosity of the product increased markedly making analysis of the material very difficult.

5.3.5.5 Effect of water on the P/L mole ratio

The results are shown in Table 5.12.

Table 5.12 Effect of water on the P/L mole ratio

Water Weight % in Mixture	P/L Mole Ratio
0	13
10	7
20	7

Without water, the P/L mole ratio (13) agrees with the data used in the regression analysis. The addition of water dropped the P/L mole ratio by approximately 50%. This segment of the work should be investigated further, as some anomalies occurred in the results. However, the trend in all cases was that the P/L mole ratio was decreased when water was present.

5.3.6 Phenolated-lignin-formaldehyde resins

Lignin was easily introduced into the resin preparation and no difficulties were experienced. In order to distinguish and clarify the characteristics of the phenolated-lignin-formaldehyde resins studied in this chapter, it is necessary to compare certain important properties with those of the other similar resins.

Phenolated-lignin-formaldehyde resins were made, as explained in Section 5.2.6.2. The resulting resins were characterised for their free phenol, free formaldehyde, hardening time and specific gravity. The physical characteristics of these phenolated-lignin-formaldehyde resins are summarised in Table 5.13.

Table 5.13 Physical properties of the phenolated-lignin-formaldehyde resins

Resins	Free Phenol (%)	Free Formaldehyde (%)	Hardening time (min, at 150°C)	Specific Gravity
Resin LPF 10A	19.8	4.63	8.30	1.17
Resin LPF 10B	21.7	0.98	10.50	1.18
Resin LPF 20A	7.3	1.33	6.29	1.16
Resin LPF 20B	4.7	0.17	6	1.17
Resin LPF 30A	4.3	3.15	6.10	1.18
Resin LPF 30B	8.9	2.20	6.15	1.18
Resin LPF 40A	9.4	0.77	1.30	1.18
Resin LPF 50A	8.2	0.86	1.35	1.19
Resin LPF 60A	6.4	0.92	1.56	1.17
Resin LPF 70A	11.2	0.77	2.48	1.19

As can be seen from Table 5.13, LPF 10A, LPF 10B and LPF 70A had an high free phenol content, which might be because there was not enough formaldehyde solution to promote the condensation reaction of the resin LPF 70A. Table 5.13 also shows the free formaldehyde 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 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.

The reaction was stopped at a desired viscosity. It was thought that there might be two scenarios in the final product that would result, based on addition of formaldehyde. If the theoretical amount of formaldehyde added was:

- Too high - then formaldehyde being in excess would appear as free formaldehyde in the final product which is undesirable and without reacting would increase the hardening time; or
- Too low - then there might be low cross linkage of phenol-phenol or P/L to phenol, which would show up in analysis as a high free phenol content. However, some free phenol might be desirable in the wood glue since it helps to create exothermic reactions with the methylolated species, when heated during board pressing (Lightbody, 1999).

5.4 CONCLUSIONS

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 in particleboard production. 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 in the resin formulations.

It was concluded that all the lignin used could be phenolated in acid, neutral or basic conditions to form a lignin-phenol combination. The amount of phenol that reacted with the lignin depends on the concentration of phenol present in the initial mixture. Below 20 weight % phenol, the resultant combination is highly viscous. At ≈20-25 weight % phenol the viscosity of the mixture of lignin-phenol plus free phenol passed through an inflection point and became easy to manage. Solvent can be used to improve the P/L mole ratio where small quantities of phenol need to be added. The solvent should be added with the phenol. There was evidence of solvation then precipitation when solvent was added to lignin on its own. It was found that increasing water content would decrease the formation of lignin-phenol combination. It was shown that the use of oxalic acid did not help to increase the P/L mole ratio but hindered it at low temperatures.

According to these results, further phenolated-lignin-formaldehyde resin formulations were made. The physical analysis of these resins such as hardening time, indicated that the resins (LPF 40A, LPF 50A and LPF 60A) had good curing properties, if compared to the properties of initial LPF resins.

Chapter 6 presents studies on the bonding properties of all the resins synthesised earlier.

CHAPTER 6
BOND STRENGTH OF RESINS

6.1 INTRODUCTION

Adhesive bonding is often regarded as the most versatile means for the joining of materials in production assembly and is ideally suited for applications requiring the attachment of dissimilar materials, thin films and delicate components and the fabrication of lightweight sandwich constructions (Epstein, 1984).

It is clear that bond strength development plays an important role in the process and its prediction is necessary for process optimisation. It is also clear, however, that there are many factors which together influence bond strength development, but not every factor plays an equally important role. The main factors influencing PF adhesive properties when related to bonding behaviour include: percentage solid content in liquid resin, pH of resin, molar ratio of phenol to formaldehyde, catalyst type and reactivity, fillers and extenders (Ren, 1988).

The adhesive is generally transformed from liquid to solid during the bonding process. This may occur by solvent evaporation or chemical reaction (polymerisation). As the adhesive hardens, stresses may develop, due to shrinkage resulting from the evaporation of solvents, or other volatiles contained in the adhesive or produced during the curing process (Epstein, 1984). Chemical reaction during hardening, as is the case in many adhesives such as phenolics, produces a molecular volumetric shrinkage.

In this chapter, the adhesion quality of PF and lignin-based PF resins was investigated. A preliminary attempt was made to predict bonding as processing proceeds during the production of particleboard. This data is only included to demonstrate the concept of relating characteristics of failure stress to forming conditions.

As seen in Chapter 5, various formulations were used in the production of LPF resins. For this reason, it was necessary to eliminate some of the poor quality resins prior to particleboard manufacture. The tests presented in this chapter were designed to investigate the bonding strength properties of lignin-based phenolic resins.

Lap shear tests using the ABES (automatic bonding evaluation system) apparatus were used in order to examine:

1) Effect of press temperature on the development of bond strength of the experimental resins.

2) Effect of press cycle time on the development of bond strength of the experimental resins.

6.2 MATERIALS AND METHODS

An experiment was designed to study the rates of bond formation under a range of time and temperature conditions. Initially, the temperature was held constant and the rate of bond formation measured over a period of time. The time was then held constant and the bonds formed were tested similarly over a range of temperatures. The effects of both temperature and time on bonding rates were then studied in this way. The experiment was specially designed to provide data, which would be used in the production of particleboards.

The bonding ability of the resins was examined in a lap joint test using an automatic bonding evaluation system (ABES) tensile tester (Figures 6.1 and 6.2). This equipment is designed to enable the bond strength development characteristics of a

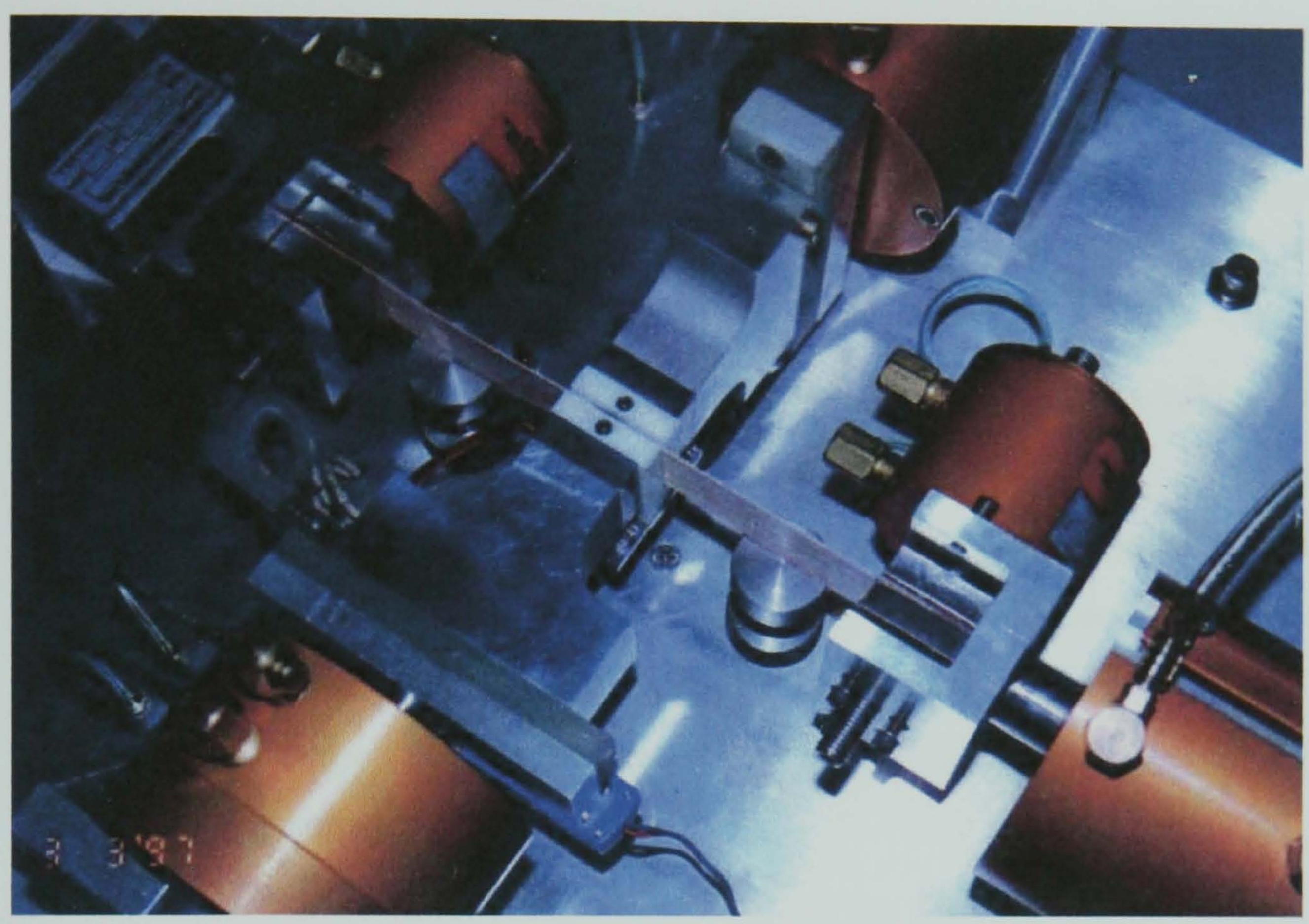


Figure 6.1 The test unit of ABES.

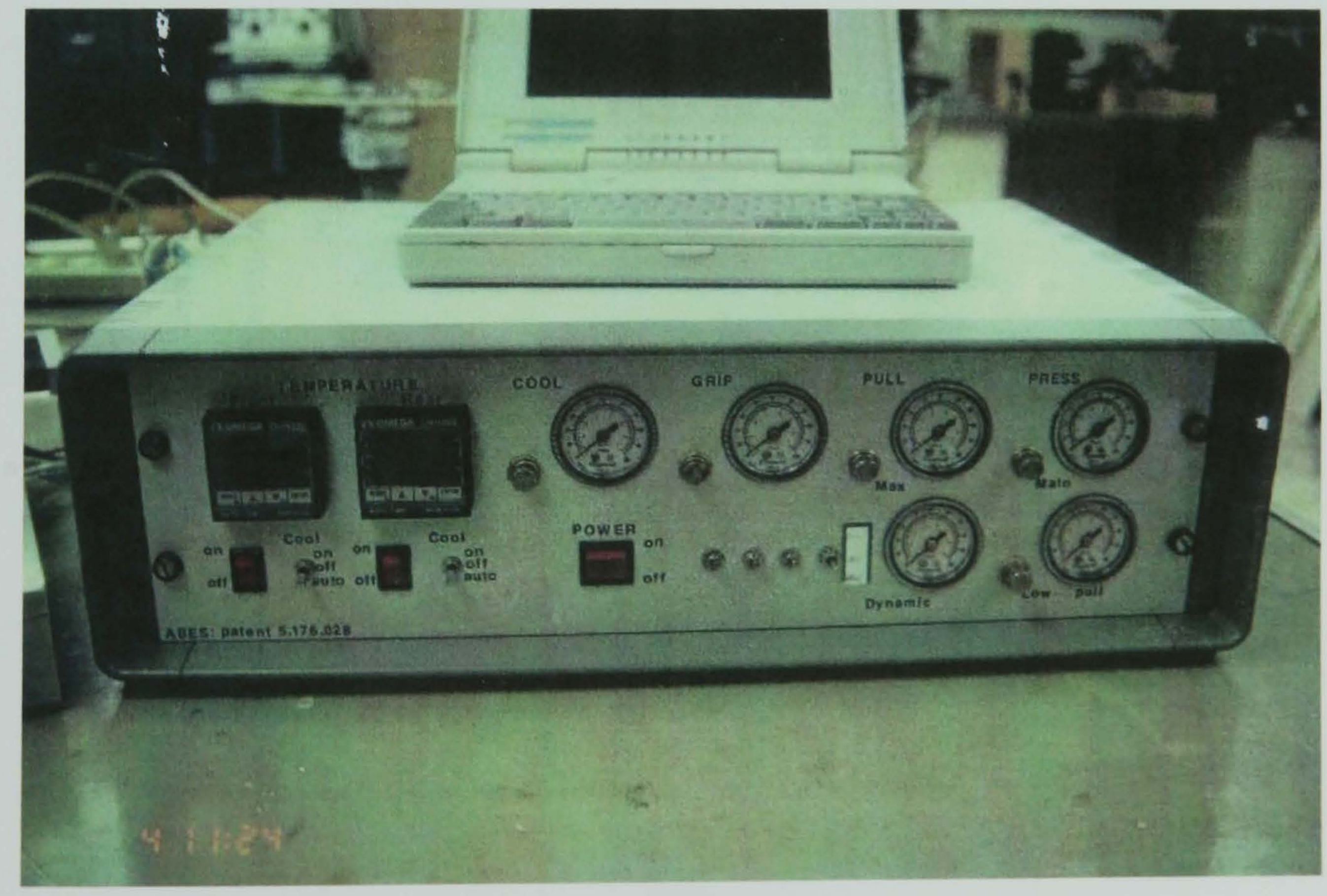


Figure 6.2 The control unit of ABES.

diverse range of adhesives to be explored, while varying the parameters. Such information enables the compatibility of adhesives for industrial manufacturing processes to be evaluated prior to expensive sample preparation, manufacture and testing.

For this purpose, relatively thin (heat diffusive) adherent birch veneer (wood strips) of thickness of 0.8 mm, cut into 104 mm (longitudinal) x 20 mm pieces were used. Resin was applied to an area of 4 mm x 20 mm on one side of one end section of the two pieces (Figure 6.3). Resin coated, over-lapped end sections of a series of specimens (pair of strips) were pressed together in a hydraulic press at a pressure of 5 kg/cm^2 using a range of curing periods at each of five temperatures (ranging from 140°C to 180°C with 10°C intervals).

Chow *et al.* (1975) and Irle (1986), recommended that PF resins should be heated in the region of 145 to 170°C to obtain complete cure. Therefore, the platen temperature was chosen to cure the strips within these limits. This temperature not only accomplished the requirements for full cure but also closely matched the conditions in which the particleboards were made, as described in Chapter 7.

At the end of the selected curing period, and while still hot, each bond was rapidly (within seconds) cooled and tested to failure in tension. For each bond forming condition (temperature and pressing time), five replicates were conducted. A graph of collected failure stress versus pressing time, could then be plotted against the temperature in question.

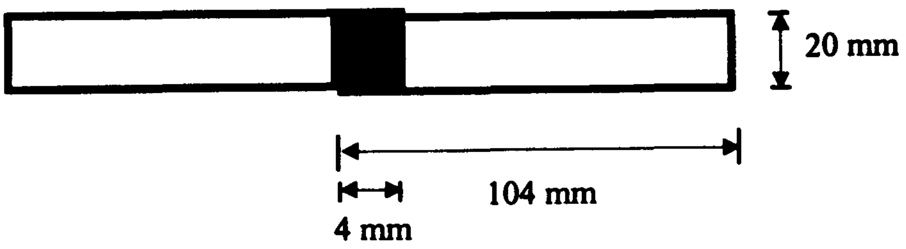


Figure 6.3 Lap-joint specimen.

The codes and the percentage lignin substitution levels of the resins used in the lap joint experiments are shown in Table 6.1.

Table 6.1 Codes and % lignin substitution levels of the resins used in a lap joint test

	Codes								
Lignin Substitution (%)	PF_com	PF_made	LPF1	LPF2	LPF3	LPF4	LPF5	LPF 10A	LPF 10B
	0	0	5	10	20	30	40	30	30
	LPF 20A	LPF 20B	LPF 30A	LPF 30B	LPF 40A	LPF 50A	LPF 60A	LPF 70A	
	60	50	50	40	20	25	30	25	

For more detailed information about the experimental resins see Appendix 2.

6.3 RESULTS AND DISCUSSION

The rates at which resin test bonds develop strength under controlled conditions were not of primary concern in this project. However, the influence that temperature and time have on the final strength of bonds, has been reviewed. This review gave some information about the failure stress as a glueability criterion. However, it was pointed out by Ren (1988) that failure stress measured in bond formation might not always be a reliable indicator of ultimate bonding quality in particleboard manufacture.

The bond forming and testing procedure for a diversity of pressing times (while holding temperature constant) were repeated for the resins manufactured, as described in Chapter 5. In this way, isothermal bond strength accumulation obtained with time was plotted. Repeating this procedure for a number of different pressing temperatures enabled a range of isothermal bond strength accumulation plots to be constructed. This allowed the reactivity of bonding systems (effect of temperature on rates of isothermal bond strength development) to be examined.

The value for each bonding strength property of the resins is graphically illustrated. The results for tensile stress at failure (N/mm^2) are shown in the figures. The PF_com resin served as a reference for evaluating standard bonding strength properties of the wood strip samples.

6.3.1 Bond strength development analysis of commercial phenol-formaldehyde resin

Firstly, the bonding strength of PF_com was evaluated. The results of the bonding tests of PF_com are shown in Figure 6.4. The relationship, between the bond strength of the bonded specimens and press cycle time at 140°C, 150°C, 160°C, 170°C and 180°C was investigated. The results indicated that the extent of bond strength development was dependent on temperature and press cycle time.

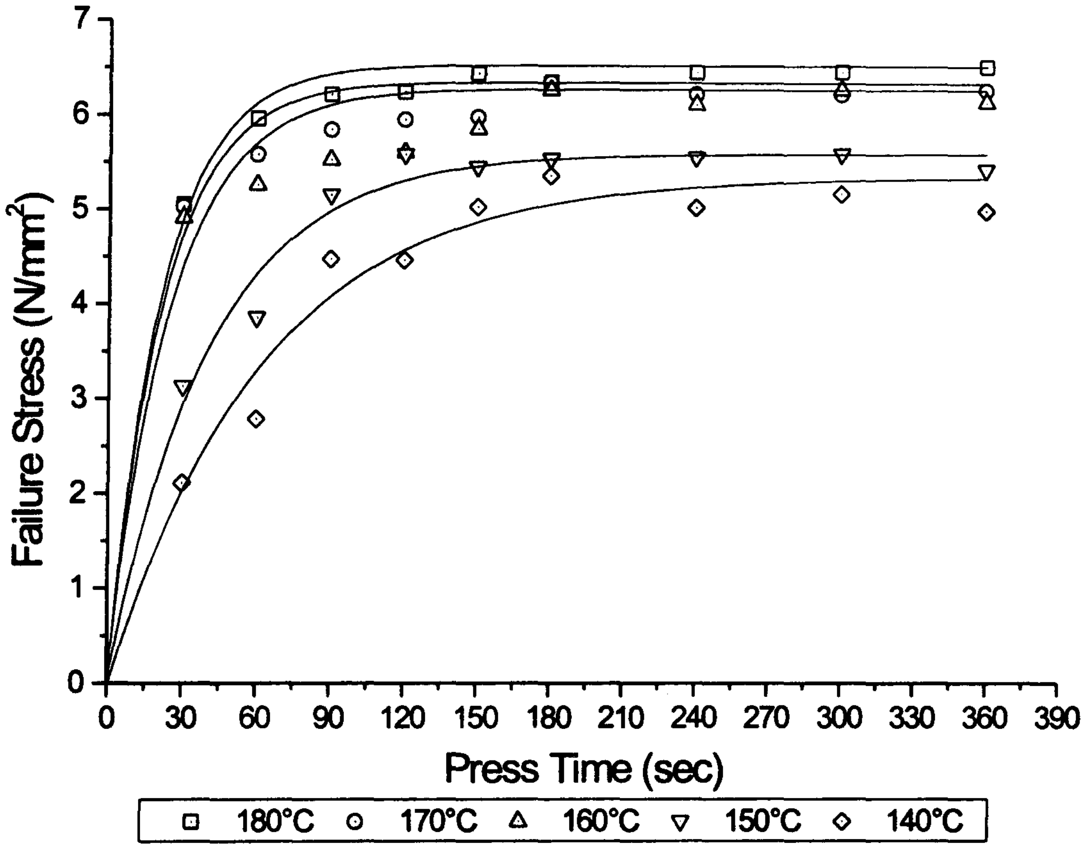


Figure 6.4 The development of bond strength of PF_com at a range of forming temperatures.

The PF_com resin did perform well with a short press cycle time and provide satisfactory bond quality at higher press temperatures, after a 60 seconds press cycle time. With increasing temperature, the bonding strength developed faster and the effect of temperature became less significant with increasing time. In Figure 6.4, it is also observed that the bonding strength curves of the lap joints bonded at 160°C, 170°C and 180°C came closer to each other with an increase in press cycle time, especially after one minute. Up to the level of stress applied, no bond nor wood failures were observed with the PF_com bonded wood strips with longer pressing times.

The effect of press temperature for the PF_com resin is shown in Figure 6.5. The failure stress of the PF_com resin increased with the press temperature. As seen from Figure 6.5, above 160°C press temperature, the failure stress and did not show any further significant increase as the press temperature was raised. These results would agree with the recommendation that PF resins should be heated in region of 160°C-180°C to obtain complete cure.

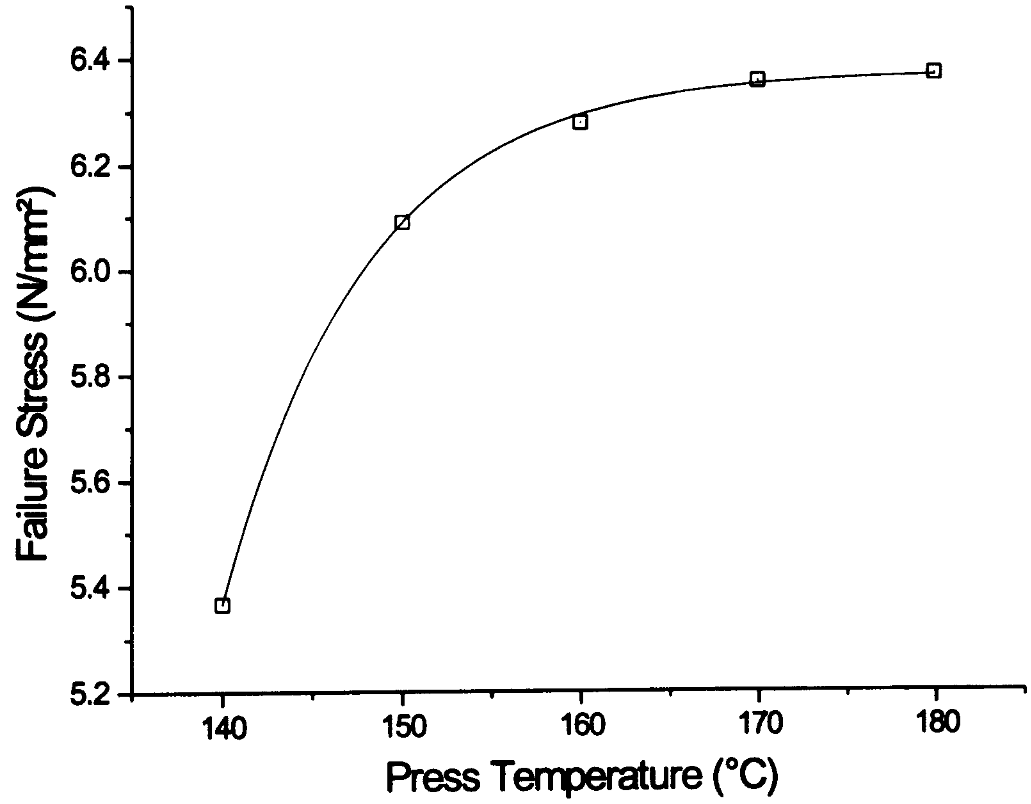


Figure 6.5 The effect of temperature on the rate of bond strength development for PF_com for 180 seconds.

6.3.2 Bond strength development analysis of laboratory made phenol-formaldehyde resin

Figure 6.6 shows a family of failure stress curves for PF_made resin at various press temperatures. The rate of cure of these thermosetting resins is clearly dependent on temperature and time of pressing.

The influence of temperature on the development of bond strength was significant, especially in the initial stage of formation. The higher the temperature, the faster the adhesive cured and the faster the bond developed strength. This is demonstrated in Figure 6.6 showing curves for the range of temperatures tested.

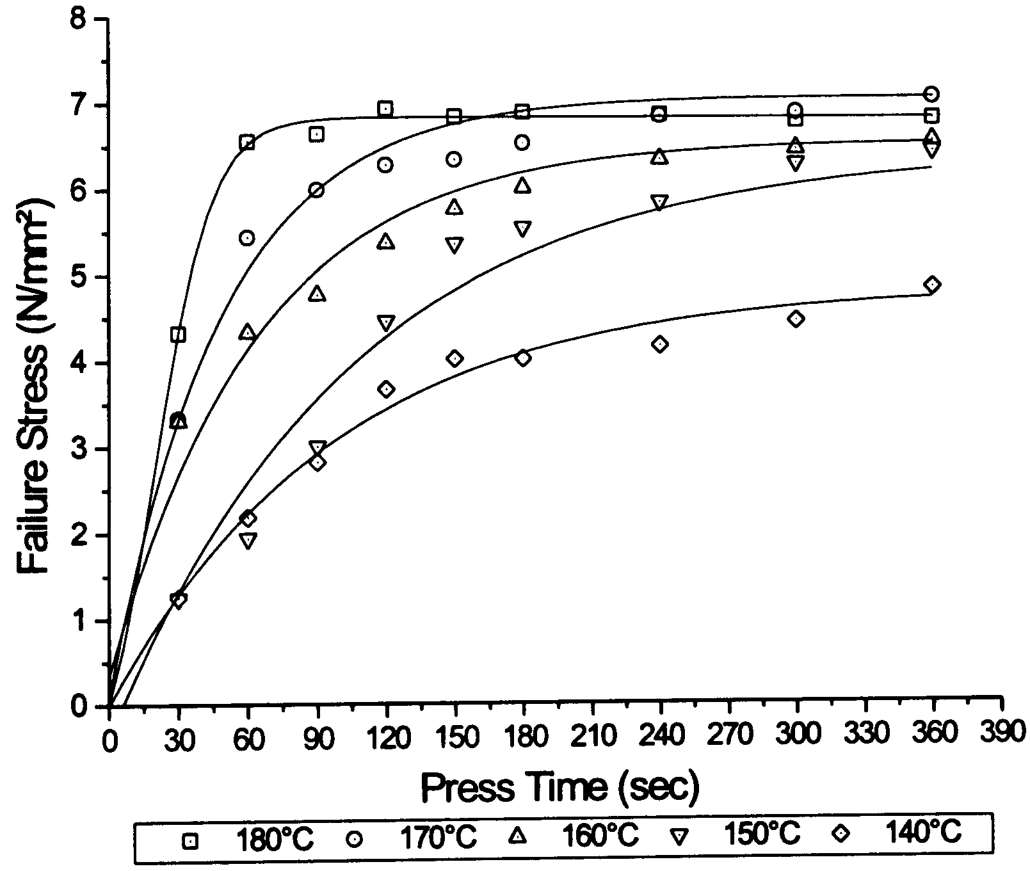


Figure 6.6 The development of bond strength of laboratory PF_made at a range of forming temperatures.

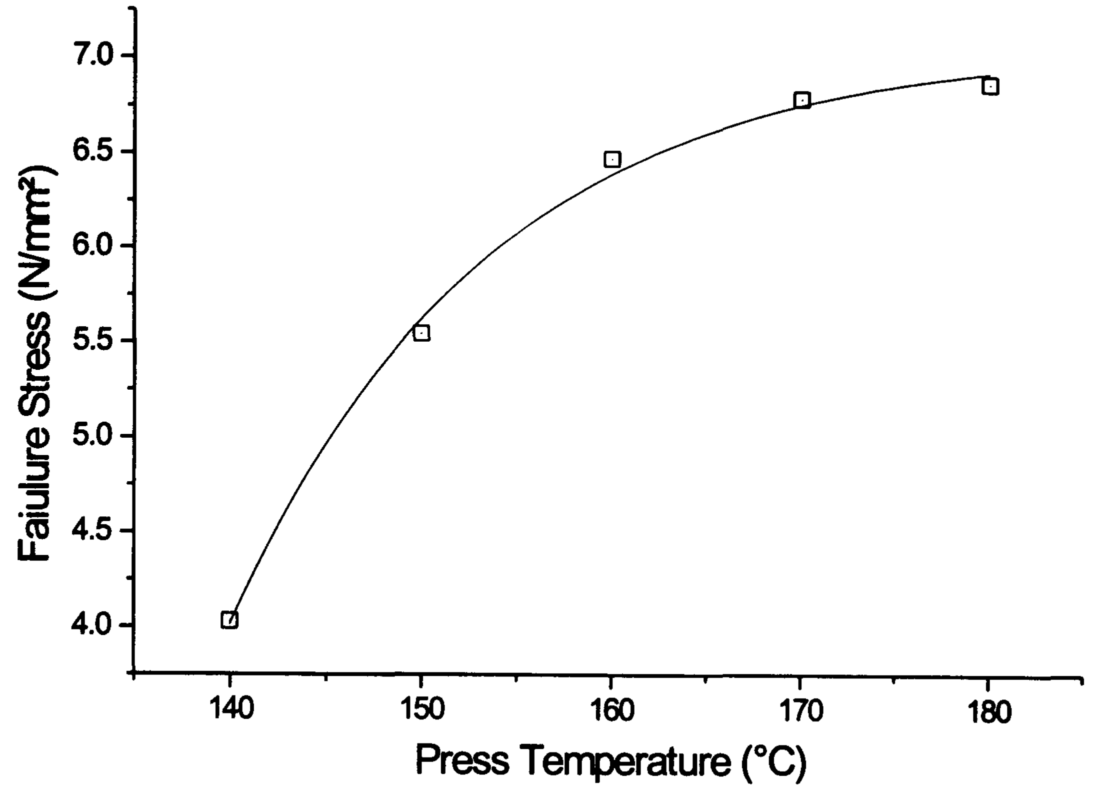


Figure 6.7 The effects of temperature on the rate of bond strength development for PF_made for 180 seconds.

Figure 6.7 depicts the failure stress values versus temperatures for the PF_made resins tested. There was a curvilinear relationship between the failure stress and press temperature. The best bond strength values were obtained at 170°C and 180°C press temperatures. It was observed that there was no further significant bond strength increase above 170°C.

6.3.3 Bond strength development analysis of lignin-phenol-formaldehyde resins

The bond strength development of the LPF resins prepared with various organosolv lignin contents (5%, 10%, 20%, 30% and 40%) were analysed using the ABES tester. Initial experimental results showed that there was no bond strength deterioration observed up to a 10% lignin substitution level. LPF1 and LPF2 (5% and 10% substituted respectively) resins had similar bond strength values and showed the same trends as noted with the PF_made resin (Table 6.2). The best bond strength values were obtained after a 60 seconds press cycle time at 160°C and above this press temperature.

Table 6.2 Bond strength values of PF_made, LPF1 and LPF2 resins

	Failure Stress (N/mm^2)					
Time	**PF_made**		**LPF1 (5%)**		**LPF2 (10%)**	
(sec)	**160°C**	**180°C**	**160°C**	**180°C**	**160°C**	**180°C**
30	3.3	4.3	3.1	4.2	2.8	3.9
60	4.3	6.6	4.1	6.1	3.8	5.7
90	4.8	6.7	4.6	6.3	4.3	6.2
120	5.4	6.9	5.2	6.6	5.2	6.4
240	6.4	6.9	6.4	6.8	6.3	6.6

For LPF3 resin (20% substitution), as shown in Figure 6.8, the effect of press temperature on the development of the bond strength was found to be highly important. The highest bond failure stress for LPF3 resin was obtained at 180°C. At higher press temperatures, LPF3 resin was cured at a faster rate and developed high bond strength. Increasing the press cycle time beyond 60 seconds did not improve the bond strength for LPF3 resin at this temperature. At lower temperatures, the bond quality of the lap joints was reduced and required a longer press cycle time to cure. Even though long press cycle times were applied at lower press temperatures such as 160°C and 170°C, the bond strength value did not reach the level of a lap joint pressed at 180°C for 60 seconds (see Figure 6.8). This effect is probably caused by less resin cure at the lower press temperatures. Increasing press temperatures from 160°C to 180°C caused the bond strength to develop at a much higher rate. This finding confirms previous work (Sellers, 1993) that lignin based resins require elevated press temperatures and a long press cycle time in order to develop strong bonds.

In fact, the tests showed that the failure stress of the resin LPF3 (20% replacement of phenol) was not significantly reduced, except where the samples were cured at low temperatures. The high press temperature, which resulted in the high failure stress, highlights that the LPF3 resin needed elevated press temperatures in order to cure.

From these results, it appears that LPF3 resins, which were bonded at high press times and temperatures, gave favourable results compared to the PF_com or PF_made resins.

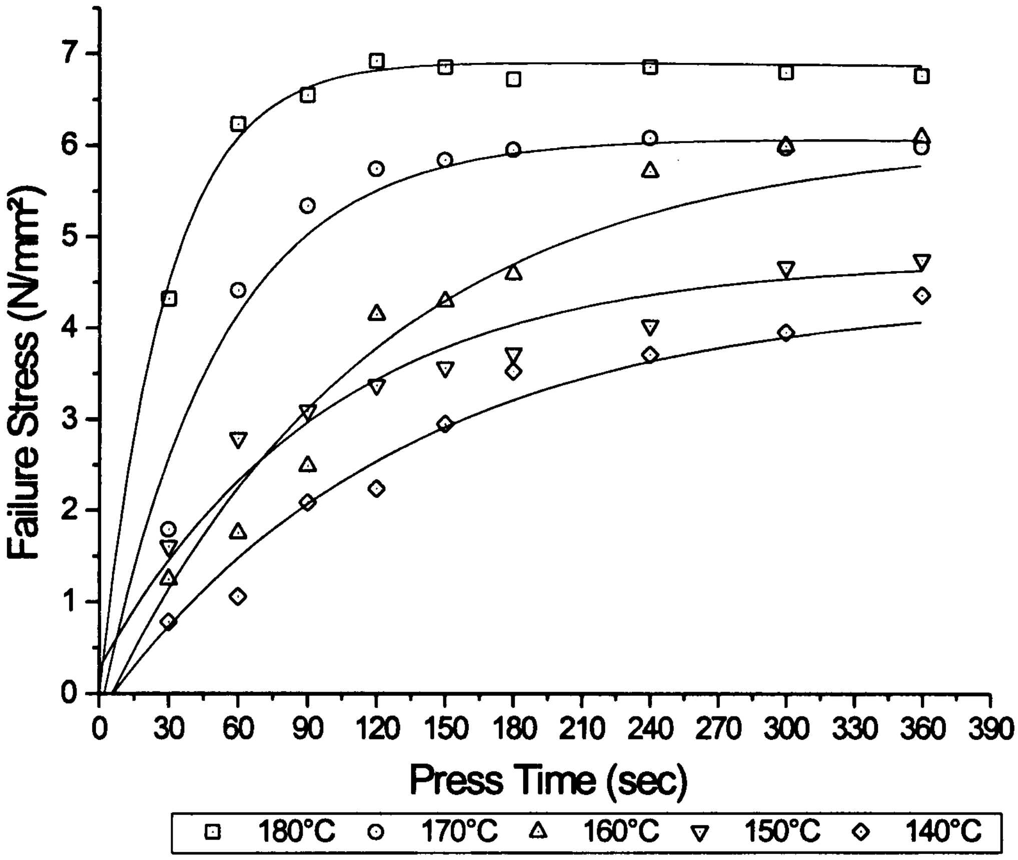


Figure 6.8 Bond failure stress values of LPF3 for various forming temperatures at various press cycle times.

The results indicated that the press temperature had a large influence on curing time. Therefore, the optimum process conditions will be achieved by increasing the press temperature and time. Clearly, the interpretation of this data would be simplified if the bond reached the required test temperature instantaneously. Time was, however, required for heat to be transferred to the glueline, and this delay affected the rate of bond strength development in the early stages of each test.

Figure 6.9 shows a typical set of bond strength values for the LPF3 resin used for forming at various temperatures at a 180 seconds press cycle time. It is quite apparent that there is an almost linear relationship between press temperature and the bond strength. An increase in the press temperature resulted in an increase in the bond strength. From this result, it can be stated that the rate of bond strength development of LPF3 resin is highly dependent on the press temperature.

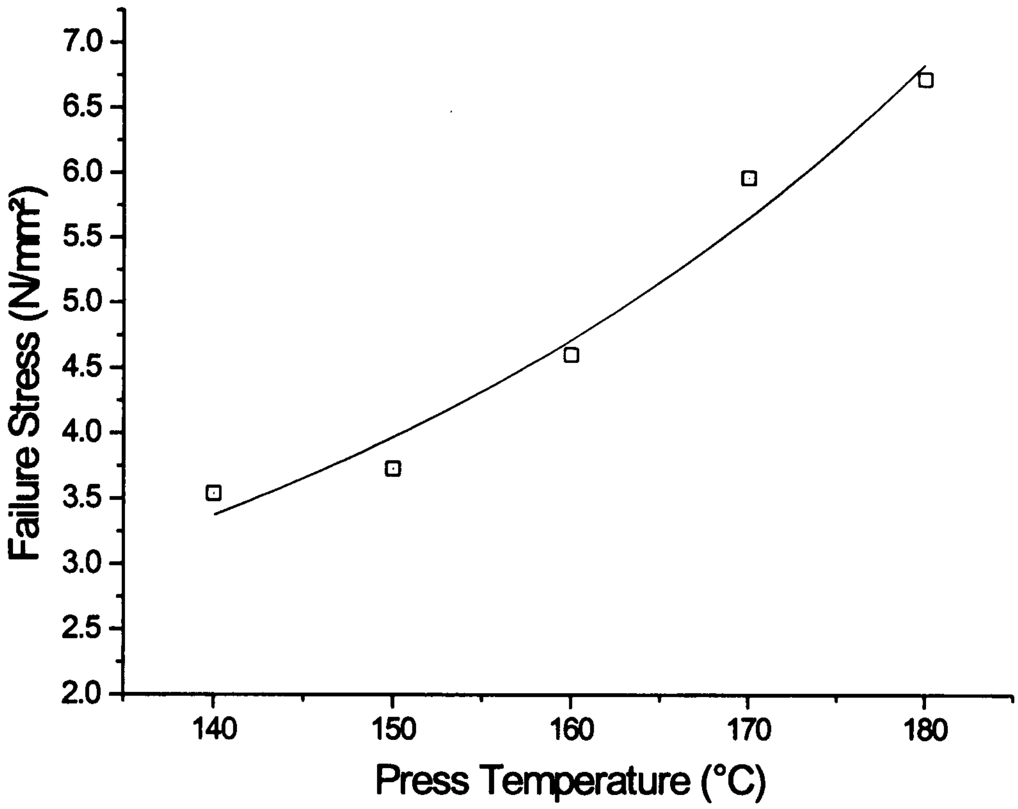


Figure 6.9 The effects of temperature on the rate of bond strength development for resin LPF3 for 180 seconds.

The LPF3 resin was equivalent in bond performance to the standard PF_com resin at 180°C. For wood strips, this work indicated that 20% of phenol in the PF resin could be replaced with organosolv lignin without detrimentally affecting adhesive properties.

The effect of press temperature on the load failure stress of LPF4 resin (30% substitution level) at various press cycle times is shown in Figure 6.10. There was a positive correlation between bond strength and press temperature. At all press temperature values studied, as press cycle time was increased, the bond failure stress of LPF4 bonded strips also increased. The best bond failure strength of LPF4 resin was obtained at 180°C press temperature, and after 180 seconds press cycle time, the bond failure stress values was comparable with PF_com resin.

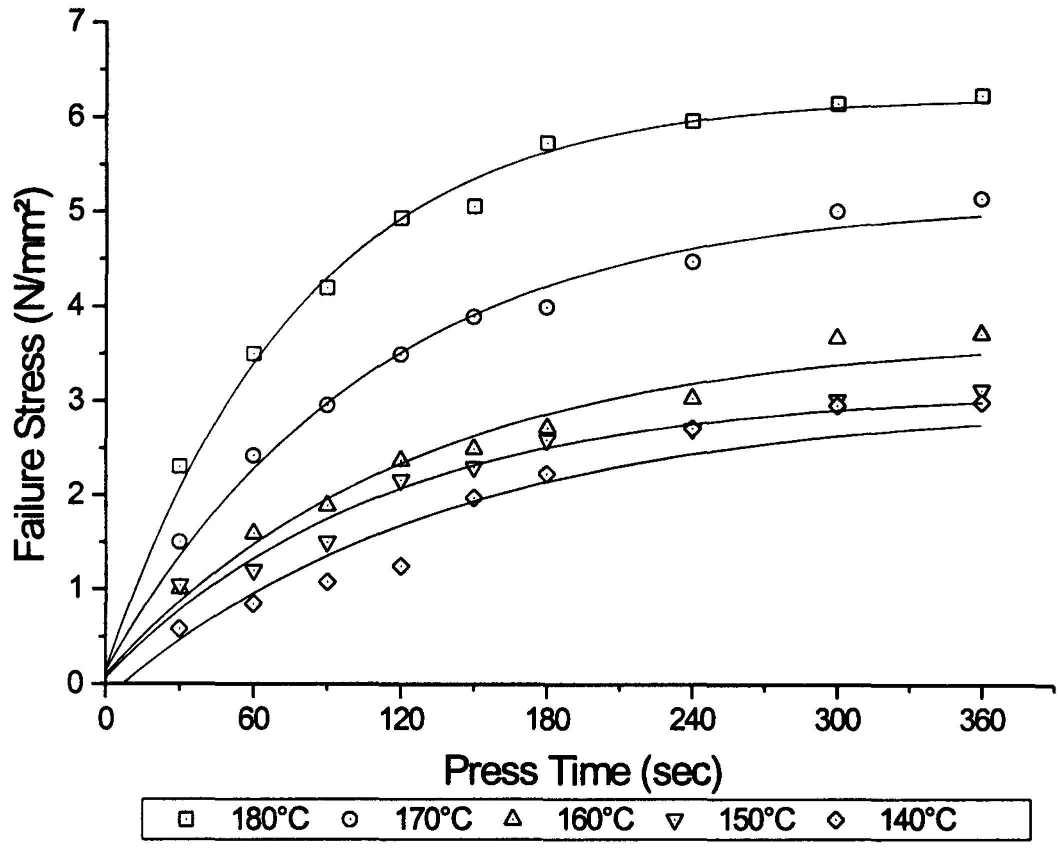


Figure 6.10 Bond failure stress values of LPF4 for various forming temperatures at various press cycle times.

The effect of press temperature on the development on bond strength of LPF4 resin at 180 seconds press cycle time is shown in Figure 6.11. As the press temperature increased, the stresses required to induce bond failure showed an exponential increase.

However, resin LPF5 (40% phenol replacement) exhibited a dramatically low failure stress, compared to the other resins. As shown in Figure 6.12, even though an increase in the press temperature resulted in an increase in the bond strength, these bond strength increases were well below the other resins studied.

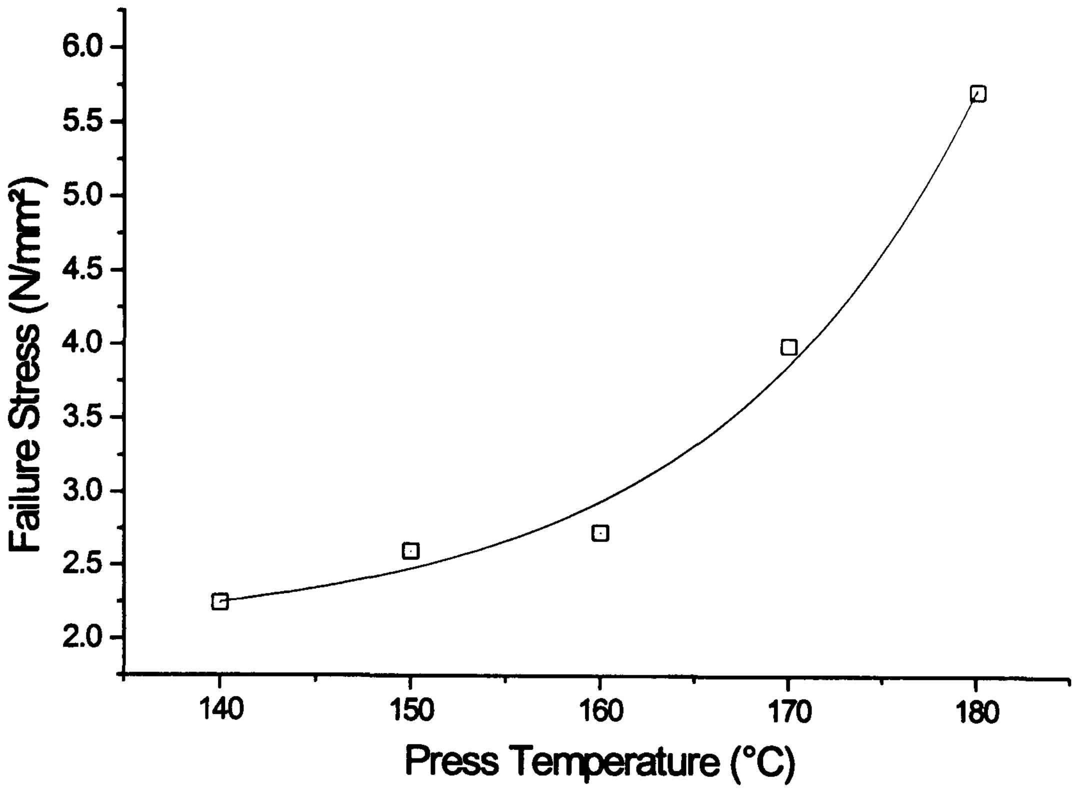


Figure 6.11 The effects of press temperature on the rate of bond strength development for resin LPF4 for 180 seconds.

It can be seen from Figure 6.12 that the failure stresses of LPF5 resin (40% phenol replacement) are quite low at low temperatures. This resin showed a distinctly poorer performance. The difference between the resins LPF3 and LPF5 are shown more clearly by their different lignin content. The failure stress at 180°C increased with increasing press cycle time up to approximately 360 seconds. However, increasing press cycle time did not improve the bond strengths to same values at the lower temperatures.

The effect of press temperature on the bond strength of LPF5 resin is shown in Figure 6.13. The bond failure stress of LPF5 resin showed an exponential growth curve as the press temperature increased (at 180 seconds press cycle time). An increase in press temperature above 160°C caused significant changes in the bond strength development.

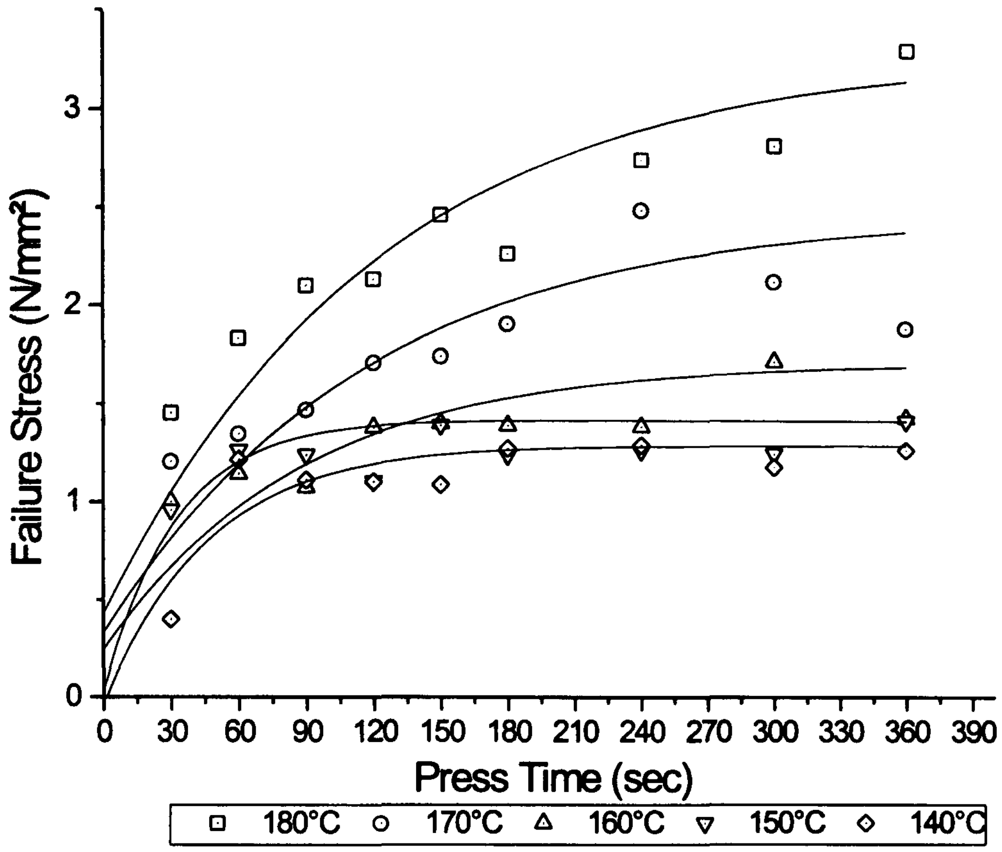


Figure 6.12 Bond failure stress values of LPF5 for various forming temperatures at various press cycle times.

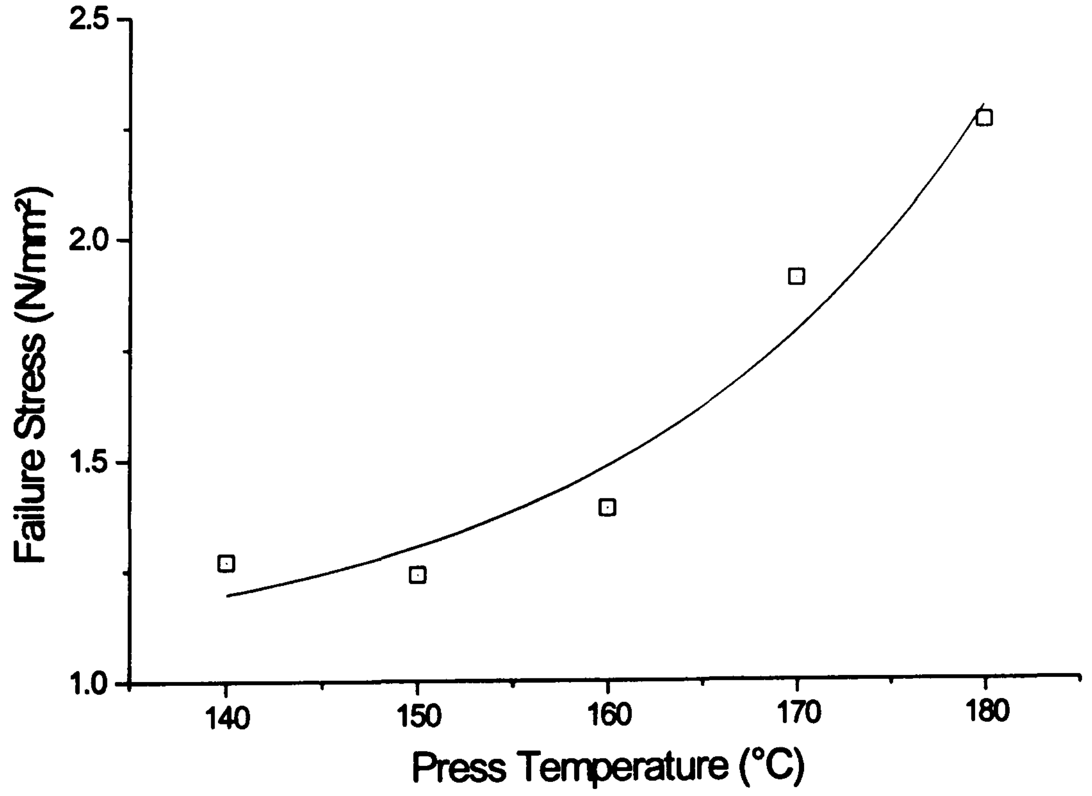


Figure 6.13 The effects of temperature on the rate of bond strength development for resin LPF5 for 180 seconds pressing time.

When the results of Figures 6.5, 6.7, 6.9, 6.11, and 6.13 are re-plotted in the same graph (see Figure 6.14), an interesting phenomenon is observed. As the lignin percentage is increased in the LPF resins, the bond strength is adversely affected and they require a higher press temperature to cure. As seen from Figure 6.14, at the 40% substitution level (LPF5 resin), the bond quality was the poorest, even at a 180°C press temperature. From these results, it is clear that up to 20% of the phenol could be substituted by lignin in the PF resin, without significantly sacrificing the bond quality of the resins, provided that an adequate pressing temperature was reached.

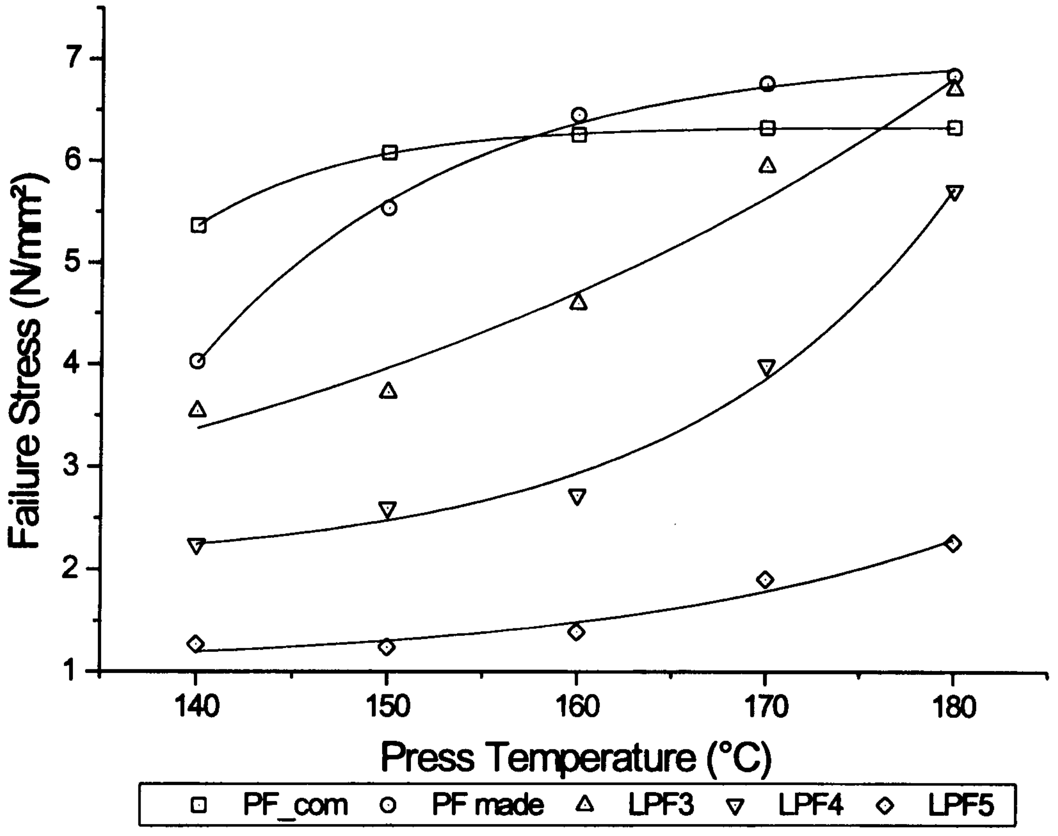


Figure 6.14 The effects of lignin substitution level on the rate of the bond strength development for LPF resins at various press temperatures for 180 second press cycle time.

6.3.4 Bond strength development analysis of phenolated-lignin-formaldehyde resins

Figure 6.15 shows the failure stress values at different press cycle times for LPF 10A (≈30% substitution with phenolated-lignin and 37.4% formaldehyde solution) and LPF 10B (29.5% formaldehyde solution) resins at 180°C. Lower press temperature tests were also used to evaluate the bond strength for these phenolated-lignin resins. Unfortunately, no equivalent or better results were obtained by low temperature pressing. As shown in Section 6.3.3, LPF resins gave best bond strength values at 180°C press temperature. For this reason, further work was done using this press temperature only.

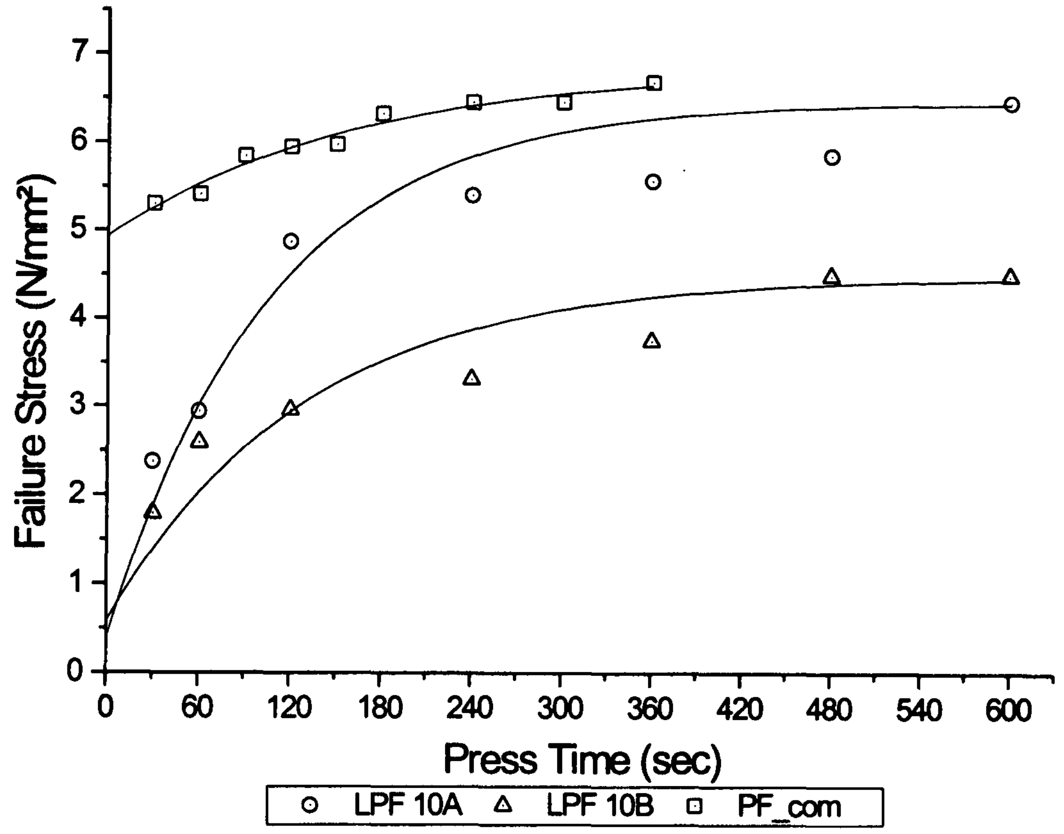


Figure 6.15 Bond failure stress values for different forming times at constant forming temperature of 180°C.

It can be seen from Figure 6.15, that as the press cycle time was increased, the bond strength also increased for LPF 10A and LPF 10B resins. LPF 10A showed higher bonding strength than LPF 10B. The reason of these high strength values might be that the LPF 10A resin contained more formaldehyde than the LPF 10B resin (see Appendix 2). The increased formaldehyde ratio improved the curing property of lignin copolymer resins to some extent. LPF 10A resin required 8 minutes press cycle time to give the same bond strength value as PF_com resins at 180°C, whereas, the PF_com resin gave this value after a 30 second press cycle time at 180°C.

The bond strength values of LPF 20A, LPF 20B, LPF 30A and LPF 30B are shown in Figure 6.16. At short press cycle times, all the LPF resins exhibited resulted in very poor bond quality. As the press cycle time was increased, the bond strength of the lap joint also increased in a curvilinear manner. The bond strength increase levelled off at 240 seconds press cycle time. It was noted again that the LPF resin needed a longer time to cure. Even though there was adequate press cycle time employed for curing the resins, the bond strength of LPF 20A, LPF 20B, LPF 30A and LPF 30B was considerably lower than the PF_com resin. The reason for the low bonding strength values might be due to high amount of lignin content (≈40%-60% phenol replacement, see Appendix 2).

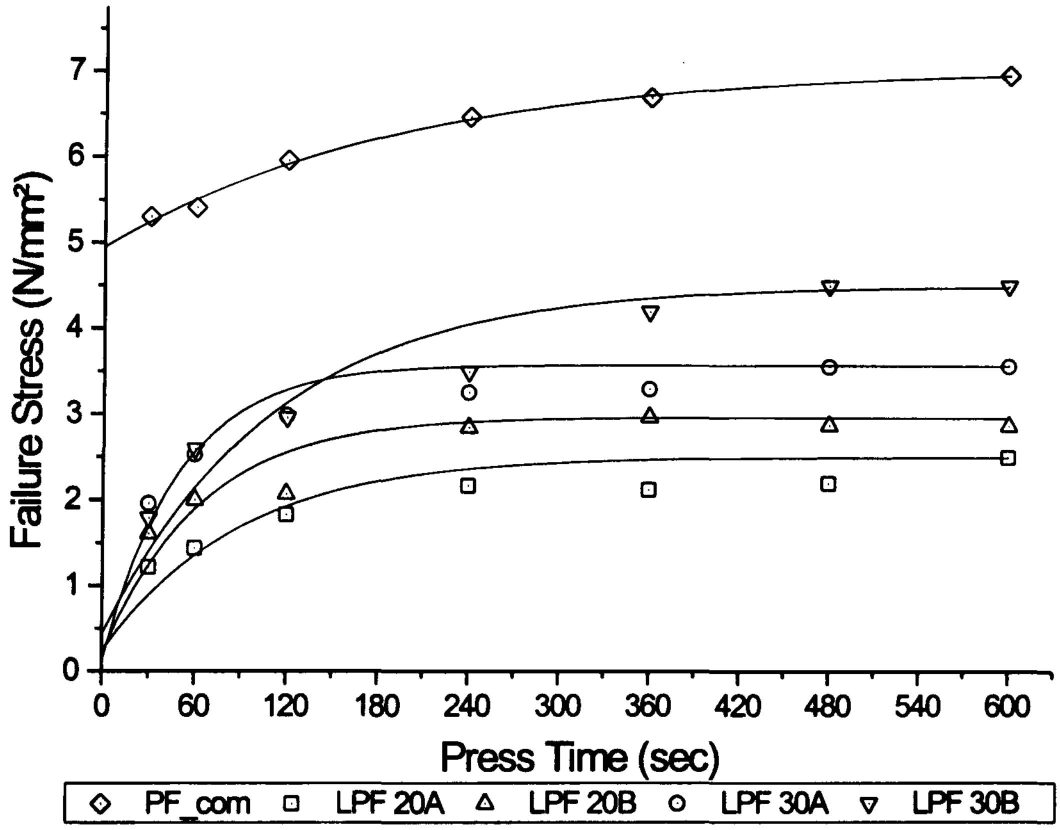


Figure 6.16 The stress failure values of LPF 20A, LPF 20B, LPF 30A and LPF 30B resins versus pressing time.

The bond strength values of LPF 40A, LPF 50A and LPF 60A resins (≈20-30% substitution with phenolated lignin and 41% formaldehyde solution, see Appendix 2) are illustrated in Table 6.3. The bond strength of these resins built up faster, and achieved higher final bonding at 60 seconds than LPF 70A did at 180 seconds. Failure stress reached ≈6.50 N/mm² in a short time. There was adhesive failure in these samples. There was no bond failure observed for these three resins after 90 seconds of bond formation. During the experiment, in some cases, it was also noted that before the bond fails, the veneer strips failed (material failure) with most of the LPF 40A, LPF 50A and LPF 60A bonded strips. Since there was no bond failure between the strips, it is an example of how strong an interaction it was, although high temperatures were needed.

Table 6.3 The bond strength values of LPF 40A, LPF 50A and LPF 60A resins (pressed at 180°C for 60, 90, 120, 180 and 360 seconds).

Time		**Failure Stress (N/mm²)**	
(sec)	**LPF 40A**	**LPF 50A**	**LPF 60A**
60	6.22	5.55	5.18
90	6.73	6.64	6.50
120	No failure	No failure	6.74
180	No failure	No failure	6.56
360	No failure	No failure	No failure

To see the effect of lignin substitution level on the bond strength, the failure stresses of LPF 40A, LPF 50A, LPF 60A are plotted and shown in Figure 6.17. It can be seen from Figure 6.17 that the higher the lignin content, the poorer the bond quality. However, the bond strength is still tolerable, at 60 second press cycle time and 180°C press temperature. In addition, when the press cycle time was increased, the high lignin content resins gave better bond strength, similar to the PF_com resin (see Table 6.3). The performance of all three of these phenolated-lignin-formaldehyde resin formulations was adequate with respect to a standard or by comparison with PF_com.

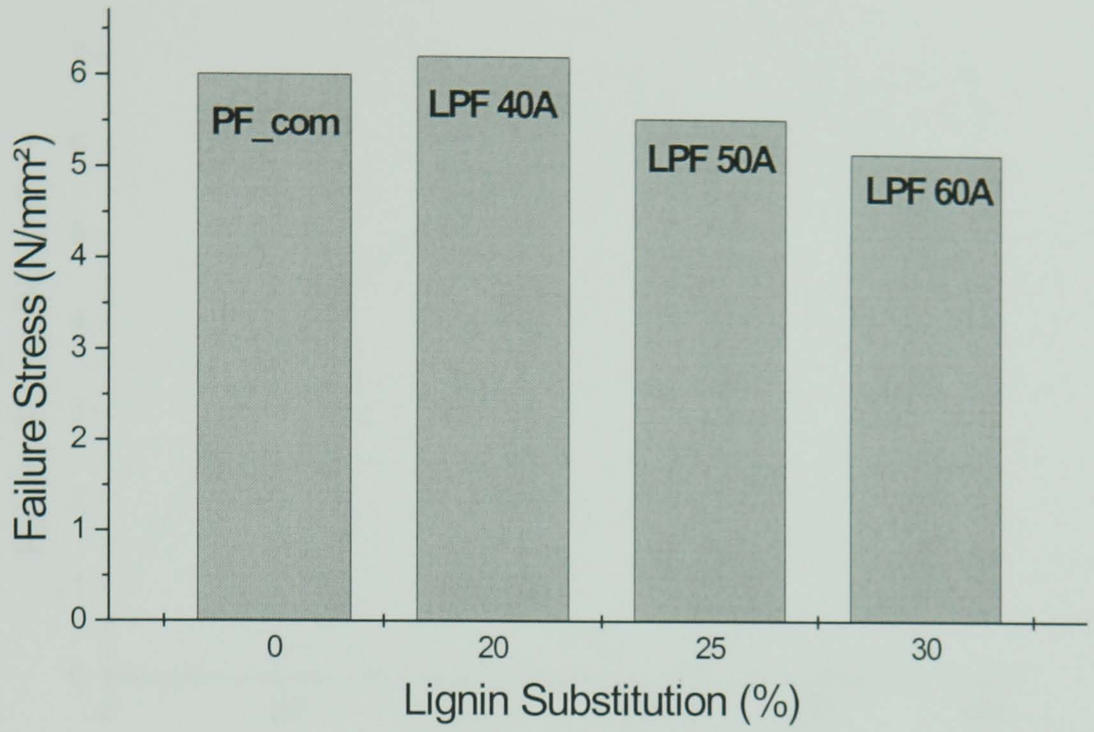


Figure 6.17 Effect of lignin substitution in phenolated-lignin formaldehyde resin (press cycle time was 60 seconds and press temperature was 180°C).

However, LPF 70A (≈25% lignin) gave lower failure stress values than those of other phenolated-lignin-formaldehyde resins. The reason for these low values might be that less formaldehyde (33%) was used in the preparation of the LPF 70A resin compared to other resins (see Appendix 2). The molar ratio of formaldehyde to lignin is clearly an important factor in the resin characteristics. As mentioned earlier, the formaldehyde concentration improved the curing property of lignin copolymer resins to some extent. In order to provide a good bonding quality, it seems that the interaction of formaldehyde/lignin (F/L) as well as the lignin/phenol (L/P) may play an important role.

Figure 6.18 shows the stress failure values for resin LPF 70A. It can be seen from the graph that in order to obtain good bond strength, resin LPF 70A needed longer pressing times than the other three resins.

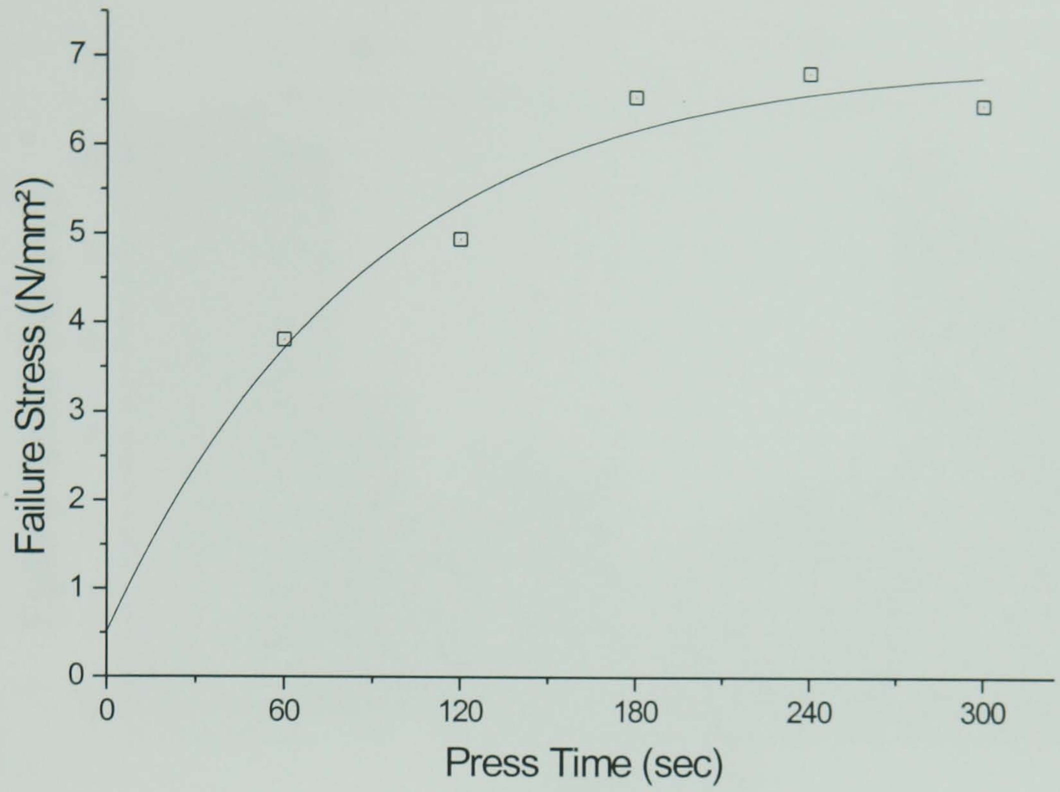


Figure 6.18 The stress failure values of LPF 70A resin versus pressing time.

It is clear that the amount of lignin contained in the copolymer resin and the formaldehyde to lignin molar ratio affected the curing property of lignin copolymer resins a great deal. The results showed that the bonding quality of copolymer resins, with the lignin to phenol weight ratios of ≈20/80, ≈25/75 and ≈30/70, were generally comparable to that of the PF_com resin.

All these experiments were carried out in order to choose the best lignin resins for production of the particleboards. To determine the best resins, the lap joint strength values of all resins at 60 seconds press cycle time and 180°C press temperature were plotted (Figure 6.19).

Figure 6.19 indicates that LPF3, LPF 40A, LPF 50A and LPF 60A resins gave more or less similar lap joint strength to PF_com or PF_made resins at 60 seconds press cycle time and 180°C press temperature.

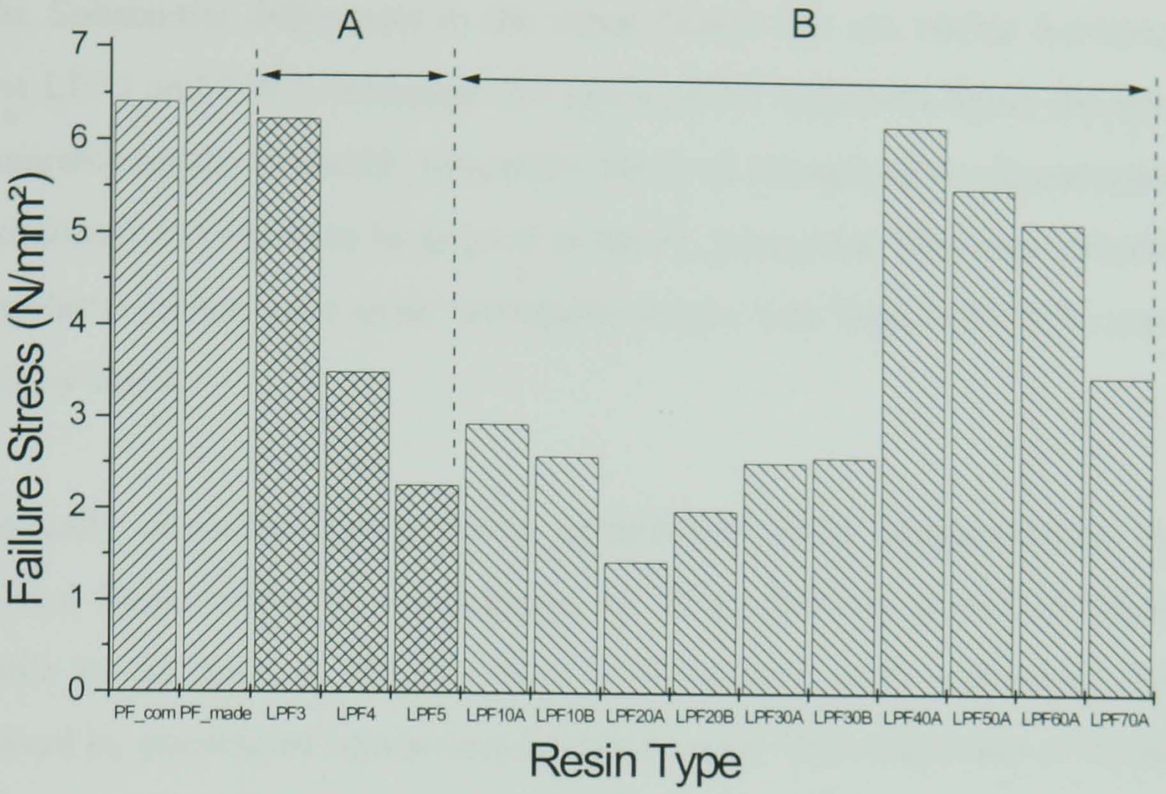


Figure 6.19 The failure stress values of PF_com, PF_made, lignin-phenol-formaldehyde (A) and phenolated-lignin-formaldehyde (B) resins at 60 seconds press cycle time and 180°C press temperature (see Appendix 2 for formulations of resins).

6.4 CONCLUSIONS

Based on the results obtained under the conditions of this research, the following could be concluded:

The results of this chapter indicate that the press temperature and time of the process are both important. Although the main effect of temperature showed very significant interactions on the failure stress of the wood strips, time also showed the same significant connection. Increasing press time beyond a certain period did not improve the bonds made at 180°C. The effect of temperature on the failure stress over the range used in this study were shown in the results of the laboratory experiment. Therefore, the optimum level of temperature and time used were those suggested by the results of the laboratory experiments.

The overall comparison of the lignin replacement procedures and the PF_com were made. Substantial differences in the stress failure rate are visible between the two resins LPF3 and LPF5. Although the lignin resins with 40% lignin did not produce comparable results to the PF_com resin, the bond strength of the lignin resins (≈20% substitution) was found to be as good as the PF_com resin. However, modified resins (phenolated resins) gave quite favourable results with high (≈20-30%) replacement levels by lignin.

Chemically modified lignin resins contributed better characteristics than non-modified lignin resins. A replacement of 20 to 30% of phenol by lignin seems feasible by this process. Higher levels of substitution with organosolv lignin were achieved by phenolated-lignin-formaldehyde resins. The molar ratio of formaldehyde to lignin, along with content, also affected the bonding property of the copolymer resins.

In the light of these studies, lignin-phenol-formaldehyde resins (LPF3 and LPF5) and phenolated-lignin-formaldehyde resins (LPF 40A, LPF 50A and LPF 60A) were chosen for production of particleboards. The results are reported in Chapter 7.

CHAPTER 7

PREPARATION AND TESTING OF PARTICLEBOARDS INCORPORATING ORGANOSOLV LIGNIN PHENOL FORMALDEHYDE RESINS

7.1 INTRODUCTION

Wood particleboard is manufactured from lignocellulosic wood material, in the form of discrete particles, combined with synthetic resin and bonded together under heat and pressure in the hot press (Maloney, 1993). In the process, the majority of the interparticle bonds are created by the added binder. In particleboard, 95%-98% of all particleboard is flat pressed and the particles lie with their longitudinal axis randomly oriented but essentially parallel to the board surface.

Bonding of thermosetting adhesives plays an important role within wood based composites. During hot pressing, there is a continuously changing state of factors such as temperature, moisture content and vapour pressure within the mattress, which affects the process of adhesion and the development of bond strength. This affects the properties of the final product, the required hot-pressing time and energy consumption (Humphrey, 1982).

In commercial practice, the amount of PF resin used is generally 5-15% w/w[1]. Even at these low concentrations, resin cost is the overriding factor affecting final product cost (Maloney, 1993, Wilson and Hill, 1978) and there have been many attempts to replace phenol with lignin in PF resins suitable for particleboards in order to reduce resin cost.

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[1] All addition rates are based on the oven-dry weight of softwood chips (ODW basis) unless otherwise stated.

This chapter covers the production and evaluation of particleboards bonded with PF, LPF and phenolated-lignin formaldehyde resins. The mechanical properties and dimensional stability of boards were measured and comparisons were drawn between the different resin types.

Resins deemed suitable for particleboard manufacture, as determined by bond evaluation (see Chapter 6), were subjected to further assessment. Preliminary work was carried out to establish a method of board making with the experimental resins. After a satisfactory method was established, the physical and mechanical properties of particleboards manufactured with the experimental lignin-based resins were compared to those made with commercial PF resin (PF_com) and laboratory made PF resin (PF_made).

7.2 MATERIALS AND METHODS

7.2.1 General experimental design

The main objective of the laboratory work was to demonstrate that the properties of particleboards bonded with resins containing organosolv lignin could equal the properties of particleboards bonded with PF_com resin.

A secondary objective was to optimise process conditions as a basis for trials. In order to achieve this objective, it was necessary to determine the effects of process variables on particleboard production. Therefore, particleboards were consolidated at a range of temperatures and times using different resins, although the bonding tests (in Chapter 6) showed significant differences for these variables.

With the aim of determining the properties of the resins, particleboards were manufactured in the laboratory. The particleboards were prepared:

Resin-only boards

Density	:	650 kg/m^3
Resin application	:	10%
Wax content	:	nil

Experimental procedure was divided into three sections. In the first section (I), control boards were produced by using PF_com and PF_made resins. The experimental design and parameters of control boards is shown in Table 7.1.

Table 7.1 Experimental design I and II:

Variables			Constants
Resin types	I	PF_com and PF_made	Density 650 kg/m^3
	II	LPF3 and LPF5	
Press temperatures		140°C, 160°C, 180°C	Resin content 10%
Press time		5 min*, 8 min, 15 min	Mat moisture content 3%
Thickness		6 mm, 12 mm	

*3 minutes press time for 6 mm particleboards

Three control replicates were made for each case. 108 control boards were prepared (2 resin types x 3 temp. x 3 press time x 2 thickness x 3 replicates).

In the second section (II), boards were prepared using two types of LPF resin (LPF3 and LPF5). The same experimental matrix of the time-temperature combinations was used as for the PF_com and PF_made resins (Table 7.1).

Three replicate boards were manufactured for each case. The total number of boards prepared was 108 (2 resin types x 3 temp. x 3 press time x 2 thickness x 3 replicates).

The third section (III) of this study was designed to measure the gluing properties of phenolated-lignin-formaldehyde resins, by board test criteria. Mechanical and water resistance tests were carried out in order to evaluate the formulated resins. The experimental design for these resins can be seen in Table 7.2.

Results gained from the second section indicated that LPF resins gave better mechanical properties at 180°C press temperature. For this reason (in the third section), press temperatures of 140°C and 160°C were eliminated and only 180°C was used to produce 6 mm and 12 mm particleboards at 3 minutes, 8 minutes and 15 minutes press time. Four types of phenolated-lignin-formaldehyde resins were used. A total of 72 boards were prepared (4 resin types x 1 temp. x 3 press time x 2 thickness x 3 replicates).

Table 7.2 Experimental design III:

Variables		Constants
Resin types III	LPF 40A, LPF 50A, LPF 60A, LPF 70A	Press temperature 180°C
Press time	5 min*, 8 min, 15 min	Density 650 kg/m^3
Thickness	6 mm, 12 mm	Resin content 10%
		Mat moisture content 3%

*3 minutes press time for 6 mm particleboards

7.2.2 Wood substrate

The chips, which are derived from a variety of species, principally softwood, were screened, in order to eliminate large chips and reduce the fines content. Chips which passed a 5 mm screen and which were retained on a 1 mm screen were used for the experiment.

7.2.3 Resins

The resins used for manufacture of boards were PF_com, PF_made and lignin-based resins. No resin hardener or wax was added. The resin solution was evenly sprayed onto the particles via a pneumatic atomising nozzle as the mixer rotated. Resins were applied at a rate of 10% (resin solids based on the oven dry weight of wood particles).

PF_com resin was obtained from an industrial supplier. PF_made and lignin-based resins were prepared as described in Chapter 5. The laboratory formulated PF resin and resins containing lignin were evaluated by comparing properties of panels bonded with these resins, against the properties of panels bonded with a PF_com resin.

7.2.4 Bond strength prediction (monitoring of core temperature)

Temperature rise in the core of the mattress was recorded before producing particleboards with resins. Temperature-time profiles were obtained from measurements made whilst pressing an unresinated particleboard, wherein moisture level was fixed to emulate resinated furnish. A type K thermocouple was used in conjunction with type K miniature thermocouple connectors. The thermocouple was placed in each board after half the wood chips had been placed in the mattress former. The remaining wood chips were then laid onto the sensor, and the mattress formed in the usual manner. 6 mm and 12 mm boards were made at 140°C, 160°C and 180°C in order to observe the effect of board thickness on temperature rise at the mattress core during pressing. Temperature rise was recorded every ten seconds.

7.2.5 Particleboard production

Particles were dried to approximately 3% moisture content. The required quantity of wood particles was placed in a rotary-drum blender and blended with resin. The resinated particles were hand formed in a circular iron frame, 312 mm in diameter, on an aluminium caul plate. Care was taken to form an even mattress to minimise variation in board density. Finally, a second caul plate was placed on top of the mat and the assembly was placed in the press. Board target thickness was either 6 mm or 12 mm; target density was 650 kg/m^3 in all cases.

7.2.6 Preparation of specimens

All boards were cut into test specimens according to the pattern shown in Figure 7.1. The pattern of sample cutting was arranged to ensure a representative distribution over the area of the panel for each group of specimens. This is important, as panel properties are known in vary according to distance from the panel centre.

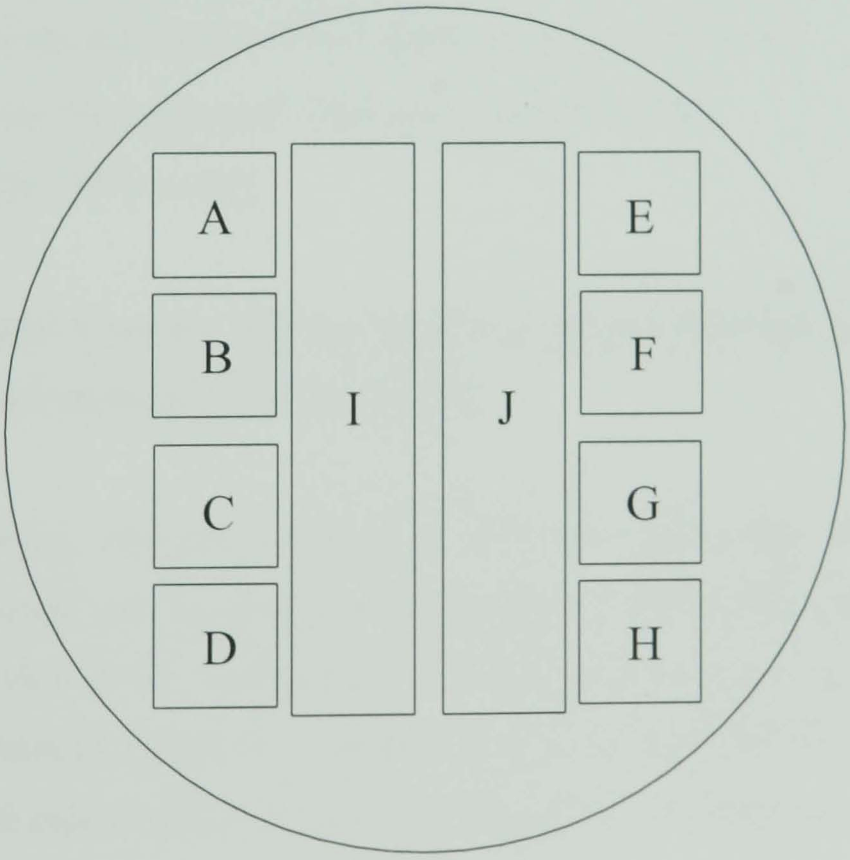

Figure 7.1 Cutting pattern for test pieces.

A, C, F, H (50 x 50 mm): Thickness swelling; B, D, E, G (50 x 50 mm): Internal Bond; I, J: Static bending (50 mm x 20t)[2]

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[2] t= thickness of the board (mm)

The particleboards were then conditioned at 65 ± 5% RH and 20 ± 2°C until weight stability was achieved. Stability is defined as change in weight ≤ 0.1% initial weight over a 24 hour period. After conditioning, sample weight and dimensions were determined.

7.2.7 Testing

All tests were carried out to the appropriate European Standards. The tests performed on the specimens were:

- Internal bond strength perpendicular to the plane of the board (IB) (EN 310:1993)
- Static bending [modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated from the data derived from these tests] (EN 317:1993)
- Thickness swelling and water absorption (EN 319:1993)
- Boil Test (EN 1087-1:1995)

- **Internal bond strength (determination of tensile strength perpendicular to the plane of the particleboard) (EN 310:1993)**

After conditioning, samples were glued using hot melt glue (ethylene vinylacetate) between two beech loading blocks mounted at their centre with brazed eye screws. This assembly was then tested to destruction on an Instron universal testing machine (model 4301), at a crosshead speed of 1 mm/min. Tensile strength perpendicular to the plane of the sample was calculated by dividing the tensile force of failure by the cross-sectional area.

$$\textit{Internal bond strength} = \frac{f}{A}$$

where:

f = the tensile force of failure (N)
A = the cross sectional area (mm^2)

Internal bond strength (IB) is an important indicator of board quality in both production and utilisation. It provides direct information on the adhesion between wood components and the bonding agent and shows the location of the weakest plane within the cross-section of the product. Thus the IB test is generally considered the most significant for determining composite quality (Ren, 1988).

- **Bending strength (EN 317:1993)**

Test samples were prepared and conditioned as described in Section 7.2.6. A single measurement of width and three measurements of thickness were taken for each sample. Mean thickness was employed to calculate the results.

Tests were carried out using an Instron universal testing machine (model 4301), at a crosshead speed of 4 mm/min for 6 mm boards and 6 mm/min for 12 mm boards. The sample was supported on parallel metal rollers with a span of 20 x t mm (thickness of the board). Load was measured at two discrete points in the straight line section of the load-deflection curve. These data were used to calculate modulus of elasticity. Modulus of rupture was calculated using the load measured at failure of the sample.

$$MOE = \frac{L^3 \Delta W}{4bt^3 \Delta S}$$

where:

MOE = modulus of elasticity (N/mm^2)
L = the distance between centres of supports (mm)
ΔW = the load increment on the straight line portion of the load-deflection curve (N)
b = the mean width of the sample (mm)
t = the mean thickness of the sample (mm)
ΔS = the increment of deflection at the mid-length of the sample corresponding to the load (mm)

$$MOR = \frac{3\, F_{\max}\, L}{2\, b\, t^2}$$

where:

MOR = modulus of rupture (N/mm^2)
F_{max} = the maximum load (N)
L = the distance between the centres of the supports (mm)
b = the width of the sample (mm)
t = the mean thickness of the sample (mm)

- **Thickness swelling (TS) and water absorption (WA) (EN 319:1993)**

Weight and thickness were measured after the specimens reached equilibrium (in an atmosphere with a mean relative humidity of (65 ± 5%) and a temperature of (20 ± 2°C). Weight was recorded to an accuracy of ± 0.01 g and thickness to ± 0.01 mm. Thickness was measured at the centre of the specimen using a digital micrometer.

All specimens were placed vertically in a water bath. Depth of water above the top most face was 25 mm. Water temperature was thermostatically maintained at 20 ± 2°C.

After the immersion time had elapsed (2 hours and 24 hours as appropriate), the samples were taken out of the water and drained for 10 minutes in order to remove excess water and thickness was determined. The swelling in thickness of each sample was calculated and expressed as a percentage of initial thickness as follows:

$$q = \frac{t_w - t_o}{t_o} x\,100$$

where:

q = total thickness swelling (%)

t_w = the mean of wet thickness (after water immersion (mm)

t_o = the mean of initial thickness (before water immersion (mm)

The values of water absorption of each sample were obtained from the same specimens prepared for the thickness swelling test. Each sample was weighed after the appropriate period of immersion. Weight gain of each sample was determined and expressed as a percentage of initial weight as follows:

$$WA = \frac{W_w - W_i}{W_i} x\,100$$

where:

WA = percentage of absorption of water the sample

W_w = the weight of the sample after immersion (g)

W_i = the weight of the sample before immersion (g)

- **Boil test (retained internal bond strength) (EN 1087-1:1995)**

Samples were submerged in boiling water for 2 hours, then were removed from the boil tank and immersed in water at 20°C ± 5°C for 1 hour. They were then removed from the water bath and dried on a paper towel. The samples were placed with faces horizontal in an oven at 70°C ± 2°C for 16 hours, after which time they were removed from the oven and allowed to cool to room temperature. Finally, an IB test was performed as described above and retained IB calculated. The mean test value and standard deviation for each type of product tested were calculated.

7.3 RESULTS AND DISCUSSION

7.3.1 Temperature in the mattress core

When the mattress surfaces come in contact with the hot platens of the press, moisture in the surface particles turns to steam and the vapour pressure (at the surface) increases; thus a vapour pressure gradient is established across the thickness of the mattress. This pressure gradient causes a flow of water vapour (in the form of steam) from the surface to the cooler interior of the mattress, where condensation takes place (Kavvouras, 1977).

The relationship of core temperature to time during pressing lends itself to division into three parts (Figure 7.2). The initial part is dominated by convection temperature, the second part by evaporation temperature and the third part by conduction temperature (the drying phase). Initial temperature rise is rapid as the condensation zone moves into the core layer of the mattress. A period of slow temperature rise follows as the zone of evaporation moves into the core layer of the mattress. Subsequently, the temperature curve levels off. In the final period of the heating process, which is characterised by a slow temperature rise, the rate of temperature increase is controlled mainly by the rate of conduction of the wood particles.

The effect of board thickness on the time-core layer temperature relationship at 140°C is shown in Figure 7.2. Thickness is shown to be an important factor; total resistance to vertical vapour flow increases and the rate of temperature rise at the mattress core decreases, as thickness increases.

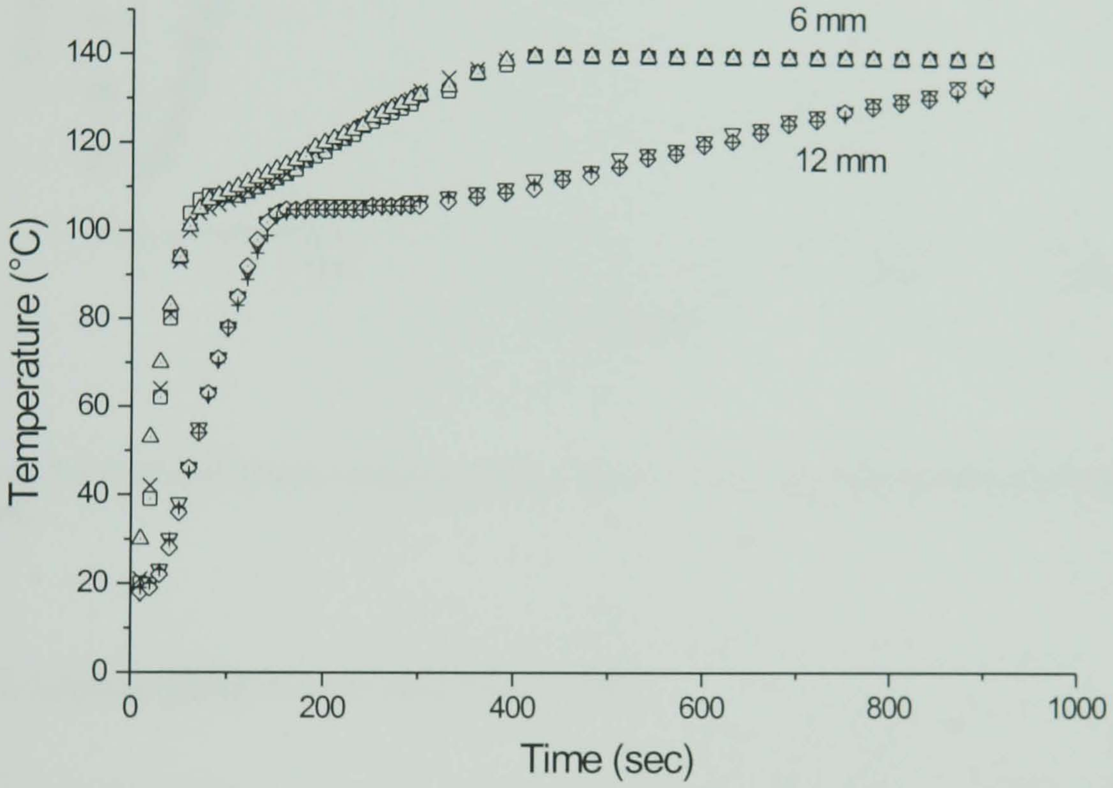


Figure 7.2 Effect of board thickness on the time-core layer temperature relationship (platen temperature 140°C).

The effect of platen temperature on the time core-layer temperature relationship for a 12 mm board is shown in Figure 7.3. An increase in platen temperature results in an increase in the rate of energy input from the platens to the particle mattress (Kavvouras, 1977). The rate of temperature rise at the mattress core, therefore, also increases.

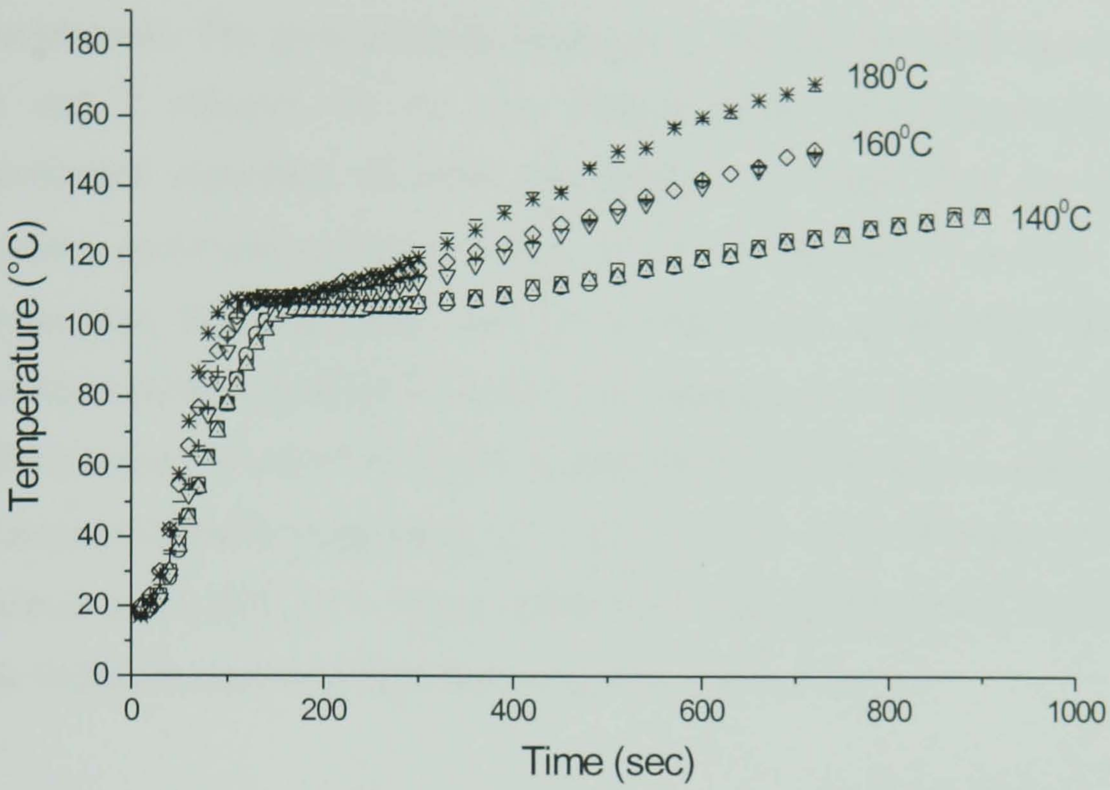


Figure 7.3 Effect of platen temperature on the time-core layer temperature relationship for 12 mm board.

7.3.2 Lignin-phenol-formaldehyde resins

Boards prepared using LPF resins were tested for their physical and mechanical properties as described in Section 7.2.7. The results of these experiments are summarised below.

7.3.2.1 Internal bond strength (IB)

The bonding ability of resins made with different additions of organosolv lignin (Alcell® lignin) was tested and compared with that of a PF_com resin and a PF_made resin.

As noted previously (Section 7.2.1), various press temperatures (140°C, 160°C and 180° C) and times (3 minutes, 8 minutes and 15 minutes and 5 minutes, 8 minutes and 15 minutes for 6 mm and 12 mm particleboards, respectively) were used for production of particleboards. The particleboards produced at the shortest press time (3 minutes for 6 mm and 5 minutes for 12 mm particleboards) were, observably, only poorly consolidated regardless of press temperature and resin type and testing was not therefore, performed on these boards. 12 mm particleboards pressed at 140°C for 8 minutes split; the conclusion made was that there was no bonding. However, at 180°C more favourable conditions exist for cross-linking in the LPF resins. This is manifested by the measured increase in the IB strength of the particleboards. The internal bond data of the particleboards made using PF_com, PF_made and LPF resins [LPF3 (20% lignin substitute and LPF5 (40% lignin substitute)] utilising 8 minutes and 15 minutes press cycle times are summarised below in Figures 7.4a to 7.4d.

Figures 7.4a and 7.4b illustrate the effect of various press times and temperatures on the internal bond strength of 12 mm particleboards. Particleboards pressed at 140°C for 8 minutes were split, therefore, no values obtained. PF_com resin gave the best internal bond values of the resins studied. But IB value of PF_made resin was similar to that of PF_com resin. Increasing levels of lignin in the resin resulted in decreasing IB values. The hardening time of LPF5 resin (40% lignin substitute) at 150°C in a test tube was 6.45 minutes, for the LPF3 resin (20% lignin substitute) 3.49 minutes and for the PF_com resin 3.2 minutes. 12 mm particleboards made at 180°C press temperature and 15 minutes press time using LPF3 and LPF5 resins showed a reduction in IB value of 21% and 33%, respectively, compared to PF_com resin. Figure 7.4a shows that increasing press temperature resulted in increased IB values of boards made using LPF3 and LPF5 resins. Linear regression (see Figure 7.5) indicated a high degree of correlation between press temperature and IB values of LPF3 (R^2= 0.89) and LPF5 (R^2= 0.84) resins.

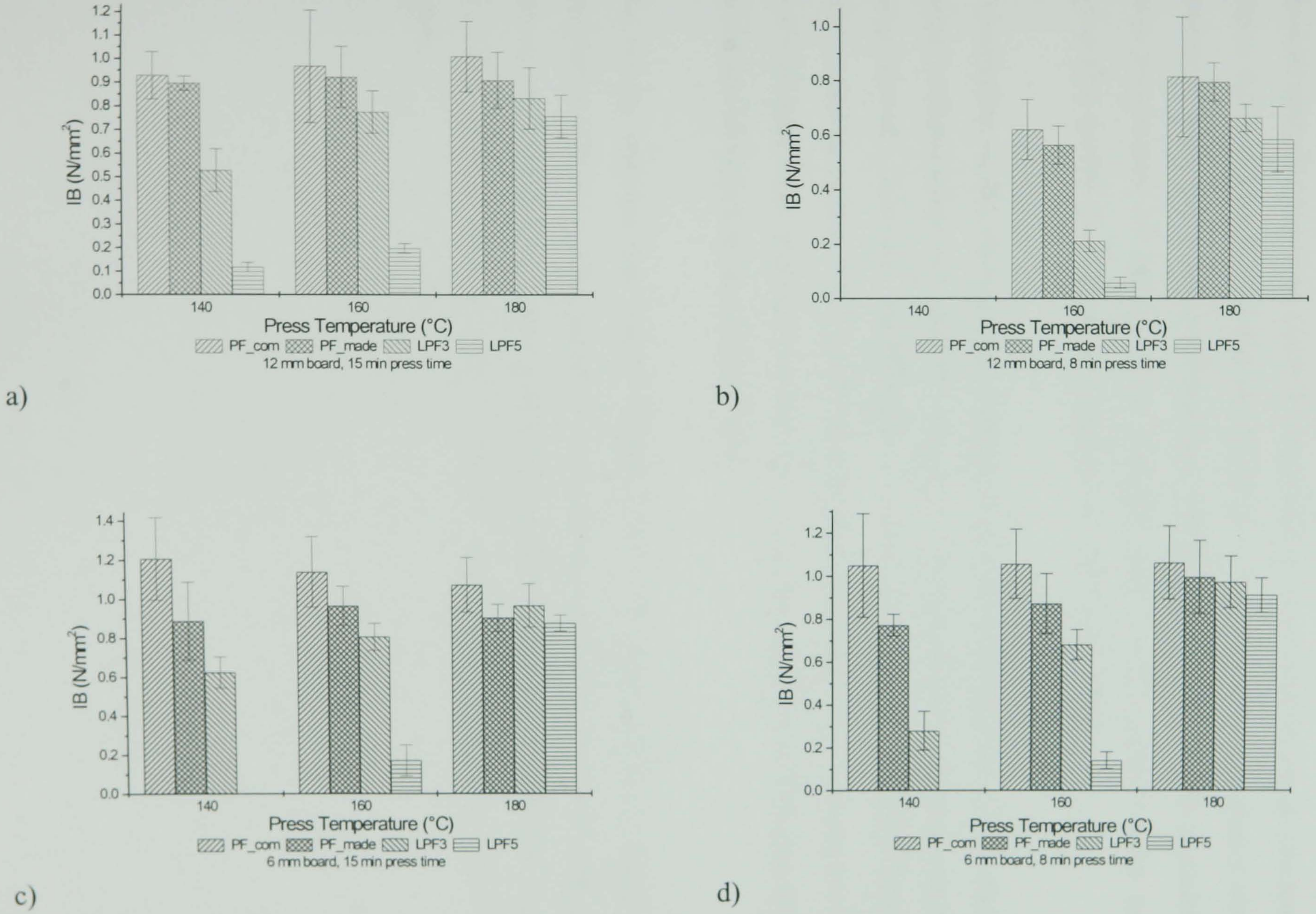


Figure 7.4 Internal bond strength properties of the resins for 12 and 6 mm boards at different press temperatures and press times.

Figures 7.4c and 7.4d illustrate the effect of press time and temperature on the internal bond strength of 6 mm particleboards. The IB of boards bonded with PF_com and pressed for 15 minutes did not vary significantly ($P>0.05$) with press temperature.

Press temperature has to be carefully controlled to ensure that the panel core temperature attains the level required to cure the adhesive without subjecting the board surface to a prolonged high, degradative temperature. In the production of 6 mm particleboards, a press temperature of 160-180°C is normally used for PF resins in order to achieve acceptable quality in all gluelines (Chow *et al.*, 1975; Irle, 1986).

Examination of the internal bond strength of 6 mm particleboards reveals that the LPF resins performed less well than PF_com resin. This mirrors the trend observed in 12 mm particleboards. However, the IB value of 6 mm specimens for the LPF3 (20% lignin) resin is similar to that of PF_made resin at press cycle times of 8 minutes and longer at 180°C (Figure 7.4c). Figures 7.4c and 7.4d, show that resin LPF5 (40% lignin) imparted the lowest IB values of the resins studied.

The results indicate that boards bonded with LPF resins exhibit a highly positive correlation with increasing platen temperature; resins containing lignin were slower to cure at low temperature. This confirms the findings of other workers (Kazayawoko *et al.*, 1992; Sellers, 1993) who have reported temperature to be a key factor for LPF resins.

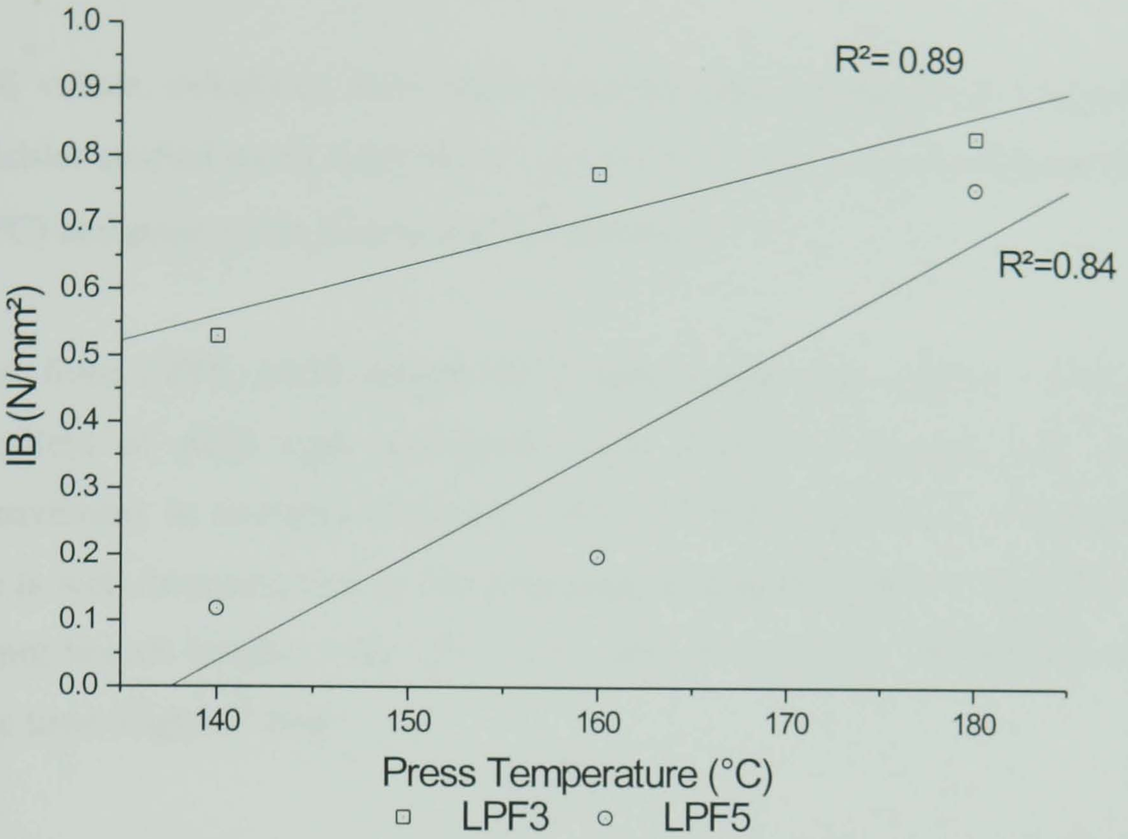


Figure 7.5 The effect of press temperature on IB of boards bonded with LPF3 or LPF5 resins (press cycle time was 15 min).

There was a clear trend of increasing IB with increasing temperature and press cycle time for both 6 mm and 12 mm boards bonded with lignin resins. Increasing press time from 8 minutes to 15 minutes increased the bonding strength of the boards produced using both LPF3 and LPF5. 6 mm particleboards bonded with LPF resins exhibited higher internal bonding strength than 12 mm boards at 15 minutes. Thin boards pressed for 8 minutes exhibited similar IB to 12 mm boards pressed for 15 minutes. This could be said to rein force the importance of core cross-linking of LPF resins. Furthermore, prolongation of press time from 3 to 15 minutes where LPF resins were used had a similar effect to that of increasing press temperature. Indeed, the use of extended press cycle times and elevated platen temperatures results in panels with IB's similar to that of a PF_com resin.

7.3.2.2 Modulus of elasticity (MOE)

MOE values, calculated from static bending tests, are shown in Figures 7.6a to 7.6d. Variables studied were; thickness (6 mm and 12 mm), press temperature (140°C, 160°C, 180°C) and press cycle time (8 and 15 minutes).

Apart from LPF5, MOE values of 12 mm boards were similar (circa 2000 N/mm^2) regardless of resin type and press cycle time (see Figures 7.6a and 7.6b). The improvement in strength of lignin resins with increasing press temperature and cycle time is well demonstrated by the behaviour of boards bonded with LPF5 (Figure 7.6a). 12 mm boards bonded with LPF5 resin split at low press temperature and short press cycle time (Figure 7.6b).

In the case of 6 mm boards (Figure 7.6c), LPF3 gave the highest MOE of all resin types at press cycle times of 8 and 15 minutes. Indeed, the MOE of 6 mm boards bonded with LPF3 was around 20% higher than boards bonded with PF_com at 160°C and 180°C using a 15 minutes press cycle. Increasing MOE of boards bonded with lignin resins is again well demonstrated by the behaviour of LPF5 (Figures 7.6c and 7.6d). It appears that, when fully cross-linked, lignin imparts elasticity to the resin.

The presence of lignin had less observable affect on the MOE of 12 mm boards pressed at 180°C for 15 minutes (Figure 7.6a). However, the best MOE results for both LPF resins were obtained at the high press temperature (180°C) and long press time (15 minutes).

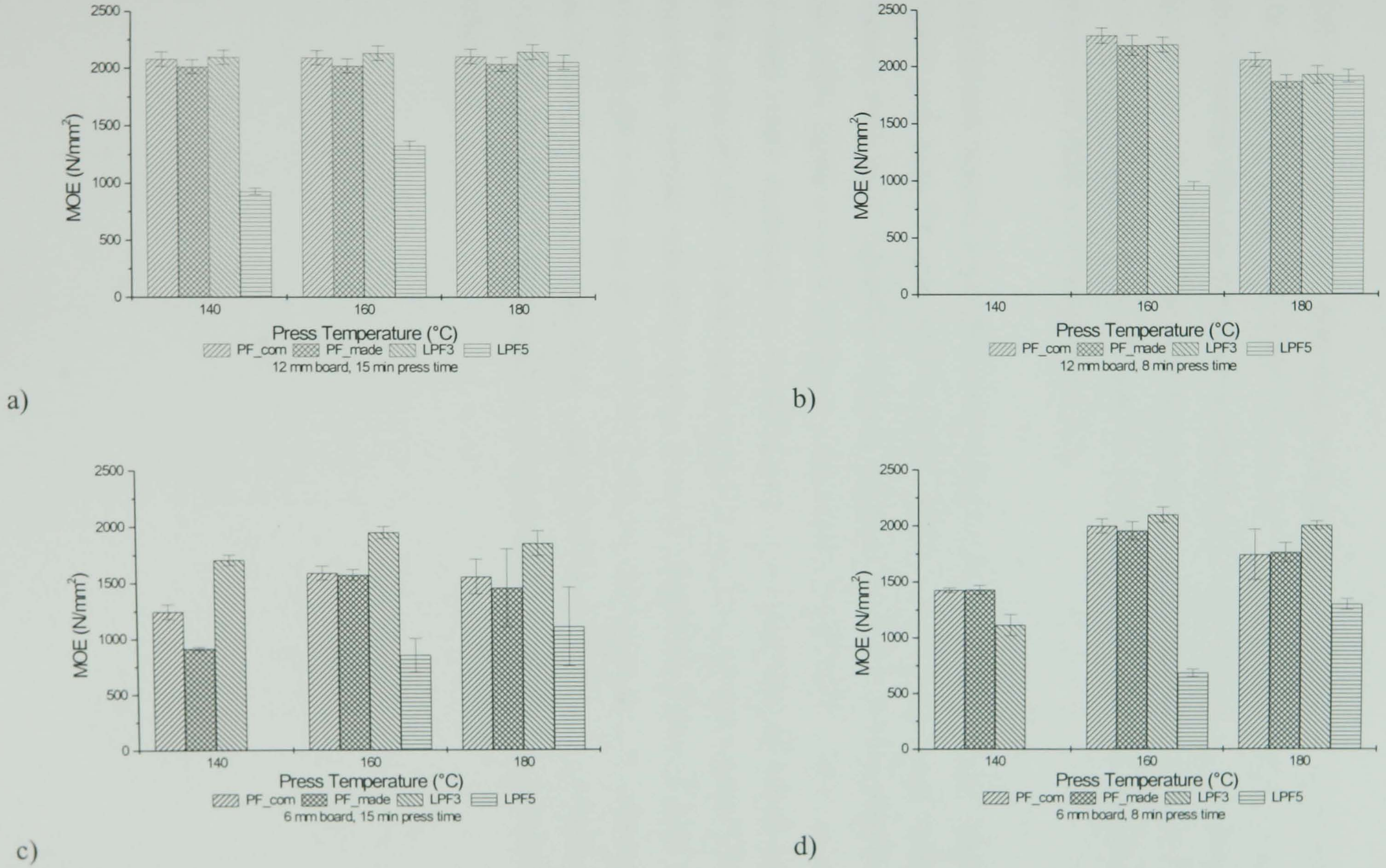


Figure 7.6 The MOE properties of the resins for 12 mm and 6 mm boards at 15 and 8 minutes press times.

7.3.2.3 Modulus of rupture (MOR)

MOR values are calculated from static bending data; results are shown in Figures 7.7a to 7.7d. Figures 7.7a and 7.7b show that 12 mm boards bonded with PF_com exhibited better bending strength than boards bonded with experimental resins. Boards bonded with PF_com showed at least 18% higher MOR values than both LPF3 and LPF5 boards at press cycle times of 8 and 15 minutes. There was no significant ($P>0.05$) difference between the MOR of PF_made and LPF3.

6 mm boards bonded with LPF3 resin exhibited similar MOR strength values to boards bonded with both PF_com and PF_made resins, where longer press cycle times (15 minutes) were used, regardless of press temperature. 6 mm boards bonded with LPF5 resin (40% lignin content) exhibited considerably lower MOR values, as compared to the other resins evaluated. As the press time and temperature increased, however, the MOR values of LPF5 bonded boards increased significantly (see Figures 7.7c and 7.7d). Regression analysis indicated a strong positive relationship between press temperature and MOR ($R^2 = 0.99$ and $R^2 = 0.99$ for 8 and 15 minutes press cycle times respectively) (see Figure 7.8). The ultimate MOR value was still well below that of other resins, but it is possible that better results would have been achieved with LPF5, given sufficient time in the press.

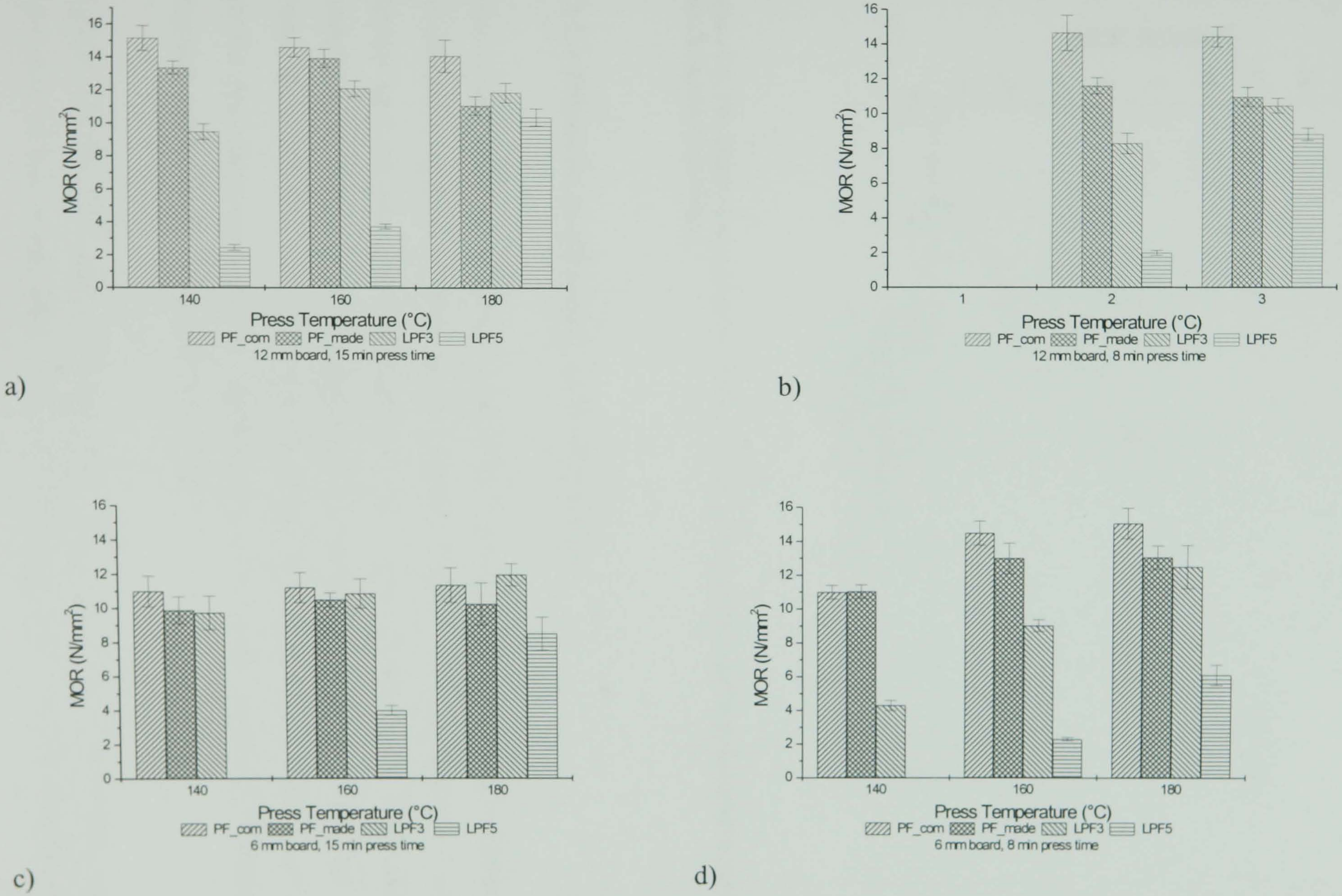


Figure 7.7 MOR strength properties of the resins for 12 and 6 mm boards at 15 and 8 minutes press times.

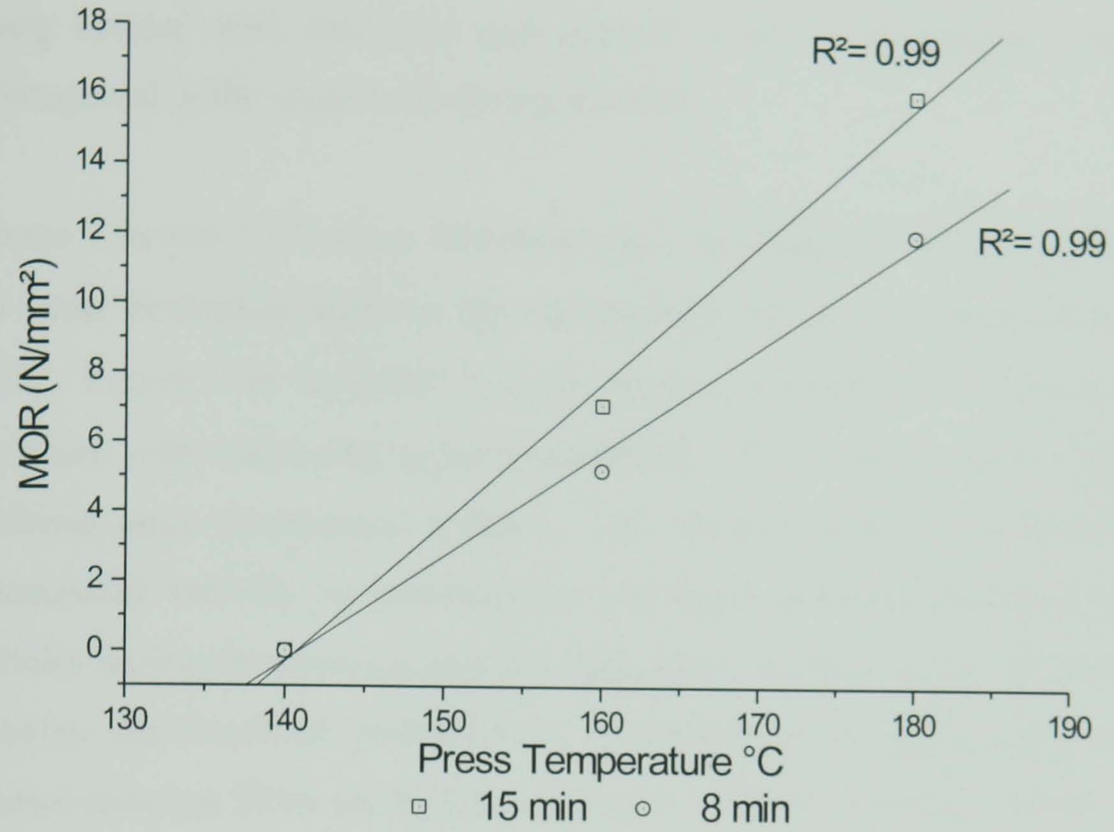


Figure 7.8 The effect of press temperature on MOR of the boards bonded with LPF5 resin (8 and 15 minutes press cycle times).

7.3.2.4 Thickness swelling and water absorption

Dimensional stability (DS) was assessed by measuring thickness swell in water, after 2 and 24 hours immersion. Dimensional stability is often a limiting factor with regard to end-use applications. Water absorption is the % weight gain by the board due to the absorption of water but is strongly related to thickness swelling (Vital and Wilson, 1980). Manufacturing variables other than resin type, for example; particle species mix; particle geometry; wax; press conditions, also affect these properties (Marian, 1958; Jongasen and Murphey, 1961; Burrows, 1961).

Figures 7.9a to 7.9d and 7.10a to 7.10d show the thickness swelling and water absorption of test boards after 2 and 24 hours immersion. Particleboards bonded with

LPF5 (40%) resin exhibited the highest thickness swell and water absorption. Indeed, panels bonded with this resin and pressed at low temperatures (140°C and 160°C) disintegrated in the water bath during the test.

Figures 7.9a and 7.10a show that there was a significant difference in thickness swelling and water absorption between the experimental 12 mm boards produced at 140°C and 180°C. Figure 7.9a indicated that the thickness swelling of the boards significantly decreases with increasing press temperature. All 12 mm boards produced at 140°C exhibited poor dimensional stability. The positive influence of press temperature on dimensional stability is enhanced by increased levels of plasticisation of the wood particles during the pressing process. This leads to lower levels of residual stress in the particles. An important contributor to the process of thickness swelling is the relief of residual stress as fibres are softened during immersion (Maloney, 1993).

When the press temperature was increased from 140°C to 180°C, there was a reduction from ≈25% to 15% in thickness swelling of the 12 mm particleboard samples bonded with PF_made and LPF3 resins after 2 hours immersion. In boards, certain temperatures are required for curing of the resins. In most cases, the curing is best achieved at the upper limit of the temperature range of the particular resin (Kazayawoko *et al.*, 1992). When higher temperatures are used therefore, there is more resin cure than at lower temperature and therefore better bonding.

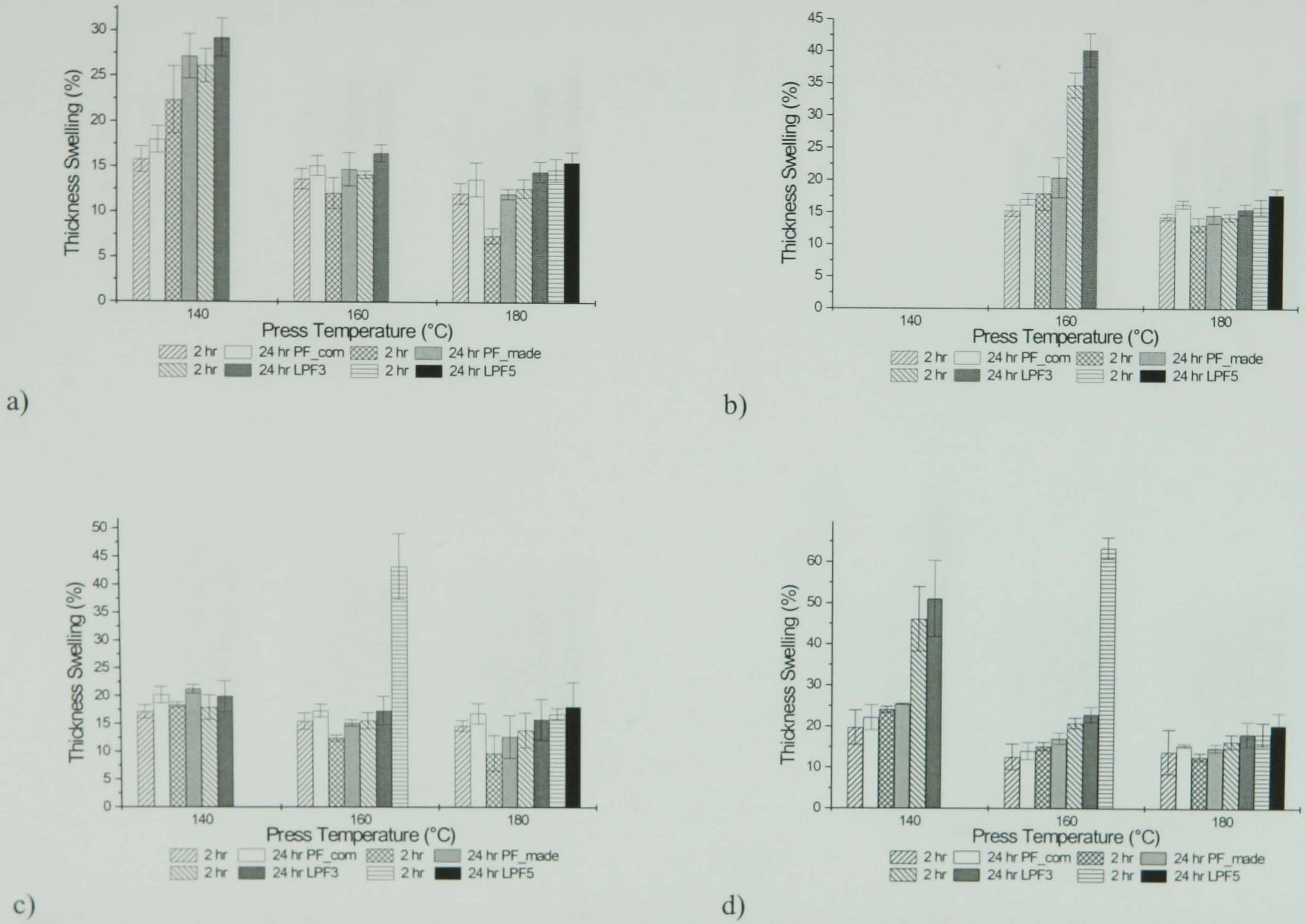
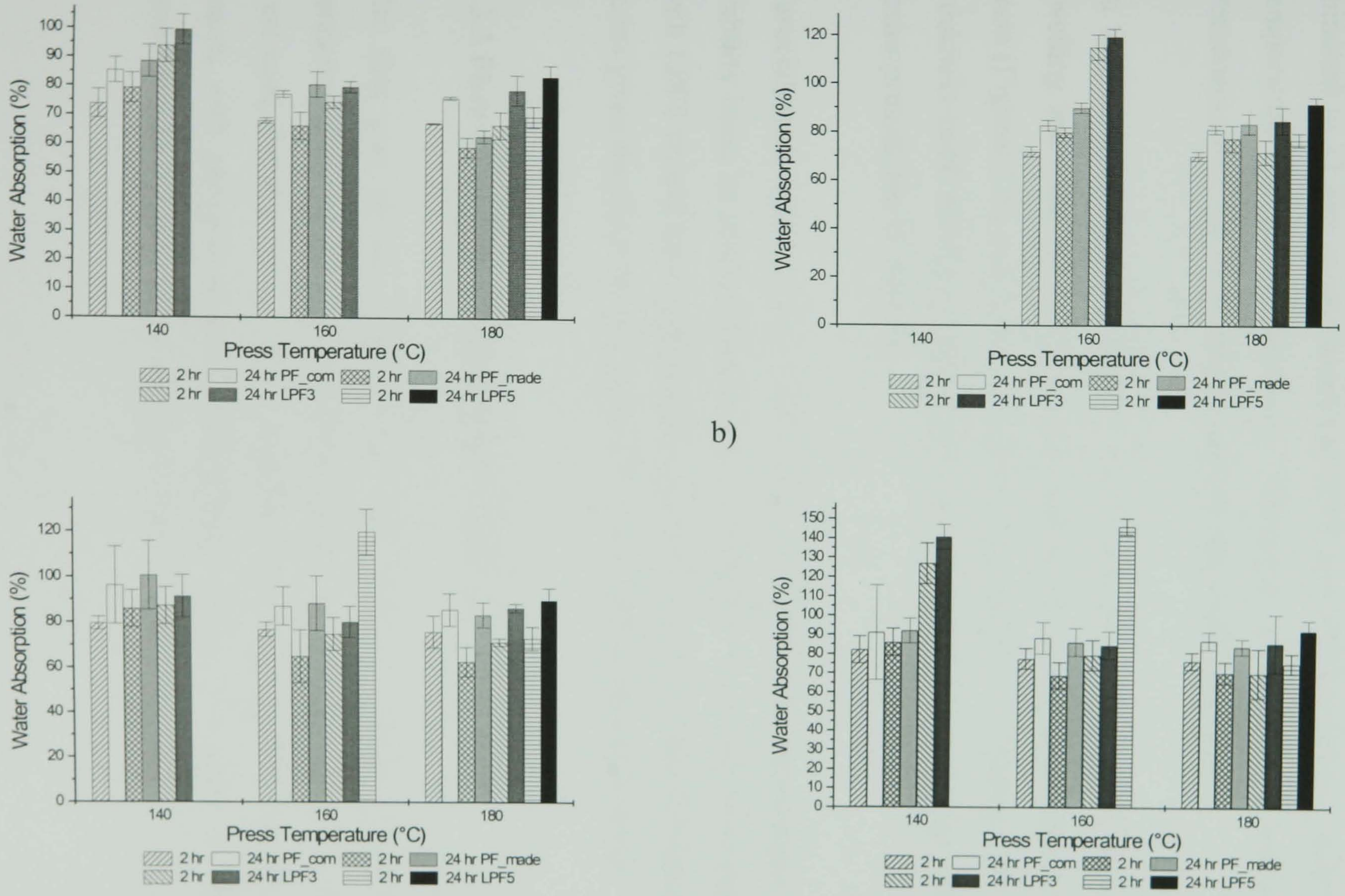


Figure 7.9 Thickness swelling values of 12 mm boards at press times of (a) 15 minutes, (b) 8 minutes; 6 mm boards at press times of (c) 15 minutes, (d) 8 minutes.



a)

b)

c)

d)

Figure 7.10 Water absorption values of 12 mm boards at press times of (a) 15 minutes, (b) 8 minutes; 6 mm boards at press times of (c) 15 minutes, (d) 8 minutes.

The results indicated that increasing press cycle time results in boards with better dimensional stability. Where short press cycle times are utilised, it appears that resin in the core of the board is not cured; this affects dimensional stability. Lower press times (8 minutes) led to significantly poorer dimensional stability than the longer press times (15 minutes) in 12 mm particleboard (at 160°C and 140°C press temperatures). At a platen temperature of 180°C, significant differences in thickness swelling after 2 hours immersion were not observed in boards bonded with LPF resins.

In the case of both 6 mm and 12 mm boards pressed at 180°C, the lowest thickness swelling and water absorption values were obtained from boards bonded with PF_made resin (Figures 7.9a and 7.10a). There were no significant differences ($P>0.05$) in 2 hours thickness swell between 6 mm and 12 mm panels bonded with the LPF3 and PF_com resins pressed for 15 minutes.

Particleboards bonded with LPF5 resin exhibited poor dimensional stability. Since stability bears an inverse relationship to strength, it is not surprising that boards bonded with LPF5 should have significantly higher % swell than boards bonded with the other resins given the observations made with regard to panel strength above.

7.3.3 Phenolated-lignin-formaldehyde resins

The first part of the experimental work showed (Section 7.3.2) that high press temperature and long press cycle times resulted in better board quality, where LPF resins were used. For this reason, only a high press temperature, (180°C), was used to produce boards with phenolated-lignin-formaldehyde resins. The types of phenolated-lignin-formaldehyde resins used are shown in Table 7.2 (Section 7.2.1).

7.3.3.1 Internal bond strength of the phenolated-lignin-formaldehyde resins

IB values of boards bonded with phenolated-lignin-formaldehyde resins were determined and compared with those of boards bonded PF_com resin. Figures 7.11 and 7.12 summarise the effect of press time and lignin content on internal bond strength. Figure 7.11 represents the effect of lignin substitution level in resins on the IB values of 12 mm particleboards. It is apparent that 5 minutes press time was not adequate to fully cure the experimental resin and low IB values resulted. As can be seen from Figure 7.11, increasing addition of lignin in all LPFA resins resulted in decreasing IB (from 1.1 N/mm^2 to 0.6 N/mm^2 for 12 mm thick boards at 15 minutes press cycle time).

Notwithstanding, the IB of 12 mm boards made with LPF 40A (≈20% lignin) were equal to or better than those bonded with PF_com resin. IB tended to decrease with increasing addition of lignin. Particleboards bonded with LPF 60A resin (≈30% lignin) showed 33% and 20% reductions in the IB values compared to particleboards bonded with PF_com resins at 8 and 15 minutes press cycle times, respectively. The influence of increasing press cycle time, again, demonstrated. Particleboards bonded with LPF 70A (≈25% lignin) showed the poorest IB values of the resins studied. These values may reflect the low formaldehyde ratio of LPF 70A resin, compared to other phenolated-lignin-formaldehyde resins (see Appendix 2). As shown in Chapter 6, an increase in formaldehyde concentration improved the curing property of lignin copolymers. Since LPF 70A had the lowest formaldehyde content among the phenolated-lignin-formaldehyde resins, it is not therefore surprising that low IB values result.

As can be seen from Figure 7.12, hot pressing of 6 mm boards at the shortest time (3 minutes) did not permit adequate curing and poor IB values resulted. In contrast, whilst increasing lignin substitution level had a detrimental effect on IB values of all 12 mm boards, it is evident that lignin content had no significant ($P>0.05$) effect on the IB values of 6 mm boards at 15 minutes press time (Figure 7.12).

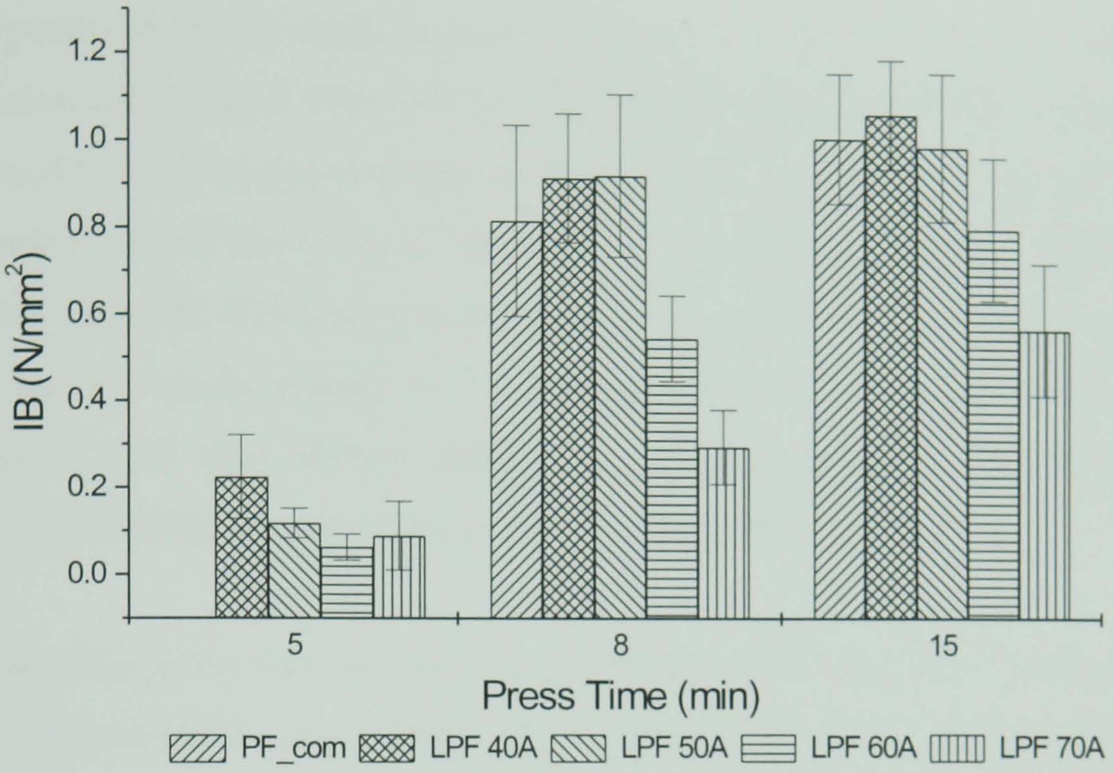


Figure 7.11 The internal bond strength of 12 mm boards bonded with phenolated-lignin-formaldehyde resins at various press cycle times.

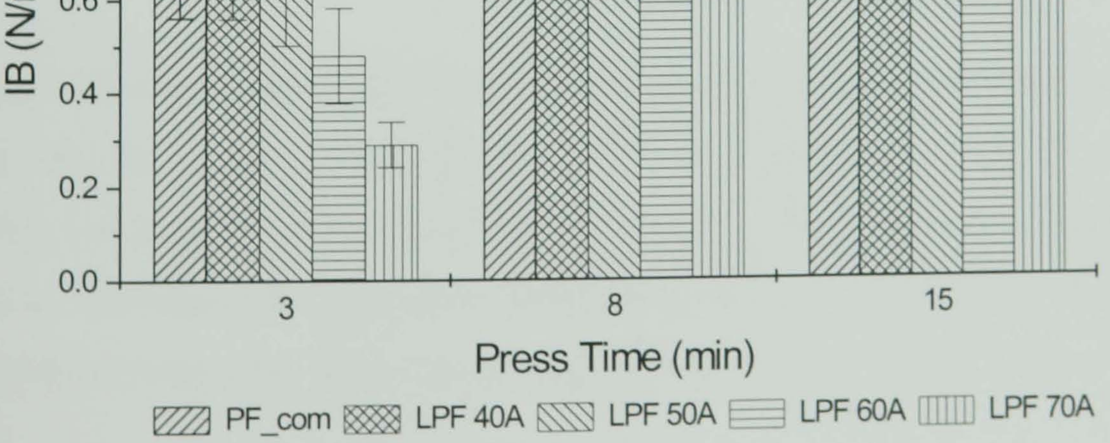


Figure 7.12 The internal bond strength of 6 mm boards bonded with phenolated-lignin-formaldehyde resins at various press cycle times.

The results from this study indicate (Figures 7.11 and 7.12) that 6 mm and 12 mm particleboards bonded with LPF 50A (made with ≈25% phenolated lignin) have almost identical ($P>0.05$) internal bonding strength to PF_com resin. When lignin content was increased beyond this level, IB decreased. It was noted that the IB values of the boards bonded with LPF 40A resin (containing ≈20% lignin) were significantly ($P<0.05$) higher than that of boards bonded with LPF 60A and LPF 70A resins. Even though the IB values of LPF 40A bonded boards were slightly higher than boards bonded with PF_com, this higher value was not statistically significant ($P>0.05$).

On the basis of the data it can be concluded that, with respect to IB, phenolated-lignin-formaldehyde resins can be used successfully as adhesives in particleboards. Satisfactory strength can be achieved at substitution levels of lignin for phenol up to 30%. Furthermore, extension of press cycle time allows the use of greater percentages of lignin in resin.

7.3.3.2 Modulus of elasticity of the phenolated-lignin-formaldehyde resins

MOE of 12 mm and 6 mm particleboards bonded with PF_com, LPF 40A, LPF 50A, LPF 60A and LPF 70A resins are summarised in Figures 7.13 and 7.14, respectively.

Figure 7.13 shows that resin LPF 40A gave the best MOE values at 8 and 15 minutes press time for 12 mm particleboards. LPF 50A (≈25% lignin) and PF_com resin gave slightly lower MOE values than LPF 40A resin. From this data, it appears that MOE tends to decrease with increasing addition of lignin. Nevertheless, values are still at acceptable levels. LPF 40A imparts higher MOE values than PF_com at all press cycle times.

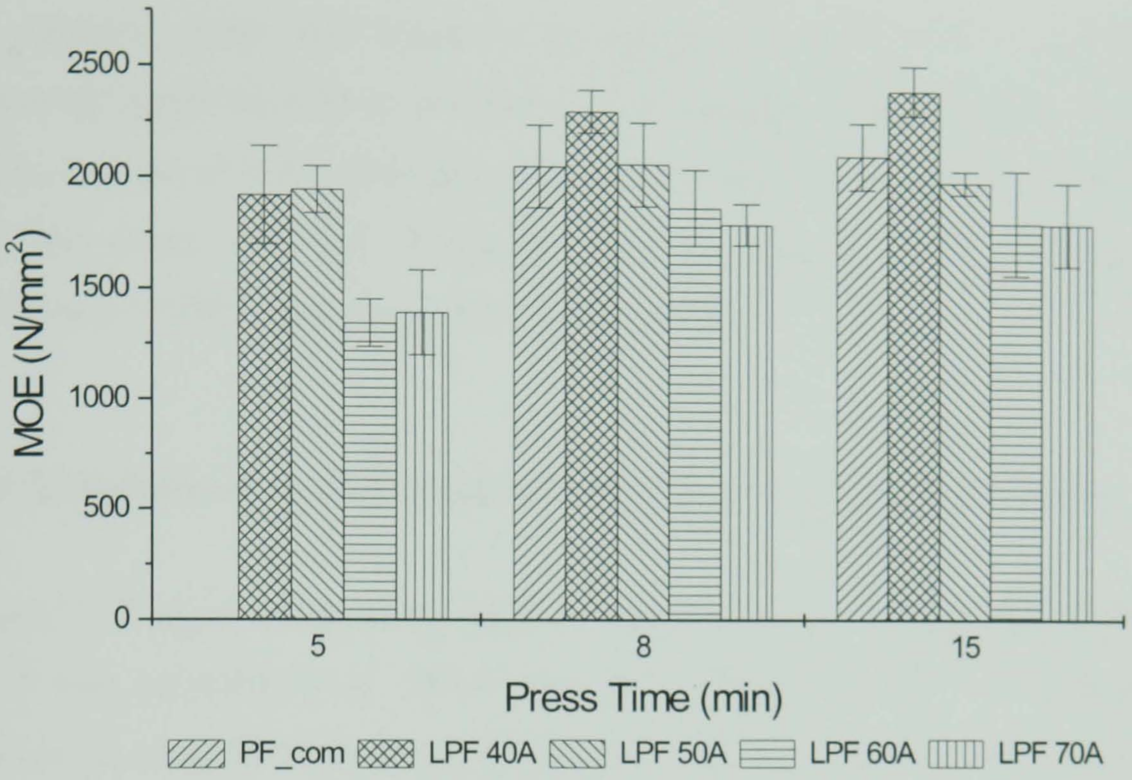


Figure 7.13 The MOE values of 12 mm particleboards made with phenolated-lignin formaldehyde and PF_com resins.

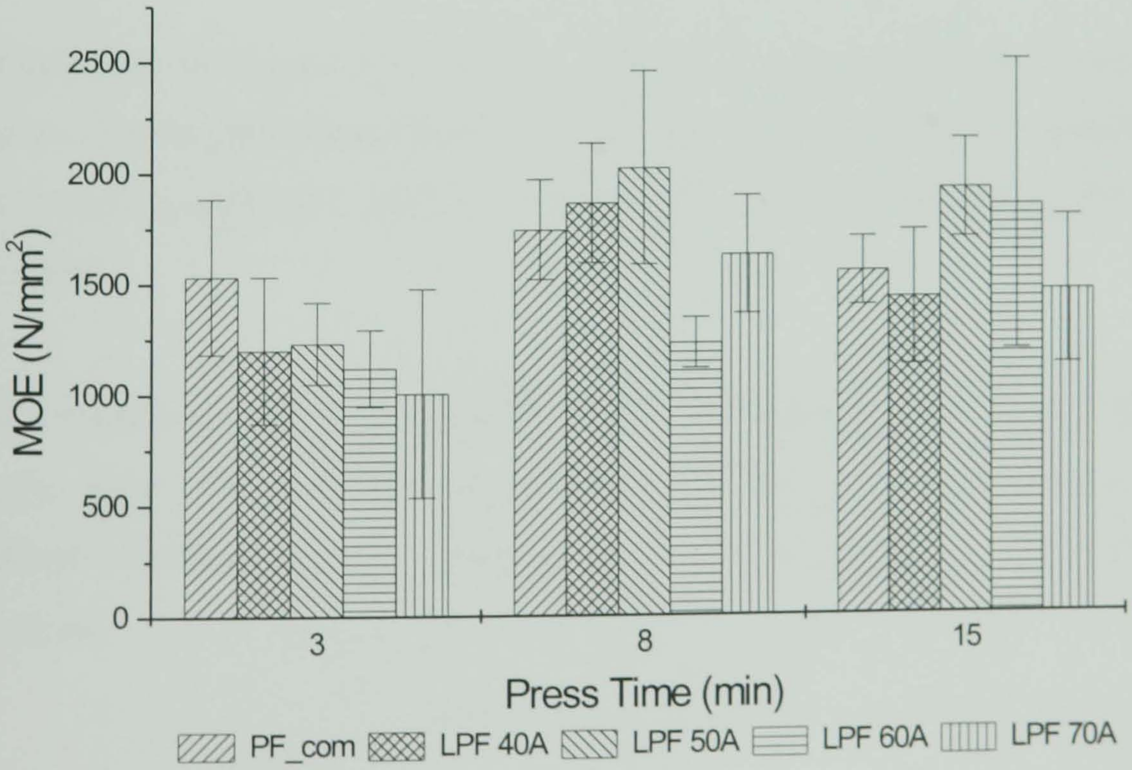


Figure 7.14 The MOE values of 6 mm particleboards made with phenolated-lignin formaldehyde and PF_com resins.

The opposite trend was observed in results obtained from 6 mm particleboards. Increasing lignin content in the resin led to improved MOE (Figure 7.14). For 6 mm boards, the use of LPF 60A resin resulted in higher MOE than PF_com, LPF 40A and LPF 50A resins at 8 and 15 minutes press time (Figure 7.14). The reason for these results may be that, lignin improved the elasticity.

7.3.3.3 Modulus of rupture of phenolated-lignin-formaldehyde resins

Figures 7.15 and 7.16 show the effect of lignin substitution in resins on the MOR of 12 and 6 mm particleboards. There were no significant ($P>0.05$) differences in MOR between 12 mm particleboards bonded with LPF 40A and PF_com. Again, it was noted that as the lignin substitution level increased, MOR values of the boards tended to decrease (Figure 7.15) except in the case of 6 mm panels pressed for 15 minutes where the trend is less obvious.

As illustrated in Figure 7.16, MOR values of 6 mm particleboards showed a similar trend to 12 mm particleboards at 8 minutes press cycle time. At 15 minutes press cycle time, however, LPF 40A and PF_com exhibited a lower MOR than LPF 50A and LPF 60A resins.

Resins containing ≈20% lignin (LPF 40A) showed higher MOE and MOR than the PF_com resin. The incorporation of lignin molecules in the resin matrix seems to give increased flexibility to the cured glueline and, consequently improved mechanical properties.

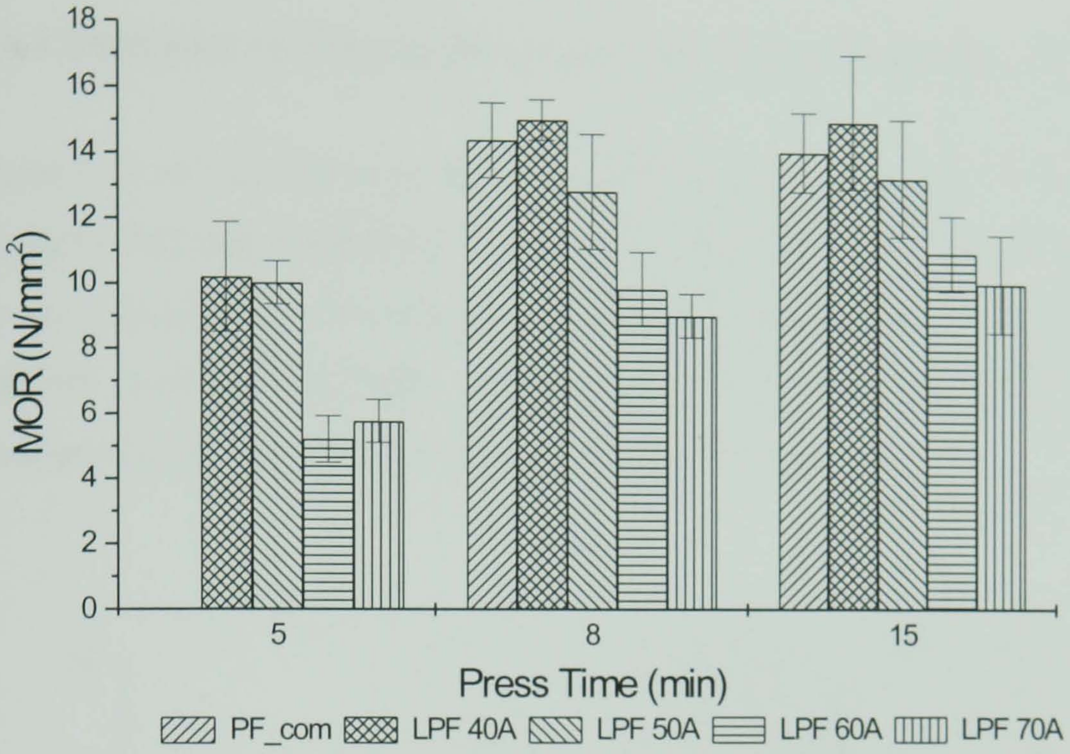


Figure 7.15 The MOR values of 12 mm particleboards made with phenolated-lignin-formaldehyde and PF_com resins.

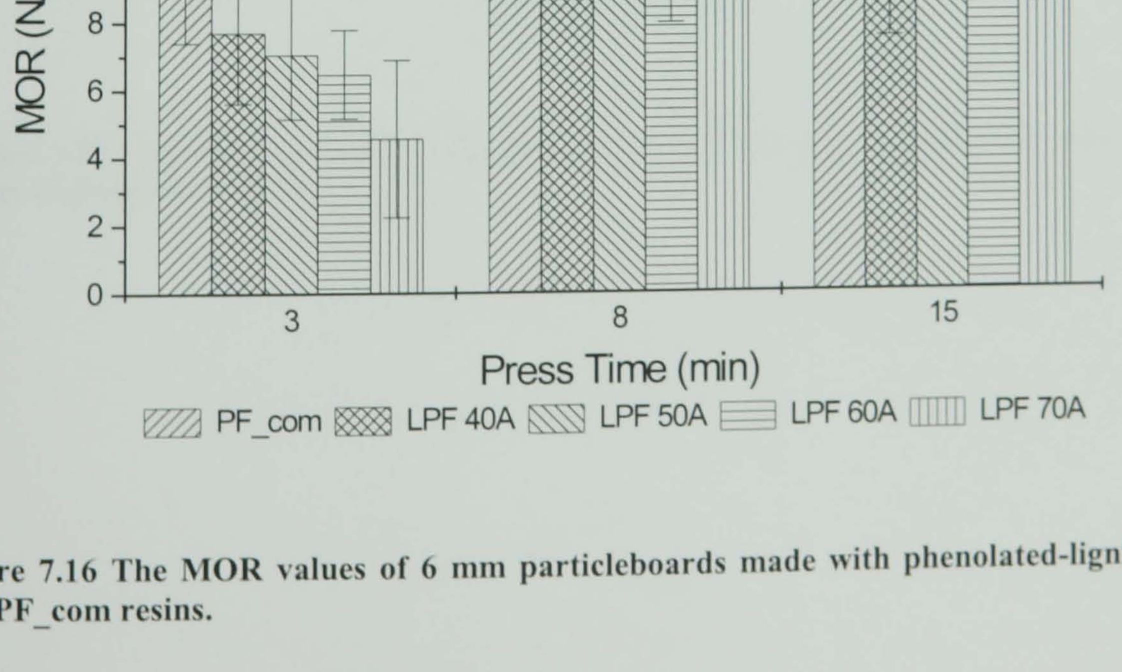


Figure 7.16 The MOR values of 6 mm particleboards made with phenolated-lignin-formaldehyde and PF_com resins.

7.3.3.4 Thickness swelling of phenolated-lignin-formaldehyde resins

Figures 7.17 to 7.20 represent the percentage thickness swell and water absorption of 12 mm and 6 mm particleboards, respectively. It has been noted that 5 minutes press time was not adequate to cure the resins in 12 mm boards. As a result, either very high thickness swelling (26.5%) and water absorption (90.8%) were recorded or disintegration occurred within 2 hours of immersion in water.

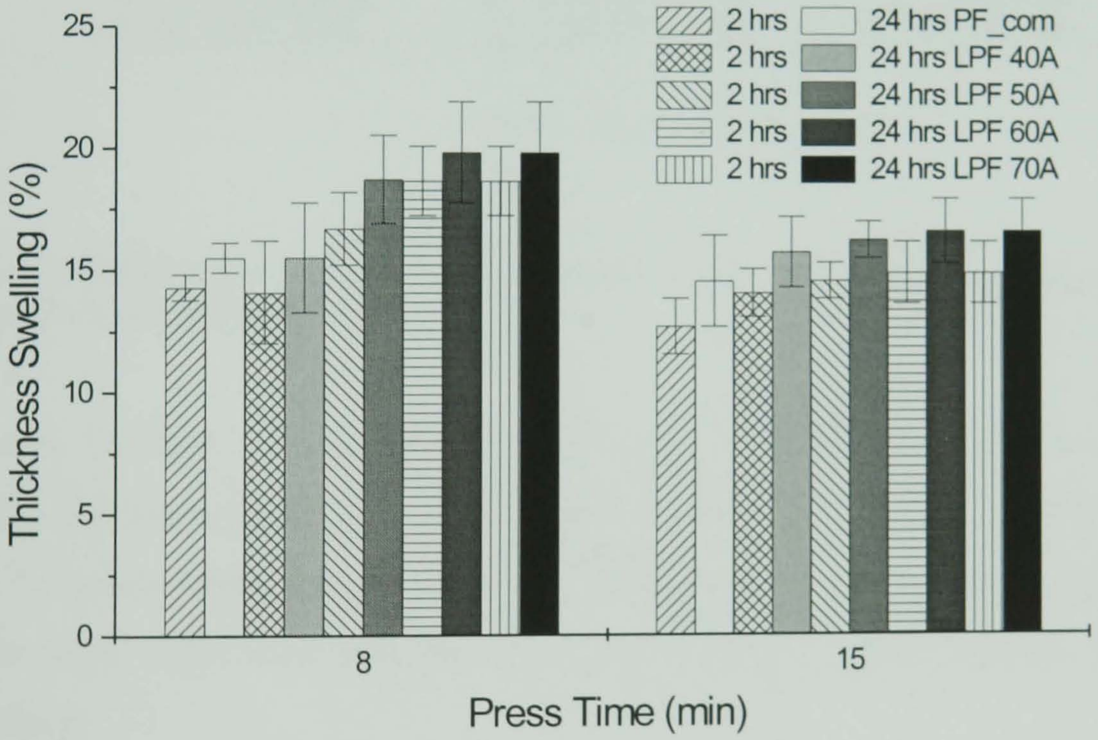


Figure 7.17 Thickness swell of 12 mm particleboard specimens bonded with various resin types at a range of press cycle times.

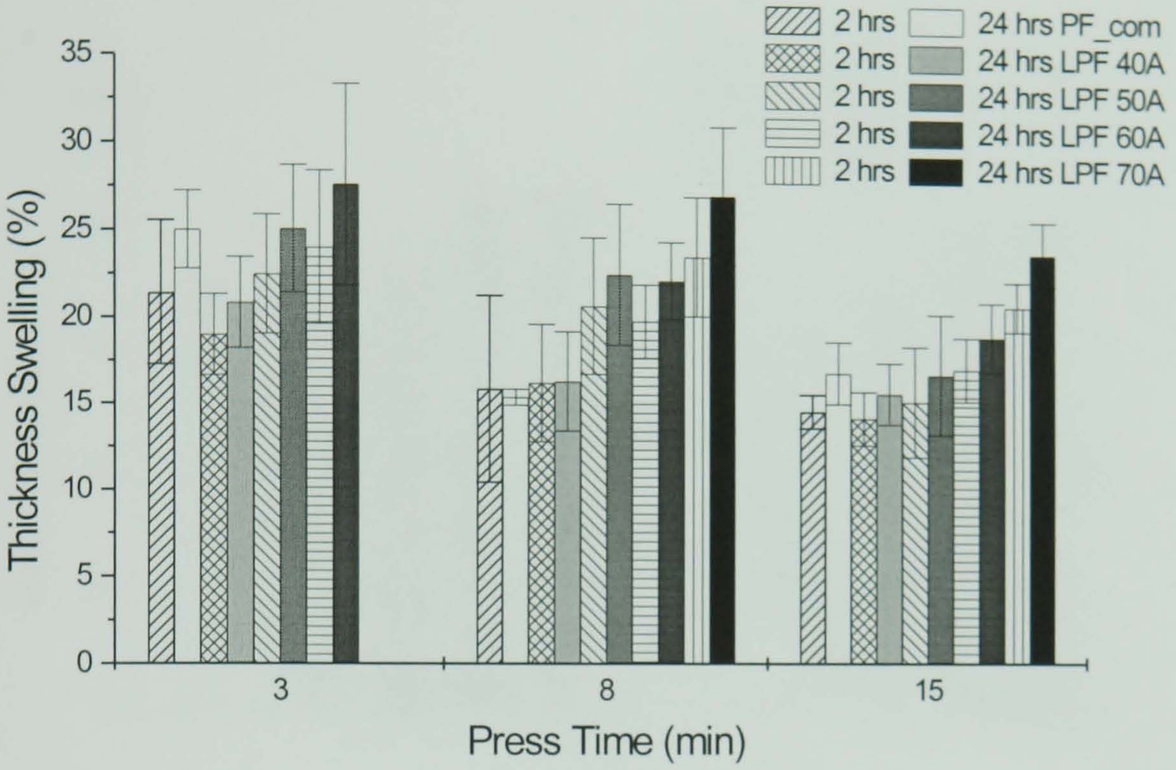


Figure 7.18 Thickness swell of 6 mm particleboard specimens bonded with various resin types at a range of press cycle times.

Figures 7.17 and 7.19 show the effects of resin type and press cycle time (8, 15 minutes) on the thickness swelling and water absorption of 12 mm particleboards after 2 hours and 24 hours immersion in water. As can be seen from Figure 7.17, for 8 minutes press cycle time, LPF 40A and PF_com resin bonded boards showed similar thickness swelling.

In contrast, differences between resins became less marked as press time was increased from 8 to 15 minutes press cycle time. Furthermore, LPF 40A and LPF 50A resin bonded boards absorbed less water than PF_com bonded board (Figure 7.19).

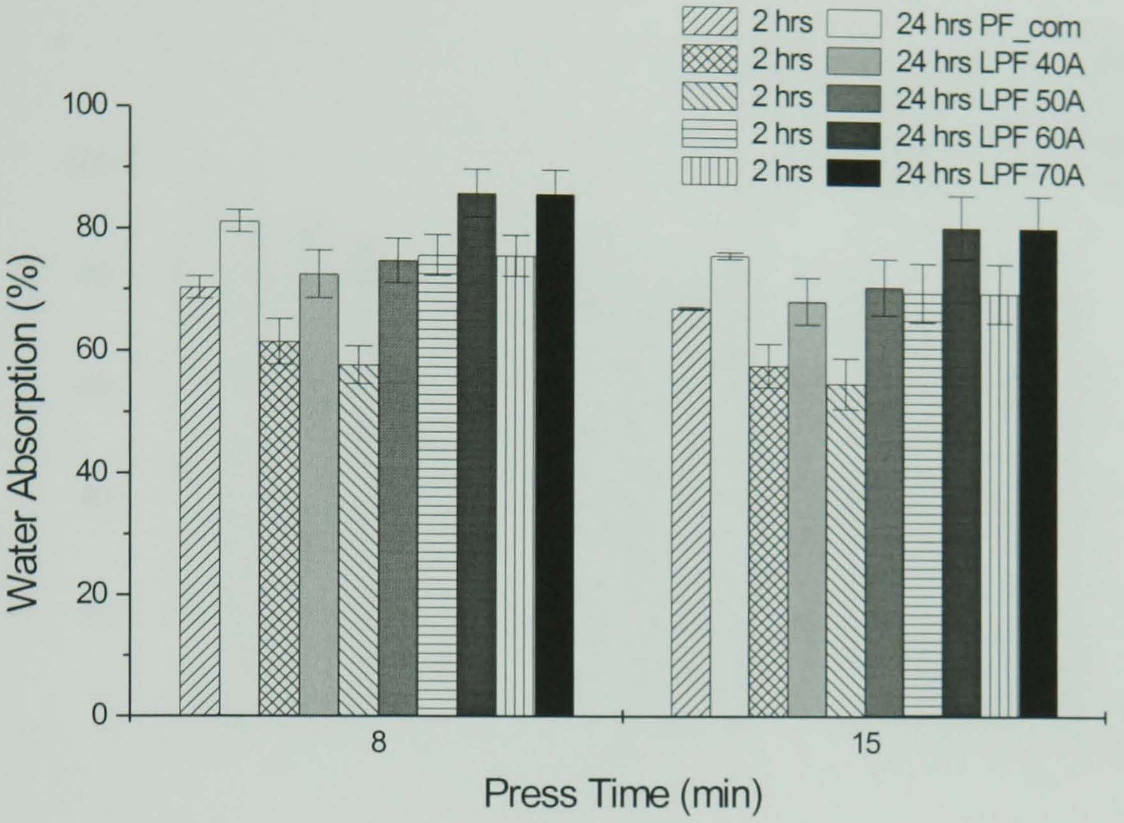


Figure 7.19 Water absorption of 12 mm particleboard specimens at various resin types and press cycle times.

Thickness swelling and water absorption of 6 mm boards are shown in Figure 7.18 and Figure 7.20 respectively. From these results, it is apparent that the boards made using LPF 70A (≈25% lignin) resin gave the highest thickness swelling. This can be explained by the fact that LPF 70A resin contains lower levels of formaldehyde (F/L = 1.9) than other LPFA resins (see Appendix 2). Again, better results were obtained from longer press times. For 8 and 15 minutes press time, there was a linear relationship between thickness swelling and the lignin ratio of the resins. For both press times, LPF 40A and PF_com exhibited similar levels of thickness swell.

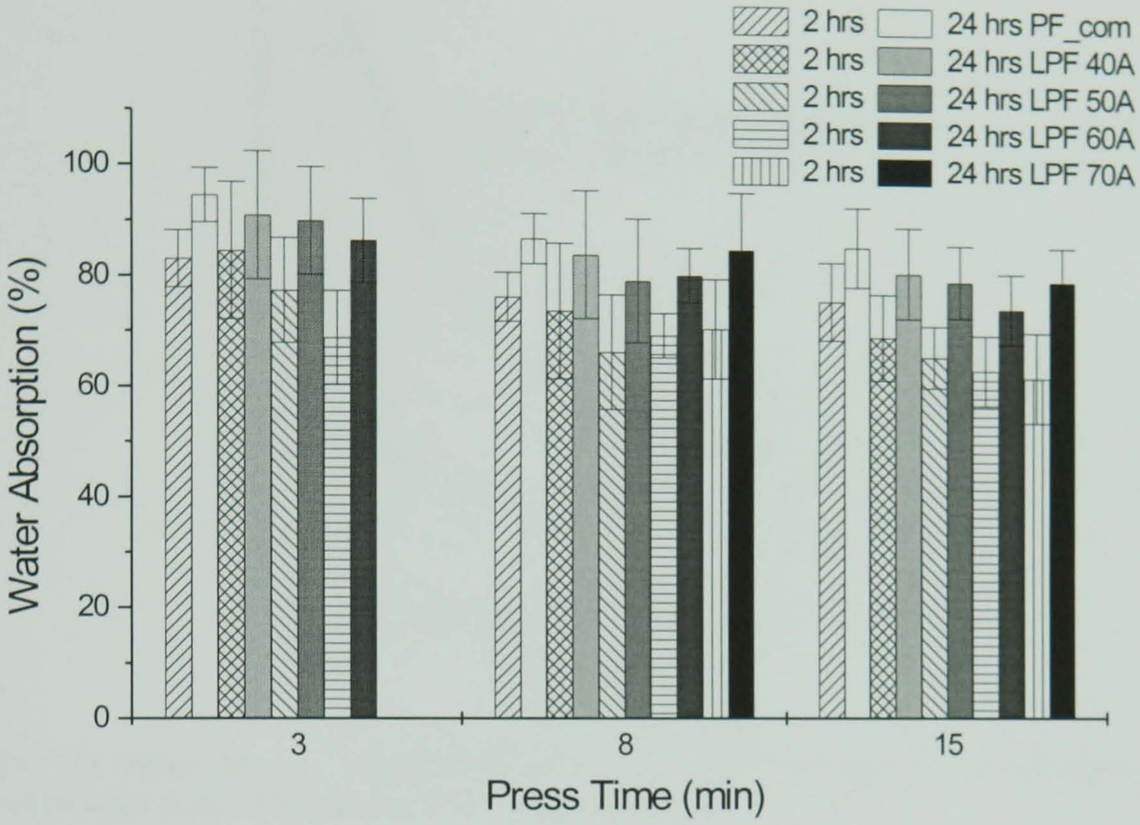


Figure 7.20 Water absorption of 6 mm particleboard specimens at various resin types and press cycle times.

As seen from Figures 7.18 and 7.19, all LPFA bonded particleboards showed high thickness swelling and water absorption values. The PF_com resin also exhibited high thickness swelling and water absorption. The reason for the overall poor performance may have resulted from the absence of a water-sizing agent. Paraffin wax was not incorporated in test panels and it is likely that this contributed to poor absolute performance with respect to dimensional stability. A 1% wax content is reported to reduce thickness swelling from *ca*. 25% to *ca*. 10% and water absorption from 75% to *ca*. 25% (Albrecht, 1968) (see Figure 7.21).

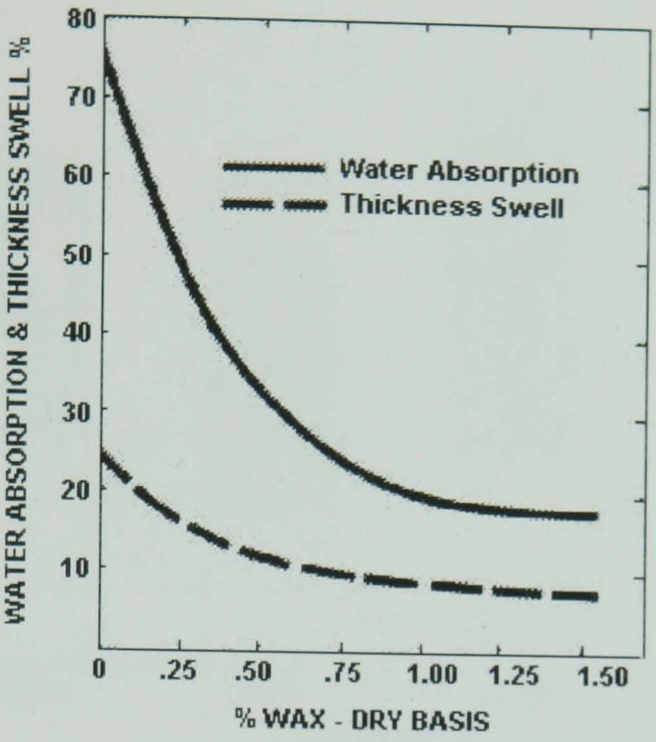


Figure 7.21 Effect of wax on particleboard sizing-water absorption and thickness swell data for aspen (24 hour test, resin content 7%) (Albrecht, 1968).

7.3.4 Dry and wet strength of the lignin-based resins bonded particleboards

Dry strength properties of particleboards bonded with LPF and phenolated-lignin-formaldehyde resins are shown in Section 7.3.2 and Section 7.3.3, respectively. LPF3, LPF 40A, and LPF 50A resins exhibited comparable dry strength properties to those of PF_com resin. The IB strength of samples bonded with these resins after boiling was also determined. These results are reported in Table 7.3.

Table 7.3 Internal bond values before and after 2 hours boil test

	IB (N/mm²)			
Resin Types*	**PF_com**	**LPF3**	**LPF 40A**	**LPF 50A**
Dry	1.01	0.84	1.07	1.00
Wet	0.45	0.31	0.43	0.41
Retention	45%	31%	40%	41%

* Codes of the resins are shown in Table 6.1 (see Chapter 6).

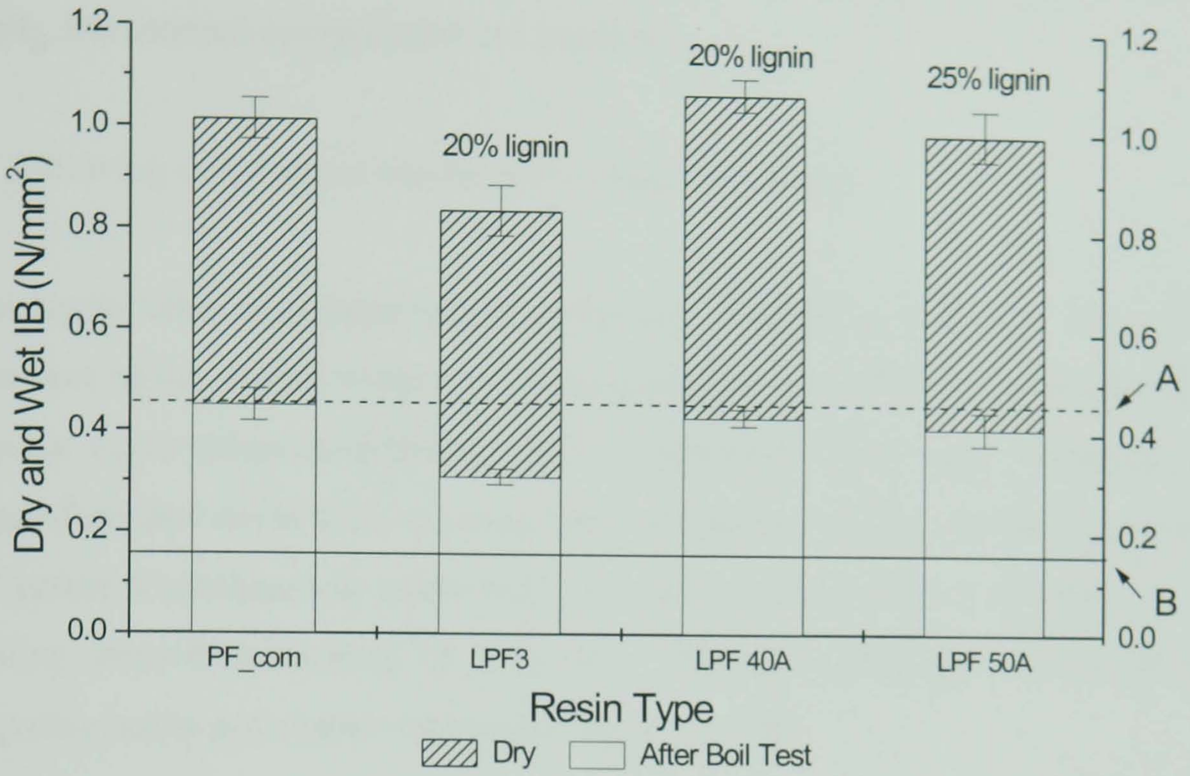


Figure 7.22 Dry and wet IB values of PF_com, LPF3 (20% lignin), LPF 40A (≈20% lignin) and LPF 50A (≈25% lignin) bonded particleboards (2 hours boil test). Arrows A and B show the required minimum IB value of load bearing boards in dry conditions and load bearing boards in humid conditions after boil test respectively (according to EN 312-4:1996 and EN 312-5:1996).

Figure 7.22 indicates that particleboards showed more or less similar IB strength retention values regardless of resin type. PF_com bonded particleboards showed significantly ($P>0.05$) higher IB strength retention values than two of the experimental resins LPF3 and LPF 40A. Minimum IB requirements, according to EN 312, for dry and after boil test are shown as arrows A and B in Figure 7.22 respectively. Figure 7.22 indicates that all particleboards exceeded these requirements.

7.4 CONCLUSIONS

Equipment and conditions for manufacturing laboratory boards were dissimilar to those of industry. For this reason, the properties of boards manufactured in the laboratory using the experimental resins may not be strictly comparable to commercially produced boards, but internal comparisons are possible.

The following conclusions can be drawn from the results:

Press cycle time and press temperatures are essential elements in the curing of any thermoset resins. Initial work with wood particles and LPF resins considered the effect of press cycle times at different press temperature. This work confirmed that press temperature and cycle time are important parameters in particleboard production using LPF resins. Particleboards made with LPF resins require higher temperature and longer pressing times than standard PF_com resin. This also correlates with the broadening of the curing peaks associated with higher lignin content.

Phenolated-lignin-formaldehyde resins impart better mechanical and physical properties than substitution by unmodified lignin. Properties comparable to those of boards bonded with PF_com resin were achieved in boards bonded with resins with up to 30% substitution of phenol by phenolated-lignin.

There is a relationship between increased addition of lignin and reduction in board mechanical properties. However, it has been demonstrated that organosolv lignin could be used to replace 20% to 30% of the phenol in PF resins used to bond particleboards, without adversely affecting bond properties.

Boards bonded with PF_com resin gave the best overall performance. Nevertheless, the novel resins gave good IB results except for the resins LPF5 and LPF 70A, which at the shortest press cycle time used, would not pass the minimum standard.

12 mm particleboards bonded with LPF3, LPF 40A, LPF 50A resins exhibited comparable mechanical properties to particleboards bonded with PF_com resin. Whereas, 12 mm particleboards bonded with LPF5 and LPF 70A resins gave the lowest

overall performance. IB values of 12 mm boards bonded with LPF3, LPF 40A, LPF 50A resins gave statistically similar results in dry tests as well as comparable IB strength retention values with PF_com after boil test.

None of the resins gave a board, which would have good properties at the shortest press cycle time. In the case of 6 mm boards only the PF_com resin would have good physical properties at the shortest press time (3 minutes). All the resins exhibited good physical properties at the other two pressing times (8 and 15 minutes). At the intermediate time resins LPF 40A and LPF 50A gave results comparable to those of the commercial resin. Resins LPF 50A and LPF 60A only gave good performance at the longest press time. For 6 mm boards, the PF_com resin at the longest press time gave a lower MOR, suggesting lignin gives elasticity. Resin LPF 70A gave the worst overall performance for the thin particleboards.

All the particleboards bonded with the experimental resins exhibited poor dimensional stability. The fact that PF_com resin gave similarly poor swelling results may indicate that values were affected by the lack of water sizing of particleboards rather than the resin.

The work has indicated that phenolated-lignin-formaldehyde resins (up to 30% substitution level) can be used successfully as a wood adhesive for constructing particleboard. The performance of these panels is comparable to those of boards made using PF_com resin. The study demonstrates that renewable resources such as lignin have potential as a substitute for phenol in PF resin systems.

CHAPTER 8

CONCLUSIONS AND FURTHER WORK

8.1 Final conclusions

The aim of this study was to use lignin as substitute for phenol in PF resins for particleboard production. The main objectives of this study were outlined in Chapter 1. These objectives have been realised.

A bioconversion technique was initially chosen for isolating lignin from wood. Large-scale experiments were set up to treat wood with two brown rot fungi (*C. puteana, Postia placenta*) to obtain lignin in sufficient quantity to use in phenolic resins. The visual evidence showed that wood deterioration only took place where the samples were in contact with the soil surface. Those that were not in contact with soil showed only slight deterioration. Brown rot fungi degraded pine, poplar and spruce wood samples, where 25%, 34% and 24% weight losses were recorded respectively. The analytical results indicated that the brown rot degraded wood samples had a higher lignin content than sound wood, but they still contained a higher percentage of holocellulose. Since complete holocellulose degradation was not obtained and since the product would need further purification, it is thus not readily usable for production of LPF resins. FTIR and NMR spectra studies of decayed wood also showed that ultimate holocellulose degradation was not achieved by brown rot fungi. The results showed that a route to accessing lignin using brown rot fungi was not readily achievable for this particular project. Furthermore, this production method is not economical, as it is not currently a by-product of any industrial process. Work on this source of lignin was discontinued and attention was focussed on isolation of lignin from black liquor produced as a waste from alkali sulphite pulping of hemp and flax.

Alkali sulphite lignin was obtained from the black liquor of a hemp/flax pulping process. In addition to this lignin, commercially available organosolv lignin was also chosen. Analysis of both lignins was carried out using UV, GPC, FTIR, NMR, HPLC and TGA. Alkali sulphite lignin had a high ash content and low purity, compared to organosolv lignin, however the reactivity of these lignins with phenol were virtually identical. Using the small-scale laboratory equipment, precipitation and filtration of black liquor was very labour intensive, requiring a long time to produce sufficient quantities for a phenolic-lignin resin trial. Since alkali sulphite lignin showed the same reactivity to phenol as organosolv lignin, it was decided to use commercially available organosolv lignin as a potential lignin resource for replacement of phenol for lignin-based resins production.

For production of lignin-based resins, organosolv lignin was introduced to PF resins in two ways. Firstly, lignin was used directly as a replacement for phenol. Various lignin substitution levels (5 to 40%) were tried. In summary, an increase in lignin content increased the hardening time of the resultant lignin-based resins. For example, the hardening time of PF_made resin was found to be 3.3 min, addition of 10% and 40% lignin increased the hardening time to 3.4 and 6.5 minutes respectively. When the lignin substitution level exceeded 20%, the hardening time of the lignin-based resins increased dramatically.

Secondly, lignin was modified by phenolation and then incorporated into the resin formulations, so that the influence of phenolated lignin on the lignin resins could be examined. Many different phenolated-lignin-formaldehyde resins were formulated. Before making phenolated lignin resins, lignin was mixed with phenol to determine the extent of the reaction taking place. GC results showed that phenol content decreased from 16% to 10%, after the reaction with lignin. Initially, phenolation of lignin was performed under three different conditions using a range of solvent or alkali or acid as a catalyst. The same level of phenolation of lignin was achieved regardless of catalyst. ≈20% to ≈60% lignin substitution levels were targeted for production of phenolated-lignin-formaldehyde resins. According to these results, further phenolated-lignin resin formulations were carried out. The physical analysis of these resins (LPF 40A, LPF 50A, LPF 60A) such as hardening time, indicated that the resins had good curing properties (*ca.* 1.3 minutes) compared to the hardening time of initial LPF resins (direct lignin added) (*ca.* 3.5 minutes).

Bond qualities of LPF, phenolated lignin formaldehyde, PF_com and PF_made resins were assessed by using the Automatic Bonding Evaluation System (ABES), in order to eliminate the resins that did not meet the specifications, prior to production of particleboards. The results indicated that the press temperature and time of the process are both important. Although the main effect of temperature showed very significant interactions on the failure stress of the wood strips, time of pressing was also significant. Increasing the press cycle time beyond a certain period did not improve the bond strengths when pressed at 180°C. The overall comparison of the lignin replacement procedures and the PF_com were made.

When lignin is used directly as a replacement for phenol, the maximum acceptable level of replacement was about 20%. However, a higher degree of replacement (30%) could be achieved using phenolated-lignin. Of all the lignin modification treatments, those that increase chemical reactivity or added reactive sites such as phenolation seemed to be the most promising.

Chemically modified lignin (phenolated-lignin-formaldehyde) resins gave better characteristics than non-modified (LPF) resins. A replacement of 20 to 30% of phenol by lignin seems feasible by this process. The molar ratio of formaldehyde to lignin, along with content, also affected bonding property of the copolymer resins.

After the selection of resins for particleboard production as determined by the bonding test using ABES, an assessment was made, based on the physical and mechanical properties of particleboards in the final part of this work.

Phenolated-lignin-formaldehyde resins impart better mechanical and physical properties than simple substitution by lignin. Properties comparable to those of boards bonded with PF_com resin were achieved in boards bonded with resins with up to 30% substitution of phenol by phenolated-lignin. It can also be concluded that there is a relationship between increased addition of lignin and reduction in board mechanical properties. However, it was demonstrated that phenolated-lignin could be used to replace 20% to 30% of the phenol in PF resins used to bond particleboards without adversely affecting bond properties.

Boards bonded with PF_com resin gave the best overall performance. Nevertheless, the novel resins gave good IB results except for resins LPF5 (40% lignin) and LPF 70A (≈25% lignin, low formaldehyde), which at the shortest press cycle time (3 minutes) used, would not pass the minimum standard.

12 mm particleboards bonded with LPF3 (20%), LPF 40A (≈20%), LPF 50A (≈25%) resins exhibited statistically equal physical and mechanical properties, when compared to particleboards bonded with PF_com resin. Whereas, 12 mm particleboards bonded with LPF5 (40%) and LPF 70A (≈25%) resins gave the lowest overall performance. IB values of 12 mm boards bonded with LPF3, LPF 40A, LPF 50A resins gave statistically similar results in dry tests, as well as similar IB strength retention values with PF_com, after the boil test.

Press cycle time and press temperatures are essential elements in the curing of any thermoset resin. The work confirmed that press temperature and cycle time were important parameters in particleboard production using lignin-based resins. Particleboards made with lignin resins require higher temperatures and longer pressing times than standard PF_com resin. This also correlates with the broadening of the curing peaks associated with a higher lignin content.

None of the lignin resins gave a board which would have good properties at the shortest press cycle time. In the case of 6 mm boards, only the PF_com resin gave good physical properties at the shortest press time (3 minutes). All the resins exhibited good physical properties at the other two pressing times (8 and 15 minutes). At the intermediate time, resins LPF 40A (20%) and LPF 50A (25%) gave results comparable to those of the commercial resin. Resins LPF 50A and LPF 60A (30%) gave the best performance at the longest press time (15 minutes). For 6 mm boards, the PF_com resin at the longest press time gave a lower MOR, suggesting lignin affords some elastic property. Resin LPF 70A (≈25%) gave the lowest overall performance for the thin particleboards, possibly due to the lower formaldehyde content when compared to the other studied resins. The overall strength properties of particleboards bonded with lignin-based resins depend not only on lignin substitution levels but also on the formaldehyde content.

All the particleboards bonded with the experimental resins exhibited poor dimensional stability, but PF_com resin also gave similarly poor swelling results. These overall poor swelling results may indicate that values were affected by the lack of water sizing (e.g. by wax addition) of the particleboards rather than the resin performance.

The work has indicated that phenolated-lignin-formaldehyde resins (up to 30% substitution level) can be used successfully as a wood adhesive for constructing particleboard. The performance of these panels is comparable to those of boards made by using PF_com resin as long as sufficient curing time and temperature were applied. The study demonstrates that renewable resources such as lignin have potential as a substitute for phenol in PF resin systems.

8.2 Problems and some recommendations for further work

The main disadvantages of lignin-based resin system can be summarised as:

1) The requirement for high press temperature and a long press regime in order to give good quality particleboards.

2) Dark colour of the final particleboards.

Point 1. Even though phenol substitution with lignin will reduce the resin cost which is an important factor affecting final product. Lignin-based resins need longer press times and high energy inputs to cure. However, in this study, the highest press temperature used was 180°C. In order to reduce press cycle time, an elevated press temperatures could be tried (>200°C).

It should also be noted that in this study no hardener or curing agent was employed. It might be possible to reduce press time and temperature for lignin based resin with the addition of curing agents.

Point 2. The other problem is the dark colour of the particleboards produced by lignin based resins compared to PF_com. But this product can be used where the colour of the material is not major concern.

In this thesis, only Alcell® organosolv lignin was used as a replacement for phenol in order to make lignin-based resins. Various types of other lignins can be used to investigate different reactivities of various lignins such as straw, hemp *etc.*, where sufficient purity can readily be obtained.

It would also be interesting to follow the reaction of lignin with the phenol during phenolation. It is suggested that methods such as NMR, FTIR might give valuable physical properties of lignin-phenol combinations.

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APPENDICES

APPENDIX 1 MANUFACTURE OF PF RESOL RESIN

1. Phenol (483 g) and formaldehyde (707.6 g) were mixed together for 10 minutes and the refractive index was checked, to ensure that it was within the given limits (sample 1, Table A1.1).

2. To these reactants, sodium hydroxide was added and allowed to mix for a further 10 minutes. The required pH was 10.2 (sample 2, Table A1.1). If the pH was too high, it was adjusted with acid (para toluene sulphonic acid); if too low, NaOH was added until it was in specification.

3. The lab apparatus was set up for reflux, and heated to 50°C. The temperature was raised to 50°C over 30 minutes. 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.

4. The temperature was held at 50°C for 1 hour.

5. The base product was then quickly cooled down, divided into three batches and frozen to prevent further reaction of the components to PF polymers.

6. Each of the batches of the base product were then taken separately, and the temperature raised slowly to 80°C. Cold water was applied to the reaction flask at 75°C to prevent overshoot. The temperature was held at 80°C and samples were taken every half an hour to check the viscosity (sample 3, Table A1.1).

7. When the sample reached the required viscosity specification, a vacuum was pulled and the flask cooled to 35°C.

8. The pH was adjusted to 7 with para toluene sulphonic acid (sample 4, Table A1.1). (Doing this maximises the pot life of the resin since at pH 7, the polymerisation reaction rate at ambient temperature is minimal).

9. 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 (sample 5, Table A1.1).

10. The flask was cooled and the vacuum released. All resins were properly secured before being 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.

Table A1.1 Tests performed during manufacture of PF_made resin

Sample 1	Refractive Index	1.445-1.450
Sample 2	pH	9.5-10.2
Sample 3	Viscosity (at 25°C)	11-13 cP
Sample 4	pH	6.7-7.2
Sample 5	Viscosity	250 cP

APPENDIX 2 COMPOSITION OF PHENOLATED-LIGNIN-FORMALDEHYDE RESINS

Table A2.1 Composition of phenolated-lignin-formaldehyde resins

Resin Names	Lignin : Phenol : Formaldehyde Parts	Lignin Substitution wt (%)	Formaldehyde in resins wt (%)
LPF 10A	1 : 2 : 1.8	33.3	37.4
LPF 10B	1 : 2 : 1.3	33.3	29.5
LPF 20A	1 : 0.7 : 0.8	58.3	32.8
LPF 20B	1 : (0.7 + 0.3*) : 1.2	50.6	38.1
LPF 30A	1 : (1.5 – 0.5*) : 1.2	50.5	38.1
LPF 30B	1 : 1.5 : 1.2	40.0	32.8
LPF 40A	1 : 4.1 : 3.6	19.7	41.2
LPF 50A	1 : 3.3 : 3	23.3	41.2
LPF 60A	1 : 2.2 : 2.2	31.4	41.2
LPF 70A	1: 2.8 : 1.9	26.3	33.3

* see Appendix 3 for addition or reduction in phenol content.

APPENDIX 3 RESIN FORMULATIONS

Table A3.1 Experimental array for phenolated-lignin phenolic resin formulations

Resins	P/L Mole Ratio	Free Phenol (wt%)	Formaldehyde (35%) Solution (wt%)
LPF 20A	5	27	32.8
LPF 20B	5	41	38.1
LPF 30A	10	27	38.1
LPF 30B	10	41	32.8

In the original PF resin prepared (section 5.2.2.1), 1 g of phenol (3 possible positions to react) reacts with 1.464 g of 35% formaldehyde solution. -----------(A)

1) In resin LPF 20A:

100 g of lignin was added to 71.6 g of phenol. This resulted in 21.6 g of phenol reacting with the lignin and 50 g free phenol in the reaction vessel.

In deciding how many positions are free to react when on the lignin (i.e. one or two), it was assumed initially that only one position was available then:

From (A) above 50 g of free phenol would require 50 x 1.464 g of formaldehyde (35%).

But if the 21.6 g of phenol combined with the lignin has only one position available then this amount of phenol i.e. (21.6 / 3) g would require 7.2 x 1.464 g of formaldehyde (35%).

i.e. (50 x 1.464) + (7.2 x 1.464) = 83.8 g of formaldehyde (35%).

Converting this weight to a percentage of the total mass in the reaction vessel wt % formaldehyde (35%) = 83.8 / (83.8 + 100 + 71.6) = 32.8%.

2) In resin LPF 20B:

Phenol (25.9 g) was added to raise the free phenol content to 41 wt %. i.e. the total phenol content would have been 75.9 g, if had it been added initially.

From (A) above 75.9 (i.e. 50 + 25.9) g of free phenol would require 75.9 x 1.464 g of formaldehyde (35%).

Again if the 21.6 g of phenol combined with the lignin has only one position available then this amount of phenol i.e. (21.6 / 3) g would require 7.2 x 1.464 g of formaldehyde (35%).

i.e. (75.9 x 1.464) + (7.2 x 1.464) = 121.6 g of formaldehyde (35%).

Converting this weight to a percentage of the total mass in the reaction vessel wt % formaldehyde (35%) = 121.6 / (121.6 + 100 + 97.5) = 38.1%.

3) In resin LPF 30A:

100 g of lignin and 150 g of phenol was reacted and as a result there was 43.2 g of phenol on the lignin + 106.8 g of free phenol.

To get the array correct, free phenol was needed to reduce from 41% to 27%. Therefore, the base combination was evaporated off until the free phenol fell to 27%.

From (A) above 54 (i.e. 106.8 – 52.8) g of free phenol would require 54 x 1.464 g of formaldehyde (35%).

If the 43.2 g of phenol combined with the lignin has only one position available then this amount of phenol i.e. (43.2 / 3) g would require 14.4 x 1.464 g of formaldehyde (35%).

i.e. (54 x 1.464) + (14.4 x 1.464) = 100 g of formaldehyde (35%).

Converting this weight to a percentage of the total mass in the reaction vessel wt % formaldehyde (35%) = 100 / (100 + 100 + 97.2) = 33.6%

But following the Taguchi method, 38.1% formaldehyde solution should be added to this base combination, therefore 122 g of 35% formaldehyde solution was added to the phenol/lignin base combination.

4) In resin LPF 30B:

100 g of lignin and 150 g of phenol was reacted and as a result there was 43.2 g of phenol on the lignin + 106.8 g of free phenol.

From (A) above 106.8 g of free phenol would require 106.8 x 1.464 g of 35% formaldehyde.

If the 43.2 g of phenol combined with the lignin has only one position available then this amount of phenol i.e. (43.2 / 3) g would require 14.4 x 1.464 g of 35% formaldehyde.

i.e. (106.8 x 1.464) + (14.4 x 1.464) = 176.6 g of formaldehyde (35%).

Converting this weight to a percentage of the total mass in the reaction vessel wt % formaldehyde (35%) = 176.6 / (176.6 + 100 + 150) = 41%

But following the Taguchi method, only 32.8% formaldehyde solution should be added to the reaction vessel, therefore 121.6 g of 35% formaldehyde solution was added.

APPENDIX 4 CALCULATION OF THE REGRESSION EQUATION

Table A4.1 Calculation of the regression equation for P/L mole ratio

P/L	Wt% Phenol	Wt% Catalyst Conc	Temp °C						
P/L	**P**	**C**	**T**	**P*P**	**P*C**	**P*T**	**C*C**	**C*T**	**T*T**
1.65	16	4	100	256	64.0	1600	16	400	1000
1.54	16.67	0	100	277.9	0.0	1667	0	0	1000
4.54	36.36	3	100	1322.0	109.1	3636	9	300	1000
4.45	37.5	0	100	1406.3	0.0	3750	0	0	1000
6.21	48.78	2.4	100	2379.5	117.1	4878	5.76	240	1000
6.59	50	0	100	2500.0	0.0	5000	0	0	1000
12.36	65.57	1.6	100	4299.4	104.9	6557	2.56	160	1000
12.92	66.67	0	100	4444.9	0.0	6667	0	0	1000
1.18	16	4	75	256.0	64.0	1200	16	300	562
0.91	16.67	0	75	277.9	0.0	1250.25	0	0	562
3.61	36.36	3	75	1322.0	109.1	2727	9	225	562
3.72	37.5	0	75	1406.3	0.0	2812.5	0	0	562
6.45	48.78	2.4	75	2379.5	117.1	3658.5	5.76	180	562
6.75	50	0	75	2500.0	0.0	3750	0	0	562
4.19	36.36	3	50	1322.0	109.1	1818	9	150	250
4.10	37.5	0	50	1406.3	0.0	1875	0	0	250
3.80	36.36	3	25	1322.0	109.1	909	9	75	625
3.41	35.29	5.9	100	1245.4	208.2	3529	34.81	590	1000

Linest calculates the statistics for a line by using the "least squares" method to calculate a straight line that best fits our data, and returns an array that describes the line.

LINEST (known_y's, known_x's, const, stats)

Using this formula with the data shown in Table A4.1, following equation was found.

y=-0.00482*P+0.249101*C-0.00457*T+0.003448*PP-0.00312*PC-0.0006*PT-0.02781*CC-0.00018*CT+0.000211*TT

From this equation, P/L mole ratio was calculated and compared with the data obtained experimental way (actual). The results are shown in Table A4.2.

Table A4.2 Actual and calculated P/L mole ratio

Actual P/L mole ratio	Calculated P/L mole ratio
1.65	1.78
1.54	1.53
4.54	3.96
4.45	4.08
6.21	6.73
6.59	7.04
12.36	12.21
12.92	12.67
1.18	1.23
0.91	0.97
3.61	3.71
3.72	3.83
6.45	6.66
6.75	6.98
4.19	3.72
4.10	3.84
3.80	4.00
3.41	3.41

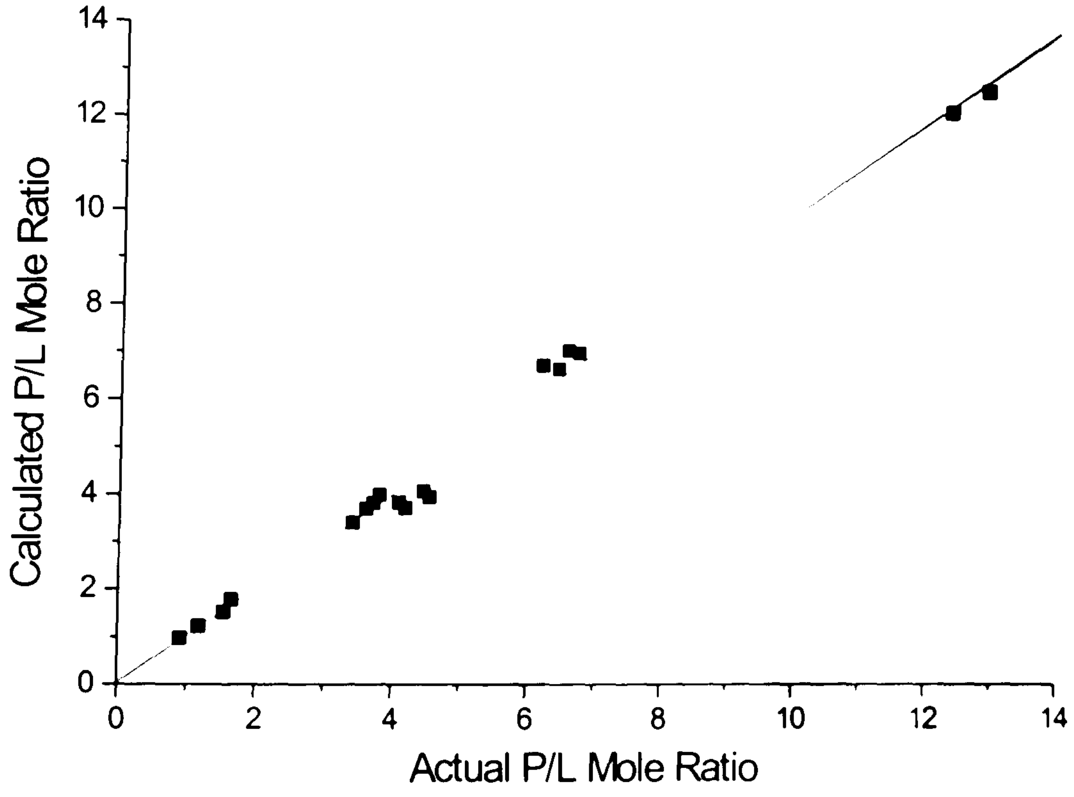

Figure A4.1 Calculated P/L mole ratio versus actual P/L mole ratio (R^2 = 0.99).