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Value-adding to cellulosic ethanol. Lignin polymers.

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Abstract

Lignocellulosic waste materials are the most promising feedstock for generation of a renewable, carbon-neutral substitute for existing liquid fuels. The development of value-added products from lignin will greatly improve the economics of producing liquid fuels from biomass. This review gives an outline of lignin chemistry, describes the current processes of lignocellulosic biomass fractionation and the lignin products obtained through these processes, then outlines current and potential value-added applications of these products, in particular as components of polymer composites.

1 Introduction

Concern about the depletion of fossil fuel resources and climate change attributed to anthropogenic carbon dioxide emissions is driving a strong global interest in renewable, carbon-neutral energy sources and chemical feedstocks derived from plant sources.

Commercial products which are capturing an increasing share of the liquid fuel market are esters of long-chain fatty acids from plant oils (biodiesel) and ethanol from the enzymatic digestion and fermentation of starch or sucrose. As an example of the use of biomass as a chemical feedstock, a consortium led by Dupont is working to convert maize starch to the

monomer, 1,3-propanediol, using genetically modified *Escherichia coli* (Caimi, 2004; Wehner et al., 2007). This monomer can then be used to prepare poly(trimethylene terephthalate), a polyester which is traditionally synthesised by the polycondensation of trimethylene glycol with either terephthalic acid or dimethyl terephthalate (Kurian, 2005; Kurian and Liang, 2008).

Industrial production of fuels and feedstocks from plant sources has concentrated on those sources that can be most readily and economically processed, such as oil palm, sugarcane, and corn. However, these compete for arable land with crops intended for human or animal consumption, putting upward pressure on food prices and accelerating environmental degradation. For this reason, current research efforts have concentrated on lignocellulosic biomass from sources that do not compete with food crops: e. g., agricultural waste products, such as sugar cane bagasse, wheat straw, rice stalk, cotton linters, and forest thinnings, or novel crops that can be grown in environments too marginal for food production, such as switchgrass and eucalypts (Sierra et al., 2008). In order for biomass to be a sustainable source of liquid fuel, technologies are required to enable economic production of suitable compounds from these sources, the dry mass of which consists primarily of a matrix of cellulose, hemicellulose, and lignin intimately mixed on the microscopic scale.

Current research is focussed on increasing the effectiveness and reducing the cost of cellulase and xylanase enzymes for cellulose and hemicellulose saccharification, (Maki et al., 2009; Oehgren et al., 2007; Rattanachomsri et al., 2009), developing enzymes capable of converting the range of sugars produced by digestion of hemicelluloses to ethanol, (Bettiga et al., 2009; Yano et al., 2009) and improving the pre-treatment process for the fractionation of cellulose, hemicellulose and lignin from biomass (Fox et al., 1987; Kim, 2009; Moxley, 2008).

Whatever the means, for producing ethanol from lignocellulosic biomass, large volumes of lignin will be produced. Current pilot plants producing ethanol from lignocellulosic material

use the residual lignin for energy generation, sequester it as 'biochar' as a carbon sink, or must dispose of it as waste. The viability of biofuel production would clearly be greatly enhanced by development of markets for lignin-derived products. Any value-added lignin derived product will improve the economics of biomass conversion, while high-volume bulk commodity applications will also address the problem of waste lignin disposal. There are a number of physicochemical factors which suggest a bright future for lignin-based products: (a) compatibility with a wide range of industrial chemicals; (b) presence of aromatic rings providing stability, good mechanical properties, and the possibility of a broad range of chemical transformations; (c) presence of other reactive functional groups allowing facile preparation of graft copolymers; (d) good rheological and viscoelastic properties for a structural material; (e) good film-forming ability; (f) small particle size; and (g) hydrophilic or hydrophobic character depending on origin, allowing a wide range of blends to be produced (Mousavioun and Doherty, 2009).

The focus of this review is the preparation of possible value-added polymers derived from the varieties of lignin likely to be generated in significant amounts from the production of cellulosic ethanol.

2. Lignin Structure

Lignocellulose materials refer to plants that are composed of cellulose, hemicellulose and lignin. The cellulose microfibrils (formed by ordered polymer chains that contain tightly packed, crystalline regions) are embedded within a matrix of hemicellulose and lignin (Figure 2.1). Covalent bonds between lignin and the carbohydrates have been suggested to consist benzyl esters, benzyl ethers and phenyl glycosides (Smook, 2002).

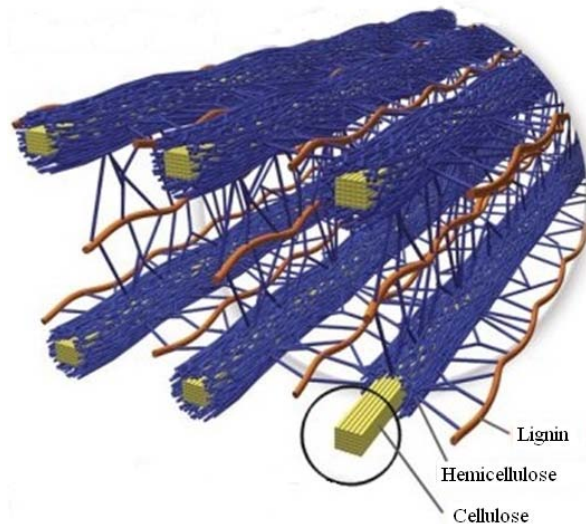


Figure 2.1 Cellulose strands surrounded by hemicellulose and lignin

Lignin is primarily a structural material to add strength and rigidity to cell walls and constitutes between 15 wt% and 40 wt% of the dry matter of woody plants. Lignin is more resistant to most forms of biological attack than cellulose and other structural polysaccharides, (Akin and Benner, 1988; Baurhoo et al., 2008; Kirk, 1971) and plants with a higher lignin content have been reported to be more resistant to direct sunlight and frost (Miidla, 1980). *In vitro*, lignin and lignin extracts have been shown to have antimicrobial and antifungal activity, (Cruz et al., 2001) act as antioxidants, (Krizkova et al., 2000; Pan et al., 2006; Ugartondo et al., 2008) absorb UV radiation, (Toh et al., 2005; Zschiegner, 1999) and exhibit flame-retardant properties (Reti et al., 2008).

Lignin is a cross-linked macromolecular material based on a phenylpropanoid monomer structure (Figure 2.2). Typical molecular masses of isolated lignin are in the range 1000 g/mol to 20,000 g/mol, but the degree of polymerisation in nature is difficult to measure, since lignin is invariably fragmented during extraction and consists of several types of substructures which repeat in an apparently haphazard manner. In this review the term

'lignin' will be used both for the *in vivo* material and the various fractions isolated from living matter, which invariably undergo some degree of chemical and physical change.

The monomer structures in lignin consist of the same phenylpropanoid skeleton, but differ in the degree of oxygen substitution on the phenyl ring. The H-structure (4-hydroxy phenyl) has a single hydroxy or methoxy group, the G-structure (guaiacyl) has two such groups, and the S-structure (syringyl) has three (Figure 2.2). The polymerisation of the phenylpropanoid monomers is initiated by oxidases or peroxidases. While the precise mechanism is obscure, it is postulated that radical-radical combination of free radicals produced by enzymatic dehydrogenation is the key reaction, either under enzymatic control (Davin et al., 2008) or in a random 'combinatorial' manner (Ralph et al., 2004).

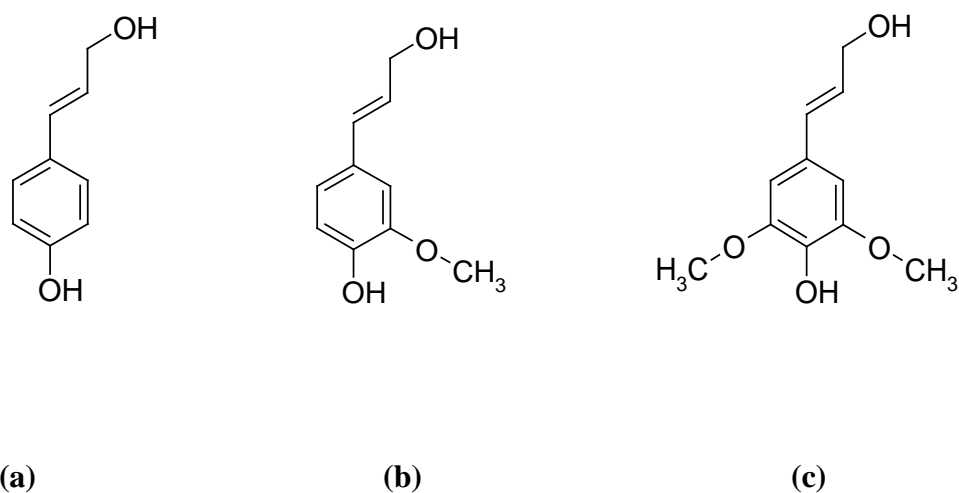


Figure 2.2 Monolignol monomer species. (a) *p*-coumaryl alcohol (4-hydroxyl phenyl, H), (b) coniferyl alcohol (guaiacyl, G), (c) sinapyl alcohol (syringyl, S).

Both carbon-carbon and carbon-oxygen bonds between monomers are found in lignin (Figure 2.3). The most common functionality, accounting for about half the bonds between monomers in lignin from most sources, is a carbon-oxygen link between a *p*-hydroxy moiety

and the β -end of the propenyl group (β -O-4) (Figure 2.3a) (Chen, 1991; Ede and Kilpelainen, 1995; Kukkola et al., 2004).

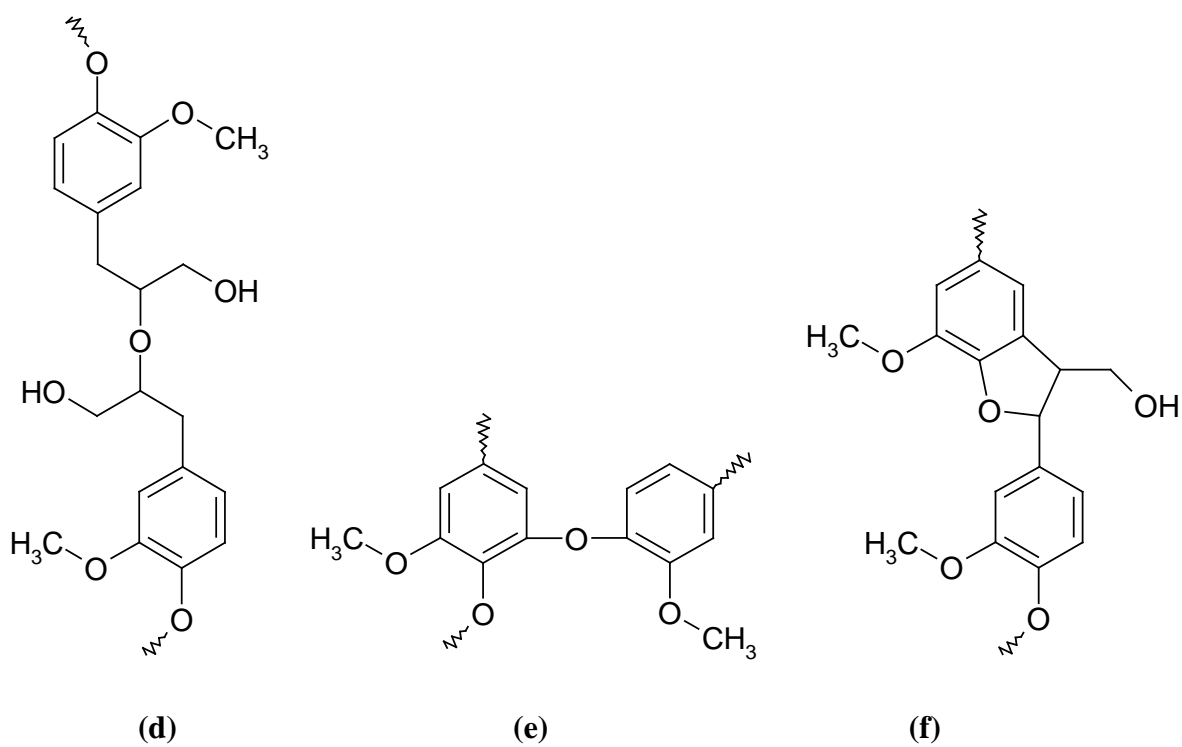
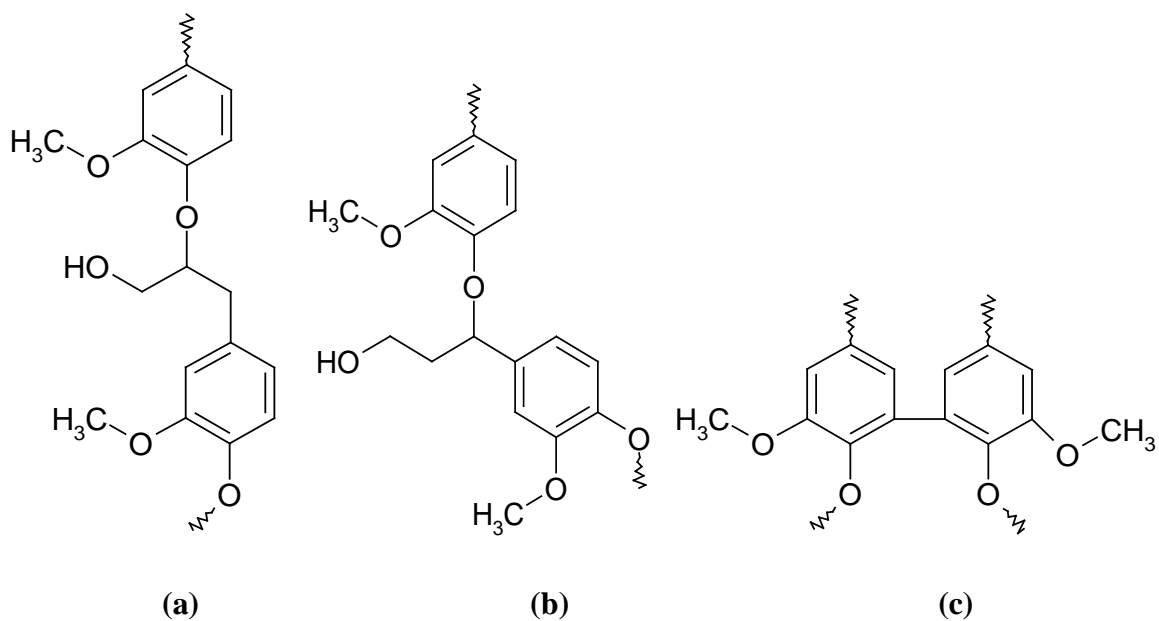


Figure 2.3 Significant lignin linkage structures. (a) β -O-4, (b) α -O-4, (c) 5-5, (d) β - β , (e) 5-O-5, (f) β -5.

The degree of cross-linking possible in lignin, and hence the rigidity of the structure, is dependent on the degree of substitution. In softwoods, the G structure is dominant, while hardwood lignins normally contain a mixture of S and G structures with S in the majority, while H structures predominate in lignins found in grasses (Wang et al., 2009).

Recent interest in lignin has been driven by the fact that it forms a large proportion of the non-food biomass under consideration for production of renewable and carbon-neutral liquid fuels and chemical feedstocks. Separation of cellulose from lignin is one of many technical hurdles which must be overcome in order for biofuels to be economically produced from cellulose-containing waste. While biotechnology allows plants to be modified to have a larger cellulose: lignin ratio (Hu et al., 1999; Sticklen, 2008) and alter lignin structure to produce lignins which can be more easily separated, (Lapierre et al., 1999) these strategies will unavoidably run into limits imposed by plant physiology and thus a significant volume of waste lignin is unavoidable.

3 Lignin Fractionation Processes

The extraction of lignin from lignocellulosic materials is conducted under conditions where lignin is progressively broken down to lower molecular weight fragments, resulting in changes to its physicochemical properties. Thus, apart from the source of the lignin, the method of extraction will have a significant influence on composition and properties of lignin. The majority of lignin extraction and delignification processes occur by either acid or base-catalysed mechanisms. The chemistry of bond cleavage in lignin by these mechanisms has been reviewed by Gratzl and Chen (2000).

3.1 Sulfite process

At present the main commercial source of lignin is from the pulp and paper industry. The sulfite process which traditionally used to be the main pulping technology involves the reaction of a metal sulfite and sulfur dioxide (Smook, 2002). The main reactions that take place during the pulping process are: (a) the reaction between lignin and free sulphurous acid to form lignosulfonic acid, (b) the formation of the relatively soluble lignosulfonates with the cations, Mg, Na or NH_4^+ , and (c) the fragmentation of the lignosulfonates. In addition to lignosulfonates, degraded carbohydrates are also produced. The pulping reactions are usually conducted between 140 °C and 160 °C and the pH of the acid sulfite process is between 1.5 and 2.0, while the bisulfite process is between pH 4.0 to 5.0 (Smook, 2002). The chemistry of the sulfite process has been exhaustively reviewed by Wong (1980) and more recently by Alen (2000). Several purification steps are required to obtain the lignosulfonate fraction with high purity, including fermentation to convert the residual sugars to ethanol and membrane filtration to reduce the metal ion content. The lignosulfonate biopolymer is typically highly cross-linked, with ~5 wt% sulfur content, and bears two types of ionising groups; sulfonates ($\text{pK}_a \leq 2$) and phenolic hydroxy groups ($\text{pK}_a \sim 10$). Because of the low pK_a for the sulfonate groups, lignosulfonates are water-soluble under most conditions. The physicochemical properties of lignosulfonates are affected by the metal cation (Na or Ca) of the sulfite salt used during the pulping process. Sodium sulfite produces more extended lignin chains that are more suitable for use as dispersants, while calcium sulfite produces more compact lignin, presumably due to a bridging effect of chelating Ca^{2+} . The sulfur content (5 wt %) of sulfite lignins is one of the major factors restricting its use in speciality applications, and so most of its lignin is currently used on co-generation.

The sulfite delignification process is an acid catalysed process in which there is cleavage of the α -ether linkages and β -ether linkages of lignin. The process goes via the quinone methide intermediate or nucleophilic substitution. Generally, less side-chain cleavage is seen under

acid-catalysed rather than alkali-catalysed reactions. The complete breakdown of the aryl ether linkages leads to the formation of a reactive resonance-stabilised benzyl carbocation. Under these conditions condensation reactions occur. The carbocation may form a C-C bond with an electron-rich carbon atom in the aromatic ring of a lignin fragment or the protonation of a benzylic oxygen atom may cause inter- or intramolecular condensation by a S_N2 mechanism. The formation of organic acids such as acetic acid during the delignification process can encourage the formation of the benzylic carbocation or lead to protonation of a benzylic oxygen atom, enhancing the S_N2 condensation pathway.

3.2 Kraft process

The kraft or sulfate process is now the main traditional method for pulping and hence produces the largest volume of lignin (Smook, 2002). It uses sodium hydroxide and sodium sulphide under strong alkaline conditions to cleave the ether bonds in lignin. The delignification process proceeds in three stages. The first phase occurs around 150 °C and is controlled by diffusion. The second stage occurs between 150 °C-170 °C, while the final stage occurs at even higher temperatures. The bulk of the delignification (90 wt%) occurs during the second stage. The lignin may be recovered from the alkaline liquid remaining after pulp extraction, the black liquor, by lowering the pH to between 5 and 7.5 with acid (usually, sulfuric acid) or carbon dioxide (Koljonen et al., 2004). Recent developments in improving the yield of the kraft process have been reviewed by Couchene (1998) and Kordsachia et al. (1999) have compared the suitability of the kraft process for different substrates with the sulfite process.

The kraft process produces lignin with aliphatic thiol groups called kraft lignin. Kraft lignin is hydrophobic and so needs to be modified to improve reactivity. The sulfur content (1 wt% - 2 wt%) of kraft is also a major reason while its main application has been co-generation, though pulp mills use this application to recover pulping chemicals in order to reduce costs.

The kraft process goes by alkaline hydrolysis in which the β -1,4 links in cellulose is cleaved, allowing the lignin component of biomass to be extracted. However, the lignin itself is also susceptible to attack by alkali and except for the diarylether linkages, ethers in lignin readily undergo base-induced hydrolysis under relatively mild conditions.

In alkaline hydrolysis α -aryl ether bonds are more easily broken than β -aryl ether bonds, particularly in situations where the substructures contain a free phenolic hydroxyl group in the para position (Baucher et al., 2003; Sakakibara et al., 1966). Simple heating of the biomass in water results in substantial cleavage of the α -ether bonds either through a quinone methide intermediate or through nucleophilic substitution by a S_N2 mechanism (Chakar and Ragauskas, 2004).

In alkaline media intermolecular condensation reactions can occur with competition between the added nucleophiles and anionic lignin fragments (e.g., phenolate anions and carbanions) (Olm and Tisdal, 1979). The extent of condensation will depend on the types of structures initially formed. If a structure contains good leaving groups at the β -carbon, neighboring group participation reactions resulting in the cleavage of β -aryl ether linkages will predominate over condensation reactions (Chakar and Ragauskas, 2004).

3.3 Soda process

The soda process (which goes by alkaline hydrolysis) was the first chemical pulping method and was patented in 1845. Soda process led kraft pulping which now dominates the chemical pulping industry. The soda process is the preferred method of chemical pulping of non-wood material such as bagasse, wheat straw, hemp, kenaf and sisal. The pulping process involves heating the biomass in a pressurised reactor to 140 °C -170 °C in the presence of 13 wt%-16 wt% alkali (typically sodium hydroxide).

Lignin recovered through extraction with sodium hydroxide is normally referred to as 'soda lignin'. Soda lignin from non-wood sources is typically difficult to recover by filtration or centrifugation because its high carboxylic acid content, arising from oxidation of aliphatic hydroxy groups, makes it a relatively good dispersant. Heating is therefore required to encourage coagulation and ensure filtrable material can be obtained. As soda lignin contains no sulfur and little hemicellulose or oxidised defect structures, it has good potential for use in high value product

3.4 Other fractionation processes

With the push to produce cellulosic ethanol and bio-diesel, additional sources of lignin will be available through various pre-treatment technologies. Promising pre-treatment technologies for lignocellulosic biomass involve a combination of physical, chemical, biochemical and thermal methods. Physical methods include steam explosion, pulverising and hydrothermolysis (Mosier et al., 2005). The principal chemical methods are the use of ammonia expansion, aqueous ammonia, dilute and concentrated acids (e.g., H_2SO_4 , HCl , HNO_3 , H_3PO_4 , SO_2) and alkali (e.g. NaOH , KOH , $\text{Ca}(\text{OH})_2$) and ionic liquids. Significantly, all the approaches under development for production of biofuels from lignocellulosics are likely to produce lignin with little or no sulfur, increasing the scope for manufacture of value-added products.

Organic solvents (e.g. ethanol, formic acid, acetic acid, methanol) produce lignin, called organosolv lignin, the benefits of organosolv lignin over sulfonated and kraft lignins include no sulfur, greater ability to be derivatised, lower ash content, generally lower molecular weight and more hydrophobic (Lora 2002).

A relatively recent development in biomass fractionation is the application of ionic liquids (IL) to fractionate lignocellulosic materials. Ionic liquids usually consist of a large

asymmetric organic cation and a small anion and typically have negligible vapour pressure, very low flammability and a wide liquidus temperature range. Most work on IL as biomass solvents has used alkyimidazolium IL for dissolving cellulose. The mechanism of dissolution involves the coordination of small hydrogen acceptors, such as chloride ions, to the hydroxy groups of cellulose, breaking the strong intramolecular H-bonding between the cellulose fibres (Spear et al., 2002; Swatloski et al., 2003). An ionic liquid mixture containing 1-ethyl-3-methylimidazolium cation and a mixture of alkylbenzenesulfonates with xylenesulfonate as the main anion has been used to extract lignin from sugarcane bagasse at atmospheric pressure and elevated temperatures (170°C-190 °C) (Tan et al., 2009). The addition of small amounts of sodium xylene sulfonate to the ionic liquid mixture aided the cleavage of ether groups in lignin. This was attributed to the sodium ions coordinating to the ether oxygen, thereby increasing the carbonium ion character of the ether carbon atoms and enhancing their susceptibility to nucleophilic attack by the arylsulfonate groups of the ionic liquid (Tan et al., 2009). Lignins were recovered from IL by precipitation, allowing the IL to be recycled. Lignins with molecular weights around 2220 g/mol obtained by this process contained between 0.6 wt% and 2 wt% ash and about ~1.5 wt% sulfur. Low levels of hemicellulose (< 0.1 wt.%) were also detected. Other classes of IL, such as alkylphosphonium IL, which we are currently investigating, solubilise lignin by similar mechanisms as those under acidic conditions. These lignins were sulfur-free and were of low molecular weights.

4 Physical Properties of Lignin

The physicochemical state of lignin dictates how and where it can be utilised in the manufacture of various products. The source from which lignin is obtained and the method of extraction has a strong bearing on its properties (Lora and Glasser, 2002). As a highly cross-linked material with widely varying functionality, lignin may not readily be

characterised to give meaningful molecular weight data, but other parameters more directly relevant to end-use properties may be assessed. Despite this, the molecular weight data does provide some useful guide. Table 4.1 gives the functional groups and molecular weight of selected lignins. The reactivities of these lignins will impact on the attributes of the end products. For example, Muller et al. (1984) found that kraft lignin-based phenol formaldehyde resins have superior properties to steam exploded lignin-based phenol formaldehyde resins.

Table 4.1 Molecular weight and functional of lignins

Lignin type	M_n (gmol^{-1})	COOH (%)	OH phenolic (%)	Methoxy (%)
Soda (bagasse)	2160	13.6	5.1	10.0
Organosolv (bagasse)	2000	7.7	3.4	15.1
Soda (wheat straw)	1700	7.2	2.6	16
Organosolv (hardwood)	800	3.6	3.7	19
Kraft (softwood)	3000	4.1	2.6	14

Another important parameter is the glass transition temperature, T_g , which is an indirect measure of crystallinity and degree of cross-linking and directly indicates whether a lignin is suitable for an application calling for a rubbery or a glassy material under particular conditions (Table 4.2) (Gargulak and Lebo, 2000).

Table 4.2 T_g of different lignin types (Gargulak and Lebo, 2000)

Types of lignin	T_g (°C)
<hr/>	
Milled wood lignin	
Hardwood	110-130
Softwood	138-160
Kraft lignin	124-174
Organosolv lignin	91-97
Steam explosion lignin	113-139
<hr/>	

Lignin T_g will depend on the amount of water and polysaccharides, as well as molecular weight and chemical functionalisation, but in general the T_g will be lower the greater the mobility of the lignin molecules. While T_g generally increases with increasing molecular weight, the impact of structural variation based on the degree of polymerisation has only recently been established. Baumberger and co-workers (2002) showed using a series of transgenic poplars that the variations in T_g were closely related to the degree of polymerisation of lignin as determined by thioacidolysis. This is illustrated in Figure 4.1, where the T_g increases with the degree of condensation, expressed as the fraction of phenylpropanoid units involved in C-C linkages.

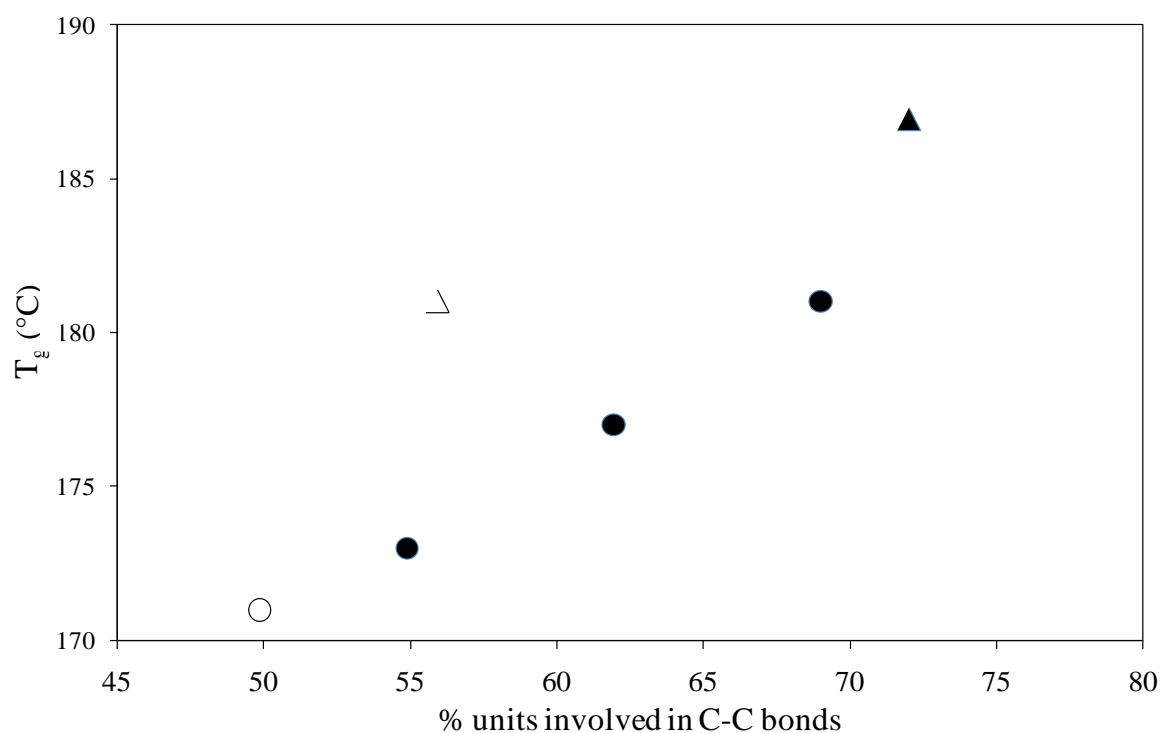


Figure 4.1 Correlation between the glass transition temperature (T_g) and the degree of condensation (% phenylpropanoid units involved in C-C linkages) of milled wood and enzyme lignins isolated from control and transgenic poplars (Baumberger et al., 2002). Data for control plants are shown as open symbols, and data for transgenic plants derived from those controls are shown as closed symbols. Figure redrawn with permission from Baumberger et al. (2002).

More potential applications of lignin can be realised if the miscibility of lignin with other polymeric materials can be improved. This may be done through chemical modification of lignin with appropriate hydrophobic groups (e.g. butyrate, hydroxypropyl, ethyl) (Ghosh et al., 2000; Uraki et al., 1997) or through formation of lignin copolymers (Wang et al., 1992). Pouteau and his coworkers (2004) examined the compatibility of lignin-polymer blends by image analysis. A strong correlation (Figure 4.2) between the solubility parameter of kraft lignin (20.5-22.5 (MPa)^{1/2}) and the solubility parameters of different polymers was obtained. The data shown does not discriminate between molecular weight of lignin fractions, but only

low molecular weight lignins are compatible with apolar and very polar matrices.

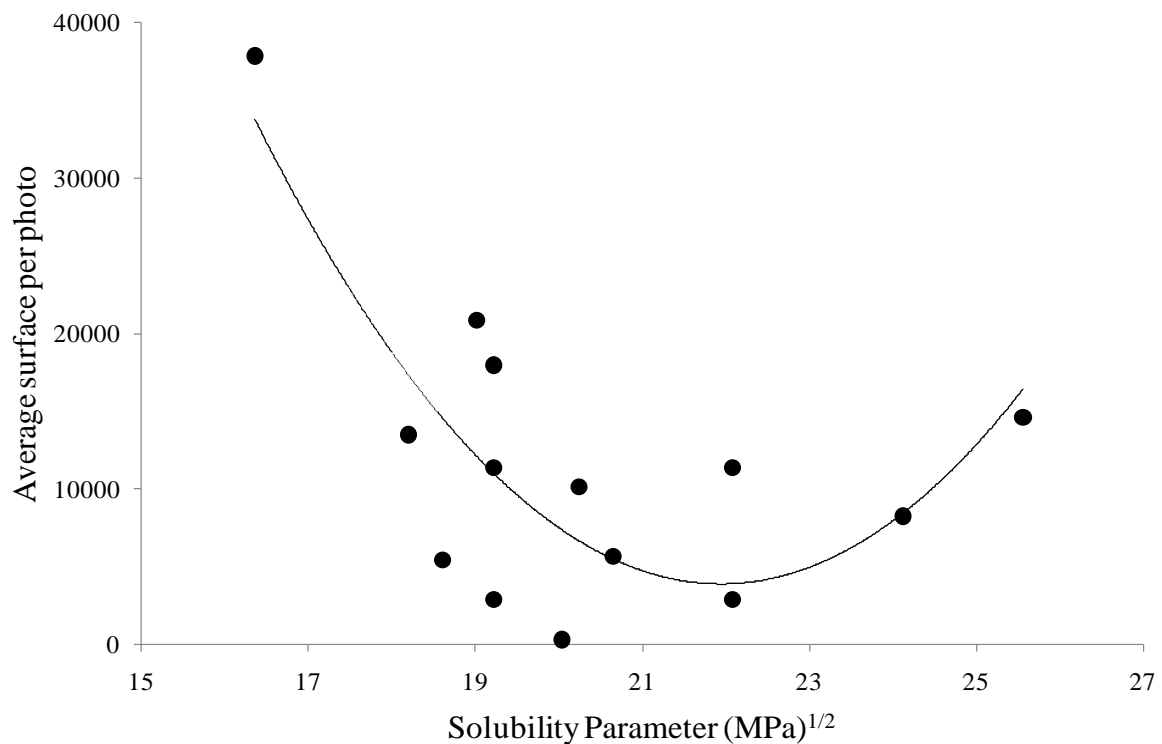


Figure 4.2 Correlation between total aggregate surface area observed per photo and the solubility parameter of the polymer matrix (Pouteau et al., 2004). Figure redrawn with permission from Pouteau et al. (2004).

5 Applications

There are many commercial applications of low value where lignins (predominantly lignosulfonates) are used because of their surface-active properties (Gargulak and Lebo, 2000; Stewart, 2008). Table 5.1 gives the variety of these lignosulfonate products.

Table 5.1 Lignosulfonate products because of their surface-active properties

Products	Reference
Concrete additives	(Sestauber et al., 1988; Shperber et al., 2004)

Animal feed pelleting aid	(Winowiski and Zajakowski, 1998)
Metallic ore processing	(Clough, 1996; Clough, 1996)
Oil well drilling muds	(Detroit and Sanford, 1989; Kelly, 1983)
Dust control	(Buchholz and Quinn, 1994; Fiske, 1992)
Phenol-formaldehyde resins	(Raskin et al., 2002)

Lignosulfonates are also used to produce a number of value-added products for specialty markets (Gargulak and Lebo, 2000). Table 5.2 gives the variety of these lignosulfonate products.

Table 5.2 Lignosulfonate products because of their speciality markets

Products	Reference
Vanillin	(Bjorsvik and Minisci, 1999; Gogotov, 2000)
Pesticides	(Lebo, 1996)
Dispersant for carbon black	(Goncharov et al., 2001)
Dyes and pigments	(Hale and Xu, 1997)
Gypsum board	(Northey, 2002)
Water treatments	(Jones, 2004; Zhuang and Walsh, 2003)
Scale inhibitors	(Ouyang et al., 2006)
Industrial cleaners	(Jones, 2008)
Emulsifiers	(Gundersen et al., 2001; Sjoblom et al., 2000)
Matrix for micronutrient fertilisers	(Docquier et al., 2007; Meier et al., 1993; Niemi et

	al., 2005)
Wood preservatives	(Dumitrescu et al., 2002; Lin and Bushar, 1991)
Battery expanders	(Pavlov et al., 2000)
Specialty chelants	(Khabarov et al., 2001)
Bricks, refractories and ceramics	(Pivinskii et al., 2006)
Retention aids in papermaking	(Vaughan et al., 1998)

The products mention in the previous section is on relatively low value applications of lignin. Blending of two or more polymers provides the ability to tailor material properties to achieve specific goals with higher value. While a particular homopolymer will have properties that can be tailored by controlling molecular weight and the degree of branching and crosslinking, blending of polymers makes a vastly greater range of potential materials properties available. As well as making simple additive properties accessible, in many instances polymer blending results in high-performance composite materials as a result of synergistic interactions between the components. Many polymer combinations are immiscible and so exist in two different phases in the polymer matrix. This separation into phases can result in poor stress transfer between the phases, thereby lowering the mechanical properties of the blend to that at least of one of the individual components. When incorporated in blends with natural and synthetic polymers, lignin generally increases the modulus and cold crystallisation temperature but decreases the melt temperature. The addition of plasticisers to such systems have been found to improve the mechanical properties by reducing the degree of self-association between lignin molecules, improving lignin-polymer miscibility (Feldman et al., 2001). Because lignin possesses easily-functionalisable hydroxyl and carboxylic acid groups,

its compatibility with different polymer types has been extensively examined. The following section presents some examples of lignin blends with natural and synthetic polymers.

Natural polymers are synthesised by living organisms or by enzymes isolated from living organisms, through sophisticated biosynthetic pathways requiring carbon dioxide consumption. These 'environmentally friendly' polymers include cellulose, hemicellulose, lignin, starch, proteins, nucleic acids and linear aliphatic polyesters. The ability to control the hydrophilicity of lignin means that it could in principle form composite materials with any of these polymers, while the physicochemical qualities of lignin means that it can in many cases improve the tensile strength and bulk modulus of these biopolymers, and protect the composite against oxidative degradation under UV light or elevated temperature.

Feldman (2002) and more recently Stewart (2008) have reviewed lignin blending with synthetic polymers. This review will discuss epoxy-lignin composites, phenol-formaldehyde resins where all or part of the phenol is derived from lignin, polyolefin-lignin blends, lignin blends with vinyl polymers, lignin-polyester blends, lignin as a component of polyurethanes, synthetic rubber-lignin blends, graft copolymers of lignin and the prospects of lignin incorporation into further polymer systems.

5.1 Protein-lignin blends

Proteins have long been used for the production of plastics and resins (Huang et al., 2004; Nagele et al., 2000). The main drawbacks of protein-based materials are high water absorption and the difficulty of separating the proteins from naturally occurring colourants without denaturation, but these obstacles are gradually being overcome (John and Bhattacharya, 1999; Otaigbe and Adams, 1997; Zhong and Sun, 2001). As a crosslinked

material with a largely aromatic structure, lignin has the capacity to increase the tensile strength, Young's modulus, thermal stability and elongation at break of protein materials.

The addition of soda lignin to soy protein plastics has been shown to reduce water absorption, as well as improving the mechanical properties of soy protein/glycerol blends. Blends containing 50 wt% soda lignin have a tensile strength twice that of unblended soy protein (Huang et al., 2003). Thermoplastic materials comprising lignin and protein blended with natural rubber, have been patented. These materials have been shown to have improved impact resistance compared to lignin-free formulations (Nagele et al., 2000).

Hydrogen-bonding interactions are often insufficient to ensure adequate mixing of lignin with protein. Huang et al. (2004) blended kraft lignin with soy protein using methylene diphenyl diisocyanate (MDI) as a compatibiliser. MDI will form urethane links between hydroxy groups on lignin molecules and in the protein. Only a slight reduction in water absorption was observed, but the addition of 2 wt% MDI caused a simultaneous enhancement of modulus, strength, and elongation at break of the polymer blends, which was attributed to graft copolymerisation and crosslinking (Huang et al., 2004).

An alternative strategy for enhancing the compatibility of lignin with protein, rather than adding a compatibiliser, is chemical or enzymatic modifications of the lignin. Blending soy protein with hydroxypropylated soda lignin resulted in a 200 % increase in the tensile strength of the blended material, (Chen et al., 2006; Wei et al., 2006) without reducing the elongation at break (Huang et al., 2006). Wei et al. (2006) suggested that improved mechanical properties of protein blended with hydroxylpropyl lignin molecules were due to: (a) formation of supramolecular domains by hydroxylpropyl lignin, (b) strong adhesion between the hydroxylpropyl group and soy protein and, (c) the interpenetration of the soy protein molecules into the supramolecular hydroxylpropyl domain. Protein has also been incorporated in more complex composite materials, e.g., an adhesive composition of low

molecular weight polyaminopolyamide-epichlorohydrin resin and protein has been patented (Spraul et al., 2008).

While most processing of gluten protein increases the degree of cross-linking, incorporation of kraft lignin in gluten reduced protein/protein interactions and prevented loss of solubility (Kunanopparat et al., 2009). This has obvious implications for processibility of gluten-based materials, suggesting kraft lignin is a promising additive for such materials. It was suggested that kraft lignin had a radical scavenging activity, reacting with the sulfur-centred radicals responsible for gluten crosslinking.

5.2 Starch-lignin blends

The use of starch-based films for packaging materials has increased recently as they degrade readily in the environment in comparison to conventional synthetic materials. However, a significant disadvantage of starch films is that they have very poor water resistance.

Blending with hydrophobic polymers can clearly improve the water resistance of starch, and lignin has a high compatibility with starch making it an obvious candidate for blending.

Baumberger (2002) has reviewed studies involving starch-lignin films, giving an overview of methods of preparation, thermomechanical properties, mechanisms of starch-lignin interactions and potential target applications of starch-lignin blends.

Lepifre et al. (2004) compared the reactivity of films of three soda lignins (one derived from sugarcane bagasse and the other two from wheat straw) with starch on exposure to radiation doses of 200 kGy and 400 kGy, using spectroscopic and chromatographic techniques.

Infrared analysis of the bagasse lignin-starch film, in contrast to the wheat straw lignin, showed evidence of condensation probably related to the presence of reactive ferulic acid, and irradiation improved compatibility of the two polymers.

Lepifre et al. (2004) found that grafting of starch films with lignin gave significant improvements in water resistance. The higher water resistance of lignin/starch blends is attributable to the partial compatibility of lignin with the amylose component of starch, the presence of hydrophobic lignin at the surface of the material due to surface activity of phenolic groups, and cross-linking between the starch-rich phase and the lignin-rich phase (Baumberger et al., 2000). The work by Baumberger et al. (1998) established that reduced water content and water solubility starch-kraft lignin blends was due to the amount of water soluble phenolics present in lignin as these hydrophilic compounds are likely to interact with the starch matrix, through hydrogen bonding, and lead to increased bonding to lignin. Figure 5.1 shows the bonding between β -1 stilbene (a component) found in lignin and the amylose portion of starch. The increase in elongation at break for the starch-kraft lignin blend compared to starch was attributed to increased plasticity of the starch matrix due to the presence of low molecular phenolics and amphiphilic fatty acids.

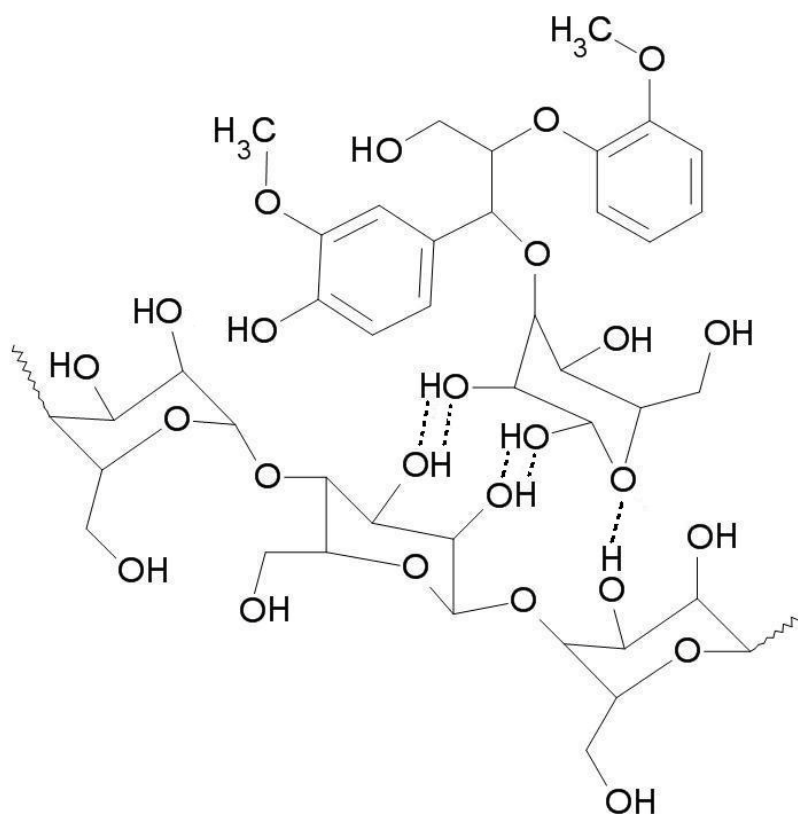


Figure 5.1 Hydrogen bonding between β -1 stilbene and amylose.

Composite films of lignin, starch, and cellulose have been cast from ionic liquid at room temperature, with the product showing good mechanical properties, thermal stability, and resistance to gas permeation(Wu et al., 2009).

Ke et al. (2003) studied the effect of amylose content on the mechanical properties and moisture up take of starch films. Four dry corn starches with different amylose contents: Amioca (0 wt% amylose); HylonV (50 wt% amylose) and HylonVII (70 wt% amylose); were blended with poly lactic acid at various starch/poly lactic acid ratios and characterized for morphology, mechanical properties and water absorption. It was shown that starch with 50 wt% or more amylose content reduced moisture uptake than those with the higher percentage amounts of amylopectin. The explanation given was that although amylopectin is more crystalline than amylose, its large branched molecules contains ~75 wt% amorphous

structure which readily absorb water (Ke et al., 2003). Moreover no significant difference in mechanical properties was observed among starches with varying amylose content, except that the blend containing 50 wt% amylose had slightly greater strength.

Based on the foregoing, to produce starch-lignin blends with improved properties research should be directed in the following areas: (a) reducing the hydrodynamic volume of lignin and increasing its phenolic hydroxyl group content, (b) attaching hydrophobic groups to both starch and lignin, (c) including high molecular weight plasticizers such as sorbitol and maltitol (Ghosh et al., 2000), (d) using starch polymer with a high amylose content and (e) forming lignin esters prior blending with starch. The use of plasticizers will minimise starch degradation and improve processability. The acetylation of the hydroxyl group in low molecular weight lignin will reduce the amount of hydroxyl groups available for water molecules to attract to and hence improve the water resistance of the blends. The attachment of acetyl groups to lignin will reduce hydrogen bonding increasing the free volume of the amorphous component of starch, thereby reducing T_g . The miscibility of the starch-lignin blends property relationships could be studied by Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and differential scanning calorimetry (DSC) in order to evaluate molecular interactions between the two components.

5.3 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) are a group of biodegradable and biocompatible linear aliphatic polyesters mainly composed of R-(−)-3-hydroxyalkanoate units, produced as carbon and energy storage materials by a range of algae and bacteria. PHA have been reported with alkanoates ranging in length from C_3 to C_{14} , but the most common are polyhydroxybutanoate (PHB, C_4) and polyhydroxyvalerate (PHV, C_5) and copolymers of C_4 and C_5 alkanoates (PHBV) (Reddy et al., 2003).

Unlike most biopolymers, PHA are insoluble in water and have low permeability towards oxygen, carbon dioxide and water. These barrier properties make PHA good candidates for the production of packaging products like bottles, bags, wrapping film and disposable nappies. These applications have not been fully realised because PHB and PHV are relatively stiff and brittle and are thermally unstable during processing.

Blending with lignin is one possible strategy for overcoming the mechanical disadvantages of PHA. Ghosh et al. (2000) investigated the thermoplastic blends of several biodegradable polymers with organosolv lignin and organosolv lignin ester based on both solvent casting and melt processing. Blends of PHB with lignin are claimed to have a high degree of recyclability (Yao, 2008). On addition of up to 20 wt% lignin to PHB, improvements were seen in T_g , melting point, Young's modulus, and the degree of crystallinity (Ghosh et al., 2000). The addition of lignin reduced the crystallinity of PHB more than addition of lignin butyrate, suggesting greater compatibility of PHB with lignin than lignin butyrate. Recently, Mousavioun et al. (2010) examined the miscibility between PHB and bagasse soda lignins (having distinct chemical group functionality) based on the T_g of their blends. A single T_g implies complete compatibility between the components, while two or more T_g values suggest that the degree of miscibility is restricted. Figure 5.2 indicates that with the lignin content <40 wt% there is compatibility between PHB and lignin. The T_g were higher for of the blends obtained from the lignin fraction containing higher xylan and phenolic hydroxyl content, but lower methoxyl and carboxylic acid content. This implies that the association between lignin and PHB is probably related to the chemical functionality of the lignin polymer as the molecular weights of these lignin fractions are similar, approximately 2400 g/mol. In fact it was shown by FTIR that the miscibility between PHB and soda lignin was due to hydrogen bond formation between the carbonyl group of PHB and the phenol hydroxyl group of lignin (Mousavioun et al., 2010).

Blends of lignin butyrate with the slightly more hydrophobic polymer PHBV gave a significant reduction in crystallinity compared to blends with PHB. Meister et al. (1993) have reported that grafting lignin with styrene-acrylonitrile copolymer improves its compatibility with PHB-PHV.

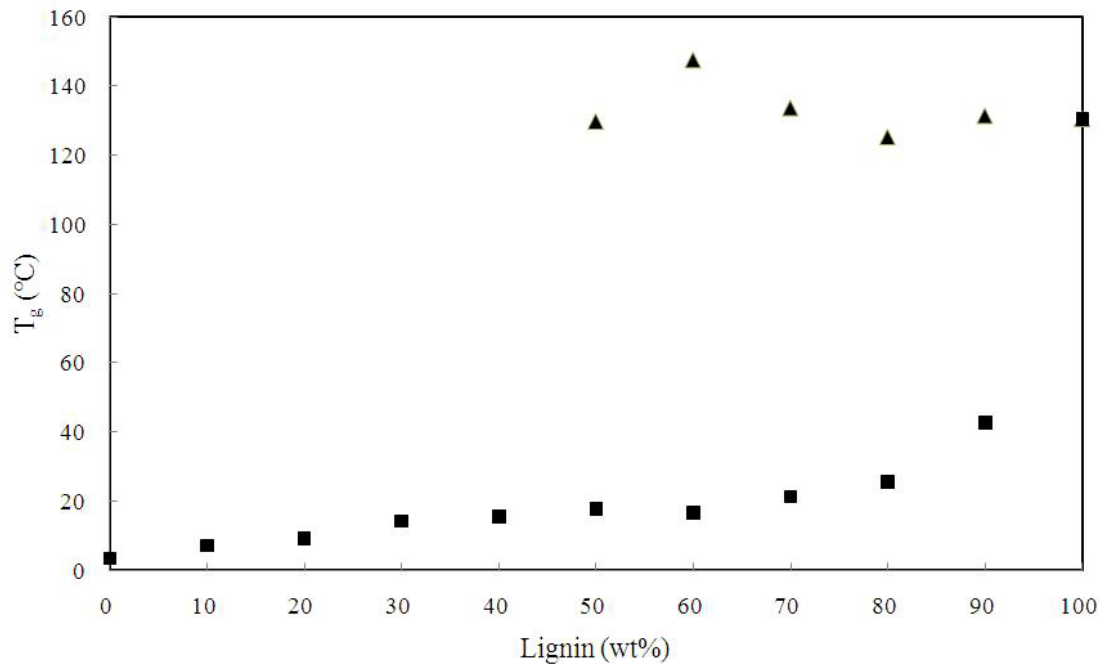


Figure 5.2 Miscibility of lignin/PHB blends based on T_g . Lignin T_g , ▲; PHB T_g , ■.

Camargo et al. (2002) investigated the thermal, mechanical and optical properties of bagasse lignin blended with PHB, as well as biodegradation of the composites. A significant increase in T_g was observed and the PHB/lignin blend was readily degraded by the common fungi species *Trametes versicolor*. The significant increase in T_g obviously related to the interactions between the reactive functional groups of lignin and the carbonyl groups of PHB. Weihua et al. (2004) investigated the effect of 1 wt% lignin on the nucleation of PHB by studying the kinetics of both isothermal and nonisothermal PHB crystallisation. DSC showed that not only did lignin act as a nucleating agent, decreasing the activation energy of crystallisation, but it reduced the size of the spherulites to give a less brittle material.

5.4 Polylactides and polyglycolides

Poly(L-lactic acid) (PLA) is a crystalline biodegradable polymer which like PHA has poor processing properties because of its high crystallinity. Copolymers of L-lactic acid and L-glycolic acid are frequently used in biomedical applications to enable tailoring of flexibility and degradation rate. Li et al. (2003) examined the thermal and mechanical properties of PLA/lignin blends, with results indicating a strong intermolecular hydrogen-bonding interaction between PLA and lignin. The tensile strength and elongation at break decreased with lignin content, while the Young's modulus remained almost constant up to a lignin content of 20 wt%. At lignin content greater than 20 wt%, thermal degradation of PLA was enhanced. More recently, ring-opening polymerisation of cyclic lactides with lignin has been used to create graft-copolymer additives that can significantly reduce the crystallinity and improve the processing and end-use performance of PLA (Uyama et al., 2008). Graupner (2008) used lignin to reinforce PLA/cotton composites and compared the mechanical properties of the composites with those of PLA/kenaf composites. Addition of lignin appeared to enhance the adhesion between the cotton fibres and PLA, improving the tensile strength and Young's modulus, though the impact resistance decreased (Graupner, 2008). Lignin has also been added to PLA in order to reduce its flammability, giving performance competitive with commercial intumescent formulations (Reti et al., 2008).

From the foregoing, it is evident that not much work has been carried out to understand the interactions between lignin and these crystalline polymers. The use of solid state nuclear magnetic resonance (NMR) and relaxation methods should be included in the analytical tools to study the interactions of lignin and these interacting polymers in order develop a better understanding of the nature of the blends for property enhancement.

5.5 Epoxy resin blends

Substitution of lignin for phenol is a possible route toward the preparation of inexpensive and renewable epoxy-resin adhesives. In fact, entirely renewable epoxy-resins have been prepared using lignin and epoxides of plant origin (Hirose, 2006; Watado et al., 2009). A very wide variety of comonomers and curing reagents have been applied to prepare lignin-derived epoxy resins (Ebata, 2004; Hirose et al., 2002).

The effect of lignin blending with epoxy resins is strongly affected by the type of lignin used (Feldman, 2002). Commercial hardwood lignins have been reported to improve adhesion to epoxy resins more than Indulin, a softwood lignin, a result which correlates well with the density of hydrogen-bonding groups in the material. Tomlinite lignin (20 wt%) gave the highest adhesive joint shear strength. In general, differences in performance could be related to the differences in molecular weight and the type and amount of functional groups (Feldman, 2002). Investigation of the viscoelastic properties of cured kraft lignin/epoxy resins has been found to have a very broad T_g , which suggests they may be suitable for application as adhesives or as damping materials for noise and vibration (Tomita, 1998). Epoxy-resins derived from lignin have also been applied in concrete formulations (Cheng et al., 2005) and in a range of fibreboard and plywood products (Okabe et al., 2006).

Feldman et al. (1991a; 1991b) studied a bisphenol A-polyamine hardener-based epoxy adhesive incorporating kraft lignin. Blends with up to 40 wt% kraft lignin cured at room temperature or above their T_g , demonstrating enhanced bonding between the components. The improvement was attributed to association between lignin and the unreacted amine groups of the hardener. In another study, Feldman and Khoury (1988) observed that epoxy blends with 10 wt% and 20 wt% of lignin improved the adhesion tensile strength of an epoxy polymer system. While blending with 5 wt% to 20 wt% lignin had little effect on the initial adhesive shear strength or the weatherability of the epoxy-lignin blend, after post-curing (4 h at 75 °C) significant improvement of adhesive strength under shear was observed.

Modifying lignin structure by ozonisation was found to have little effect on the properties of epoxy resins prepared from soda lignin and epoxy compounds (polyethylene glycol diglycidyl ether and bisphenol A diglycidyl ether) which could be prepared with acceptable shear strengths in applications as wood adhesive (Nonaka et al., 1996). Only one T_g was observed in resins of this kind, suggesting formation of interpenetrating polymer networks (Nonaka et al., 1997). Epoxy resins prepared from lignin, glycerol, and succinic anhydride cured with dimethylbenzylamine at a range of ratios showed a constant decomposition temperature, regardless of lignin and glycerol content (Hirose and Hatakeyama, 2006).

5.6 Phenol-formaldehyde resins

Extensive work has been carried out with a number of different lignin types as substitutes for phenol in phenol-formaldehyde resins. These have primarily been considered for use in adhesive applications, though there has been some application of lignin-containing phenol-formaldehyde resins as foams (Frollini et al., 2004). The state of work in this field to 2002 has been comprehensively reviewed by Feldman (2002). The properties of wood adhesive products produced with lignin-based phenol-formaldehyde resins have been found to be comparable with those of commercial resins at up to 35 wt% partial replacement with (Kulshreshtha and Vasile, 2002). A range of different lignins, including organosolv lignin, soda lignin, and liginosulfonates, have been used in phenol-formaldehyde resin preparation, and black liquor has even been applied directly (Nada et al., 2003; Wang et al., 2006). A number of methods for lignin derivatisation for forming phenol-formaldehyde resins are described in the literature. These phenolysis methods are (a) the lignin reacts with phenol and the lignin-phenol complex is then reacted with formaldehyde, (b) the lignin with reacts with phenol and formaldehyde, and the pre-polymer is then reacted with phenol, (c) phenol reacts with formaldehyde and the mixture is then reacted with lignin, and (d) the lignin reacts with formaldehyde and the hydroxymethylated lignin is then reacted with phenol. The

phenolation process may be acid or base catalysed. The condensation reaction occurs between the ortho or para position of phenol and the side chain of the phenylpropane units of lignin in which the α - position is substituted by hydroxyl, etherified lignin residue or a double bond-carbon linked lignin residue. Incorporation of lignin into phenol-formaldehyde resins has been demonstrated to delay the first glass transition and speed up curing (Khan and Ashraf, 2006; Khan and Ashraf, 2007).

Vazquez et al. (1999) and Cetin and Ozman (2002), have shown phenol-formaldehyde resins prepared using organosolv lignin and subsequent plywood board formation produced board knife-test results better than those obtained with a commercial phenol-formaldehyde resin. In contrast, Gardner and McGinnis (1988) prepared lignin-based resins with kraft lignin and steam-exploded hardwood lignin showing lower reactivity and poorer physical properties than the pure phenol resin. This variation in results is consistent with other reports indicating that the method of extraction and the source from which the lignin is derived has a strong bearing on the properties of the phenol-formaldehyde resin. For example, Olivares et al. (1988) reported that different fractions of softwood lignin separated by ultrafiltration after methylation and demethylation gave different reactivities toward formaldehyde, leading to different mechanical and water absorption properties. In another example, Piccolo et al. (1997) showed that during resol synthesis organosolv bagasse lignin acted as a chain extender. As a result, molded resins prepared with 40 wt% lignin exhibited modulus extension at elevated temperatures.

Park et al. (2008) studied the partial substitution of phenol in phenol formaldehyde resin with high-purity bagasse organosolv lignin. Purification by extraction with cyclohexane/ethanol removed waxes, lipids, tannins in the lignin prior to synthesis. The T_g of the resins were between 125 °C and 150 °C, and this transition was clearly evident in the resins when the lignin content was increased from 10 wt% to 40 wt%. Conversion profiles for lignin/phenol-

formaldehyde resins obtained in the authors' laboratory are shown below, demonstrating that partial replacement of phenol with lignin increases the rate of polymer formation (Figure 5.3). The conversion profile is relatively unchanged with the addition of 10 wt% lignin, however, the initial rate of conversion increases markedly upon increase in lignin concentration to 20 wt% and even further when the concentration is increased to 30 wt%. Further addition of lignin to 40 wt% decreases the rate of conversion from the 30 wt% value, but the conversion rate is still higher than the phenol-formaldehyde resin. In the same study, cardboard coated with lignin/phenol-formaldehyde showed water resistance properties far superior to untreated cardboard or cardboard treated with an equivalent phenol-formaldehyde resin (Park et al., 2008). Phenol-formaldehyde-type adhesives prepared from liginosulfonate derived from grasses (bagasse, kaigrass and wheat straw) have demonstrated acceptable performance qualities at up to 70 wt% liginosulfonate content (Akhtar et al., 2009; Liu et al., 2006). The best adhesive properties on incorporation into phenol-formaldehyde resins of wheat straw soda-lignin were found for the lower molecular weight fractions (Liu et al., 2008).

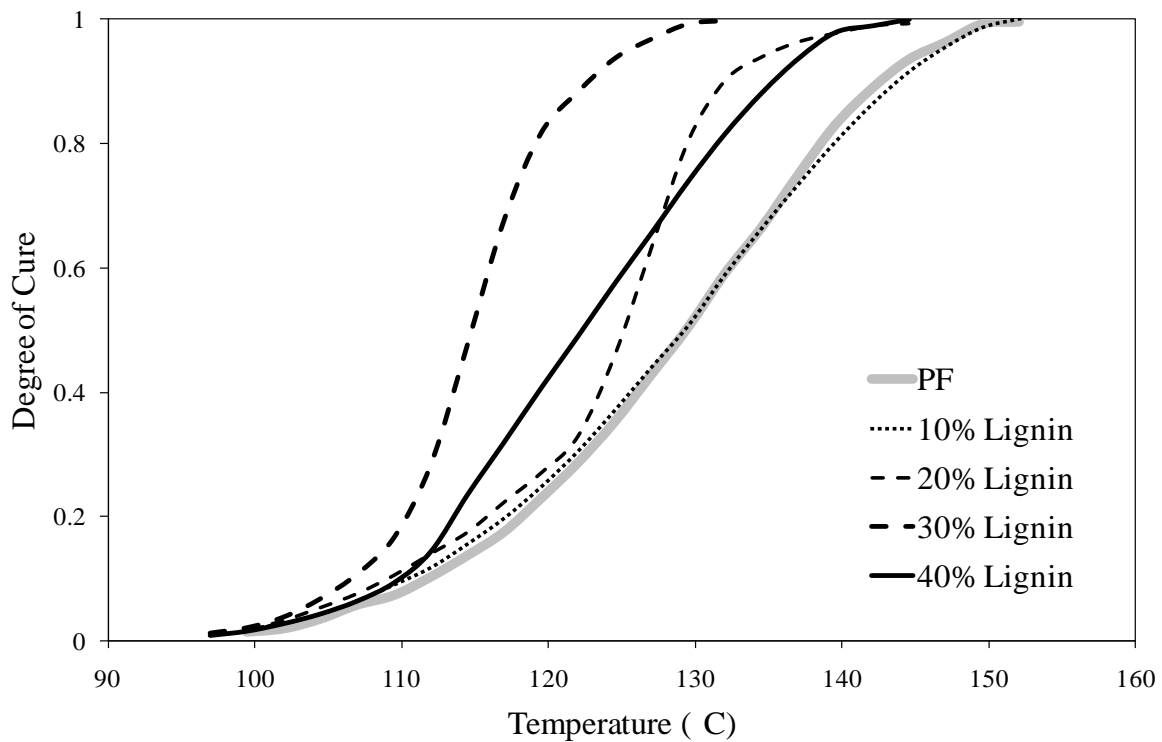


Figure 5.3 Conversion profiles of lignin-based phenol formaldehyde resins

Peng and Riedl (1994) have shown that the reactivity of liginosulfonate with formaldehyde is increased when wheat starch was added as a filler, and less condensation was apparent.

Hydroxymethylation has been reported to produce resins with improved properties in comparison to unmodified lignin (Yang and Liu, 2002). It would be interesting to see if the addition of starch to the hydroxymethylation procedure of lignin described by Muller and Glasser (1984) would further enhance the reactivity of the hydroxymethylated lignin and produce resins of improved quality. In another application of multiple natural products in a composite material, pulverised lignocellulosic materials such as sisal fibre have been applied as fillers in lignin-based phenolic resin (Frollini et al., 2004).

From an environmental point of view, an important advantage of using lignin in partial replacement of phenol-formaldehyde resin is the decrease in formaldehyde emission during

processing (Kulshreshtha and Vasile, 2002). It is also possible to avoid this volatile and toxic compound entirely, with good materials properties having been demonstrated for a resin composed of lignin and the non-volatile aldehyde glyoxal (Mansouri et al., 2007). The overall consensus is that lignin-based resins generally have weaker adhesive properties, and a high degree of variability in adhesion performance (Cyr and Ritchie, 1989). The presence of plasticisers or contaminants, such as very low molecular weight lignin, is suspected to be largely responsible for the low bond strengths obtained, (Hiro-kuni and Kenichi, 1989; Lora, 2002) while the variability is probably due to the sensitive dependence of properties on the source and history of the lignin, as mentioned above.

5.7 Lignin-polyolefin blends

The main objectives of incorporating lignin in polyolefins are to act as a stabiliser against oxidation under UV radiation or at elevated temperatures, or conversely, to enable the biodegradation of the material. Early investigations of polymer blending found good compatibility between hydrophobic lignin and high density polyethylene (HDPE) with little change in properties, but poor compatibility with low density polyethylene (LDPE) (Deanin et al., 1978). Some improvements in the tensile modulus of LDPE were found with greater than 20 wt% lignin incorporation, but tensile strength was poor. The differences observed between HDPE and LDPE suggest that molecular architecture may play as large a role as chemical structure in determining the compatibility of lignin in blends, as the interactions between lignin and the many short branching chains of LDPE may be entropically unfavourable.

Blends of up to 70 wt% hydrophilic lignin were similar for both HDPE and LDPE, with increases in Young's modulus and decrease in elongation at break for both classes of blend, with sugar-rich lignosulfonates giving the largest increase in modulus (Kubat and Stroemvall,

1983). Scanning electron microscopy of these blends suggested a morphology of thin HDPE/LDPE fibres in a lignosulfonate matrix.

Straw lignin obtained by steam-explosion has been blended with LDPE, HDPE, and linear low density polyethylene (LLDPE), giving blends that are stabilised against UV radiation and can be processed by conventional thermoplastic methods. While modulus was slightly increased in the blends, tensile strength and elongation at break were impaired (Pucciariello et al., 2004). Significant improvements have been observed in the thermal oxidative stability of polyethylene blended with lignosulfonate, and incorporation of lignosulfonate also had a significant impact on the rheology of the polymer melt (Levon et al., 1987).

Ammonium lignosulfonate and epoxy-modified lignosulfonate can act as nucleating agents in polypropylene (PP) processing as well as plasticisers and controllers of melt flow (Darie et al., 2007). Košíková et al. (1993) investigated sulfur-free lignins as composites of PP films. PP films containing 2 wt% - 10 wt% of spruce organosolv lignin and/or beech wood prehydrolysis lignin showed good compatibility between lignin and PP and sufficient tensile strength. The films acted as good UV absorbers (Kosikova and Demianova, 1992). The influence of lignin on the oxidative stability of PP has been examined by Gregorova et al. (2005) by differential scanning calorimetry under non-isothermal conditions. It was found that lignin exerts a stabilizing effect in both virgin and recycled PP, with a protection factor increasing with lignin content in the PP matrix, though the increases with small quantities of lignin were less significant than for polyethylene (PE) (Chodak et al., 1986). Surface modification of lignin/PP blends by treatment with silicon tetrachloride plasma increased tensile and impact strength by introducing surface cross-linking (Toriz et al., 2002).

Alexy et al. (2000) used lignin as a filler for both LDPE and PP at concentrations up to 30 wt%, with only small impacts on tensile strength and melt flow index, but improvements in processing stability and modulus. Resistance to light and heat degradation was improved for

both PE-lignin and PP-lignin blends. Kraft lignins acylated with long hydrophobic substituents have been used to compatibilise fractions of different polyolefins in recycled household waste, giving good values of tensile strength and elongation at break for blends of LDPE and PP (Tinnemans and Greidanus, 1984). Compatibility of lignin and hydroxypropyl lignin with polyethylene is low in comparison with more polar monomers, making them relatively ineffective in improving bulk modulus (Ciemniecki and Glasser, 1989; Glasser et al., 1988). The compatibility between lignin and PE/PP can be improved by grafting ethylene/propylene monomers onto lignin prior to blending to the polyolefin (Casenave et al., 1996). The Young's modulus of the lignin-grafted material prepared by Casenave (1996), Ait-Kadi and Riedl was similar to that of pure polyethylene at up to 64 wt% lignin content. Chemical modification of soda lignin with stearyl chloride has also been effective in increasing its compatibility with LDPE, giving significant mixing attested to by improvements in mechanical properties (Vasile et al., 2006).

Organosolv lignin blends based on the compatibilisation of polyethylene with ethylene-vinyl acetate copolymer (EVA) have been investigated by Alexy et al. (2004). The addition of 10 wt% EVA gave an approximate 200 wt% increase in tensile strength and a 1300 wt% increase in elongation at break in comparison to blends without EVA. A composite material prepared containing 33.6 wt % lignin displayed acceptable processing and mechanical properties, and was used successfully in preparing blown films. The compatibility of lignin and EVA was found to increase with increasing content of vinyl acetate for both soda lignin and hydroxypropyl lignin by Glasser, Knudsen, and Chang. (Glasser et al., 1988) Tensile properties were inferior with less than 10 wt % vinyl acetate and the best tensile properties were obtained with materials containing between 5 wt % and 20 wt % hydroxypropyl lignin and greater than 25 wt % vinyl acetate. Ciemniecki and Glasser (1989) also observed that

blends of EVA and hydroxypropyl lignin showed superior strength properties as the proportion of the polar vinyl acetate component increased.

In another application of EVA, lignin was added to an EVA/LDPE blend to form a homogeneous blend exhibiting a single glass transition temperature that could be used to prepare a foam (Zhou and Luo, 2007). LDPE grafted with maleic anhydride is another compatibiliser that has been successfully used to mix LDPE and lignin, with scanning electron microscopy indicating more dispersed lignin in smaller domains in the presence of maleated LDPE, decreasing the melting temperature and improving stability to thermal oxidation (Li and Luo, 2005). At 25 wt % loading of lignin and 10 wt % maleated LDPE, blown films could be prepared with excellent properties.

Processes for preparing degradable plastic blends of ethylene copolymers and organosolv lignin have been patented by Bono (1994) Lignin was incorporated in the form of powder having a grain diameter of about 1 μm - 5 μm , and homogeneous films with a thickness of about 15 μm - 25 μm were obtained showing improved degradation with photoactive and oxidizing agents. The ability of the lignin-degrading microorganism *Phanerochaete chrysosporium* to degrade lignin-PE blends has been reported by Košíková et al. (2001). The isolation of oligomer fraction from biodegraded polymer blends indicated that the biotransformation of lignin during the cultivation process was accompanied with degradation of the PE matrix.

5.8 Lignin-vinyl polymer blends

As with polyolefins, vinyl lignin polymers have attracted interest primarily as a UV and thermal stabiliser. In general, unmodified lignin has poor compatibility with non-polar vinyl polymers; while the modulus of these blends is increased, reductions in tensile strength and elongation at break are obtained. Early work found good compatibility between hydrophobic

lignin and relatively polar poly(vinyl chloride) (PVC), but poor compatibility with polystyrene (Deanin et al., 1978). However, the source of the lignin can have a considerable impact on miscibility, and steam-explosion lignin powder has more recently been successfully blended with atactic polystyrene into a readily processible material (Pucciariello et al., 2004). Improved blending of polystyrene and lignin has also been achieved using a copolymer of styrene and vinyl phenol (Henry and Dadmun, 2009) or cellulose phthalate (Hechenleitner et al., 1997) as compatibilising agents. In the latter case, a strong dependence of thermal stability on the hydrophobicity of the lignin used was observed, with the more hydrophobic lignin fraction promoting stability and the more hydrophilic fraction reducing stability.

A significant body of research has been carried out on the blending of lignin and PVC (Banu et al., 2006; El Raggi et al., 2000; Feldman and Banu, 2003; Mishra et al., 2007). One rationale for this has been to increase the resistance of PVC-based floor coverings to attack by fungi that can degrade phthalate-based plasticisers to generate potentially toxic products (Feldman et al., 2003). Generally homogeneous PVC/lignin blends can be prepared at low lignin content, with increased rigidity due to the lignin component improving impact resistance and scratch hardness while reducing flexibility (Mishra et al., 2007). Larger quantities of lignin with concomitant changes in properties towards rigidity can be achieved by using plasticisers that can disrupt intermolecular hydrogen bonding in lignin, (Feldman and Banu, 2003) and in general lignin may have either an antiplasticising or plasticising effect depending on its molecular weight and how it is dispersed through the PVC matrix (Banu et al., 2006; Feldman et al., 2003). There are reports that thermal stability of PVC can be improved by addition of lignin (Szalay and Johnson, 1969). Conversely, a negative impact of lignin on stability of PVC to weathering has been attributed to degradation of lignin under PVC processing conditions (Feldman and Banu, 1997). There is some evidence that softwood

lignins, generally having a higher proportion of crosslinked phenol groups, are more effective in promoting properties of PVC/lignin blends than hardwood lignins (Feldman and Banu, 1997).

Polymer blends of hydroxypropyl lignin with poly(methyl methacrylate) (PMMA), and poly(vinyl alcohol) (PVA) were investigated by Ciemniecki and Glasser (1989). In both cases compatibility was high, with the lignin able to contribute to modulus, while depending on molecular weight the effect of lignin incorporation could be either plasticising or antiplasticising. In all cases two-phase materials were produced, but T_g values nevertheless suggest a high degree of compatibilisation. Blends prepared using injection moulding showed generally better properties than blends formed by solution casting from organic solvent (Ciemniecki and Glasser, 1988).

Li et al. (1997) reported a blend of 85 wt % underivatised kraft lignin and poly(vinyl acetate), prepared with indene and diethyleneglycol benzoate as plasticizers, which exhibited promising mechanical properties. The modulus and tensile strength of these blends was strongly influenced by the degree of association between the lignin molecules. Lignins dissociated by prolonged incubation in 0.10 M NaOH gave much poorer mechanical properties in the blends, while lignins associated by incubation in 0.40 M NaOH with a high ionic strength gave blends with excellent mechanical properties. This work has significant implications for the entire field of lignin-polymer blends, implying that the effect of the blended copolymer on non-covalent interactions between lignin molecules could play a critical role in the properties of blended materials (Chen and Sarkanen, 2006).

Blends of hydrophobic lignin with water-swellaable alternating copolymers of maleic anhydride have attracted interest as matrices for delivery of agricultural actives. Acylated kraft lignin was blended with poly(maleic anhydride-*alt*-styrene) by solvent casting to give

brittle films which could be swollen to up to 50 times their dry weight in water or dilute aqueous ammonia (Tinnemans and Greidanus, 1984).

There has been interest in blends of lignin with hydrophilic polymers such as poly(vinyl alcohol) (PVA) and poly(ethylene oxide) for application in carbon fibre synthesis (Kubo et al., 2005; Kubo and Kadla, 2004; Kubo and Kadla, 2005). While kraft or organosolv lignins can be spun into fibres, they produce carbon fibres that are brittle and difficult to handle, and morphological properties can be significantly improved using miscible (e.g., PEO) or immiscible (e.g., PVA) blends of hydrophilic polymer with lignin (Kubo et al., 2005). Incorporation of lignin in PVA greatly reduces the crystallinity of the PVA and reduces T_g , suggesting there are strong hydrogen-bonding interactions between lignin and PVA despite the fact the these blends remain two-phase systems (Kubo and Kadla, 2003).

A 'polyionic complex' of liginosulfonic acid and poly(vinyl pyridine) can be cast into a thin film and shows good adhesive properties (Hasegawa et al., 2008).

As with polyolefin/lignin blends, blends of lignin with vinyl polymers have been shown to be biodegradable, with poly(methyl methacrylate) (PMMA) and polystyrene blends with as little as 10 wt % lignin degrading under the action of a number of 'white rot' fungus species (Milstein et al., 1996). Conversely, lignin blending with poly(vinyl alcohol) had little effect on its rate of bidegradation (Pseja et al., 2006). Incorporation of small amounts of lignin has also been demonstrated to accelerate the thermal depolymerisation of polystyrene and PMMA (Mansour, 1992).

5.9 Lignin-polyester blends

Blends of lignin have been prepared with a wide variety of synthetic polyesters, in addition to the poly(hydroxy alkanates) and polylactides/polyglycolides already discussed. These

include poly(ethylene terephthalate) (PET), (Agafitei et al., 1999) poly(butylene terephthalate), (Xu et al., 2007) poly(trimethylene succinate) (Li and Sarkanen, 2005) and poly(ϵ -caprolactone) (Nitz et al., 2001).

Blending of poly(butylene adipate) and poly(trimethylene succinate) with acylated, methylated and ethylated kraft lignin is most effective when the lignin has a broad molecular weight distribution (Li and Sarkanen, 2005). These polyesters appear to be relatively less effective plasticisers of lignin than PEG. On the other hand, alkylated lignin in combination with aliphatic polyester plasticisers has produced materials with tensile properties very similar to polystyrene (Sarkanen and Li, 1999).

Blends of methylated and ethylated kraft lignins with aliphatic polyesters seem appear to be a potentially versatile class of thermoplastics, with homogeneous blends obtained when the ratio of methylene/carboxylate ester in the polyester is between 2 and 4 (Li and Sarkanen, 2003). As with kraft lignin/poly(vinyl acetate) blends, the association of the lignin molecules into supramolecular structures is postulated to be largely responsible for the properties of these blends (Li et al., 1997). The amount of alkylated kraft lignin necessary to disrupt crystalline domains of the polyester is least when the ratio of methylene/carboxylate ester in the polyester is between 2.5 and 3.0 (Li and Sarkanen, 2002).

Lignin can form homogeneous blends with poly(butylene terephthalate) (Xu et al., 2007) and PET (Kadla and Kubo, 2004). Soda lignin decreases the melting temperature and T_g of PET, improving its processability, and accelerates crystallisation implying it can play a role in PET nucleation (Chaudhari et al., 2006). The compatibility of lignin epoxy-modified with epichlorohydrin with PET and a poly(ethylene terephthalate/isophthalate) copolymer was studied by Agafitei et al. (1999). Optimum compatibility with significant increases in surface and bulk electrical resistivity, reductions in crystallisation temperature, and increases in melting temperature, were achieved using 4 wt % -10 wt % lignin (Agafitei et al., 1999).

Organosolv lignin alkylated with propyl, butyl, or pentyl groups formed homogeneous blends with poly(ϵ -caprolactone) (PCL), with crystallisation studies suggesting the miscibility improved as the length of the alkyl chain increased. Good elongation at break values were obtained even in blends with 50 wt % alkylated lignin (Teramoto et al., 2009). Unmodified straw lignin strongly stabilised PCL against UV radiation and increased the blend modulus, but decreased the observed elongation at break, and the two components of the blend were shown to be immiscible by dynamic mechanical analysis (Pucciariello et al., 2008).

Compatibilisation of PCL with lignin and wood flour could be achieved by incorporation of PCL grafted with maleic anhydride, giving a blend with a five-fold improvement in modulus and 100 wt % improvement in yield stress (Nitz et al., 2001). Lignin was found to retard the rate of decomposition of these biodegradable composites (Nitz et al., 2001).

Sulfur-free lignin compounded with poly(butylene-co-adipate-co-terephthalate) gave improved mechanical properties, but marked differences were seen between lignin obtained by alkaline pulping of fibre plants such as sisal and abaca and alkaline pulping of wood, with the lignin derived from the fibre plants giving superior modulus and yield stress (Nitz et al., 2001). The blends obtained were heterogeneous, with the dispersed lignin phase occurring in larger domains when wood lignin was used.

5.10 Lignin-containing polyurethanes and lignin-polyurethane blends

The incorporation of lignin and lignin derivatives into polyurethanes has been investigated in order to (a) increase crosslinking of the polyurethane networks, (b) increase T_g , (c) increase tensile strength, (d) increase curing rates and, (e) increase thermal stability (Hatakeyama and Hatakeyama, 2005).

Extensive work has been done on the development and characterisation of polyurethanes from lignin grafted with polycaprolactone, which gave two-phase systems with properties controlled by the degree of association of the PCL chains (Hatakeyama et al., 1998;

Hatakeyama et al., 2001; Hatakeyama et al., 2001). Lignin extended with polyethylene oxide has also been used as a basis for producing polyurethanes, notably in interpenetrating network systems with PMMA (Kelley et al., 1989; Kelley et al., 1990). Liu et al. (2002) used propylene oxide-modified lignin with ethylene glycol and methylene diisocyanate to prepare polyurethane resins potentially suitable for use in hard foams, with lignin content of 30 wt % or less. One intriguing application as a geoengineering material is *in situ* polyurethane/inorganic composites generated by injecting lignin and isocyanates into sand (Hatakeyama et al., 2005).

Polyurethane/lignin blends have also been investigated. The morphology of such blends has been studied by Feldman and Lacasse (1989) While SEM revealed an even distribution of lignin particles in the polyurethane matrix, the different morphologies of the constituent phases could clearly be observed, with differential scanning calorimetry (DSC) confirming immiscibility. Polyurethane lignin blends have also been obtained by treating steam explosion lignin from straw with a range of isocyanates. The presence of ethylene glycol reduced the yields, and the best results were obtained using an isocyanate terminated poly(butylene terephthalate) (Bonini and D'Auria, 2007). Ciobanu et al. (2004) used a polyurethane elastomer blended with flax soda lignin to form homogeneous solvent-cast films containing between 4.2 wt % and 23.2 wt % lignin. While the thermal degradation ranges of unmodified polyurethane and the blends were similar, the presence of lignin accelerated decomposition at lower temperatures. The tensile strength increased up to 370 wt %, toughness up to 470 wt % and elongation at break up to 160 wt %, for the blends compared to the unmodified polyurethane film.

5.11 Rubber-lignin blends

Lignin has attracted most attention as filler in natural and synthetic rubbers - that is, as a component of a multiphase mixture, not in a homogeneous blend. It has been applied as a

filler in butadiene-styrene-butadiene and isoprene-styrene-butadiene rubbers for shoe soles, (Savel'eva et al., 1983) in styrene-butadiene elastomer, (Kosikova et al., 2003; Kramarova et al., 2007) and in natural rubber (Kramarova et al., 2007). Soda lignin and calcium lignosulfonate were compared as fillers in natural rubber, and though neither had properties entirely comparable to carbon black, soda lignin had better filler properties than calcium lignosulfonate and showed potential as a low-cost substitute for carbon black (Lazic et al., 1986). Low molecular weight lignins have been shown to be more effective in improving the tensile strength of natural rubber than of styrene-butadiene rubber, being significantly more effective than starch or protein as a filler for natural rubber but not for styrene-butadiene rubber (Kramarova et al., 2007).

Lignin-based phenol-formaldehyde resin has demonstrated good mechanical properties, oil resistance, and resistance to environmental oxidation when used as a filler in nitrile rubber (Wang et al., 1992).

Lignin has also been applied in combination with an oligomeric polyester as a modifier of isoprene rubber and methylstyrene-butadiene rubber (Savel'eva et al., 1988). The vulcanization rate of the rubbers increased and optimum vulcanization time decreased, and improvements were obtained in the mechanical properties suitable for applications as tire rubber (fatigue strength, adhesion to reinforcing cord). Improved adhesion to textiles in blends with lignin has also been observed in blends of lignosulfate with natural rubber (Piaskiewicz et al., 1998) and styrene-butadiene rubber (Lora et al., 1991). While in these applications lignin incorporation increases the adhesiveness of the material, a hydrophobically modified lignin has been applied to pre-vulcanised natural rubber latex in order to decrease the stickiness of natural rubber latex as a paperboard coating material (Wang et al., 2008).

5.12 Lignin-graft-copolymers

Apart from the uses of lignin as a filler in thermoplastics and as a copolymer in thermosetting polymers, there is the potential for lignin to be used in free-radical copolymerisation with unsaturated polymers. This potential is limited by the ability of the phenolic hydroxyl groups in lignin to act as radical scavengers, initiating the formation of quinonic structures (Barclay et al., 1997; Lu et al., 1998).

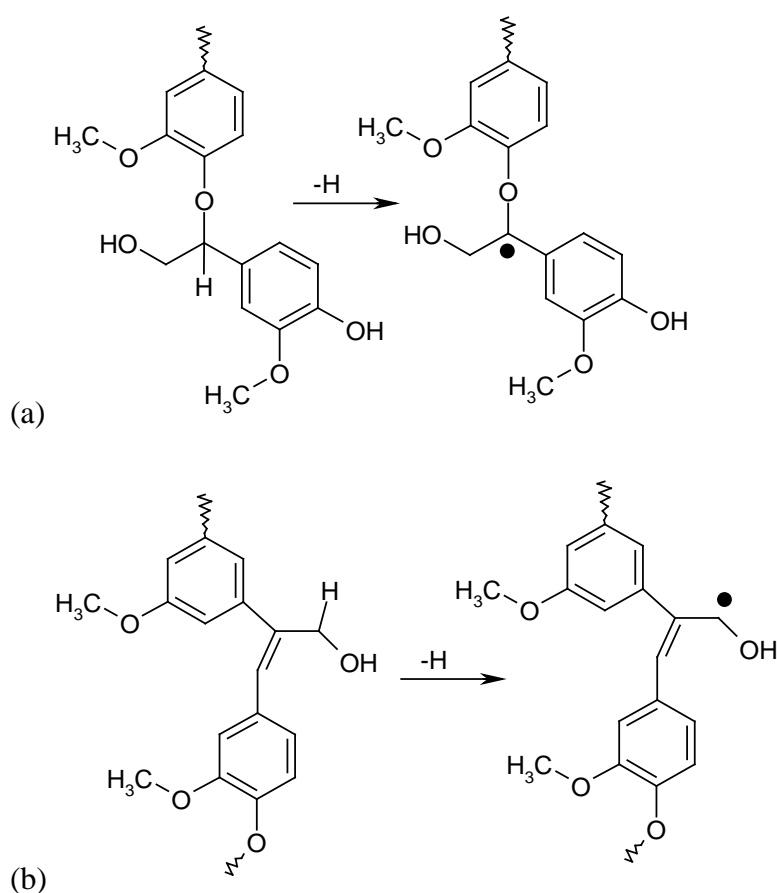


Figure 5.4 Potential sites for hydrogen abstraction for free-radical grafting from lignin; (a) benzylic hydrogen, (b) allylic hydrogen from double bond from dehydroxylation

The residual double bonds in lignin are 1,2-disubstituted and hence not reactive towards free-radical attack, but lignin has a high concentration of benzylic sites that should be susceptible

to hydrogen abstraction and hence afford grafting sites (Figure 5.4). The chief limitation on achieving grafted copolymers based on free-radical monomers and lignin is hence not normally the intrinsic reactivity of the ligand, but that the high polarity of the hydroxyl groups leads to a molecule insoluble in non-polar comonomers such as styrene and methyl methacrylate.

Lignin has been shown to retard the polymerisation of styrene and methyl methacrylate, (Rizk et al., 1984) but good yields of PMMA-grafted lignin have been prepared, (Meister and Zhao, 1992) and successful grafting using conventional radical initiation has also been achieved with acrylamide, (Ibrahim et al., 2006; Meister et al., 1991) vinyl acetate, (Corti et al., 2003) cationic vinyl monomers, (Meister and Li, 1990) acrylic acid, (Maelkki et al., 2002), acrylonitrile (Chen et al., 1996) and sodium acrylate (Potapov et al., 1990). Interest in grafting polyelectrolytes to lignin arises from the possibility of incorporating the thermal and mechanical resistance of lignin into polyelectrolyte applications for extreme environments, such as additives for drilling muds (Ibrahim et al., 2006). Chemical grafting of PMMA or polystyrene to lignin produces surface-active materials which have possible applications as wood coatings (Chen et al., 1995; Gardner et al., 1993). Contact angle on wood surfaces coated with lignin-PMMA graft copolymer, a measure of hydrophobicity, increased with lignin content, and copolymers of relatively low molecular weight gave larger contact angles than copolymers of low molecular weight (Gardner et al., 1993). Sailaja (2005) has reported that lignin grafted with PMMA using manganese pyrophosphate initiator gave much improved mechanical properties in blends at up to 50 wt % with polyethylene, in comparison to blends of polyethylene with unmodified lignin.

A promising means for producing graft copolymers of lignin and free-radical monomers appears to be initial derivatisation of lignin with more readily polymerisable moieties, e.g., with isocyanatomethacrylate to give pendant methacrylate groups readily polymerisable with

methyl methacrylate or styrene, (Glasser and Wang, 1989) or with chloromethylstyrene and methacryloyl chloride (Da Cunha et al., 1993). Feldman et al. (1991) carried out free-radical grafting of maleic anhydride onto lignin in order to facilitate incorporation of the modified lignin into a polyurethane. They reported both free-radical grafting to the lignin backbone and a degree of esterification of the phenol hydroxy groups on treatment with maleic anhydride and a persulfate radical source.

Grafting of methyl methacrylate to lignin using radiation was first reported by Koshijima and Muraki (1964). Alkoxylation of the phenol groups improved the effectiveness of radiation grafting, and radiation-curable coatings have been produced using acrylic acid and propoxylated lignin (Reich et al., 1996). Radiation-induced grafting of styrene to lignin was facilitated in the presence of an organic solvent, with better efficiency as the proportion of methanol in the reactants was increased (Phillips et al., 1972). Increasing moisture content in wood was correlated with increasing radiation-induced grafting of PMMA to lignin, presumably a phenomenon related to monomer diffusion within the matrix (Sutyagina et al., 1987).

Grafting to lignin has also been accomplished through anionic and cationic chain polymerisation, and chemical (De Oliveira and Glasser, 1994a) or enzymatic (Huttermann et al., 2000) grafting of complete polymer chains. Oliveira and Glasser prepared star-like graft copolymers of lignin and poly(caprolactone) using anionic polymerization (De Oliveira and Glasser, 1994b) and heterogeneous composites of these copolymers with poly(vinyl chloride) (De Oliveira and Glasser, 1994c). While these lignin-PCL copolymers were brittle and had poor mechanical strength on their own (De Oliveira and Glasser, 1990), they were found to exhibit good plasticization properties with PVC. Anionic polymerisation has been used to graft well-characterised polystyrene chains onto mesylated lignin, producing copolymers

suitable for use as compatibilisers for blends of kraft lignin and polystyrene (Narayan et al., 1989).

Another route to lignin-PCL graft copolymers is by enzymatic polymerisation of ϵ -caprolactone (Enoki and Aida, 2007). A similar chemo-enzymatic polymerisation pathway has also been reported as a means of grafting acrylamide (Mai et al., 2000a) and acrylic acid (Mai et al., 2001) onto lignin, in a process where the role of the laccase enzyme appears to be primarily to catalyse the production of peroxide-derived radicals (Mai et al., 2002). Although grafting of acrylic acid to calcium lignosulfonates could be successfully carried out with a hydroperoxide initiator alone, the process was much more effective when the initiator was used in combination with laccase (Mai et al., 2000b).

6 Conclusions

Lignin is a very abundant naturally occurring polymer with good properties for many materials applications, which can play a role in replacing or part replacing petroleum-based components in a broad range of composite materials. Lignin can be isolated in fractions of varying molecular weight and may readily be functionalised to play a role in a broad range of composite materials. In addition, lignin can serve as a feedstock for the production of both liquid fuel and a broad range of commodity chemicals. The importance of lignin in these applications is likely to increase, as society becomes less tolerant of product streams that dispose of lignin by landfill or burning and as the exploitation of lignocellulosic sources for biofuels increase the amount of lignin generated. Widespread exploitation of these lignocellulosic sources would also dramatically change the nature of the lignin isolated: today most lignin is hydrophilic sulfated material produced as a by-product of the pulp and paper industry, but the thermal, chemical, and biological methods employed in digesting lignocellulosic material are all likely to give rise to unfunctionalised lignin. For many

applications, this material will be of superior quality, and hence the emergence of a viable lignocellulosic biofuels industry will afford a significant opportunity to apply lignin to a much greater extent in polymer composites, controlled-release formulations, and as a feedstock for fuels and commodity chemicals. Conversely, the development of these applications on a commercially viable scale will exert a ‘pull’ effect on lignocellulosic biofuel development, making the industry economically viable at an earlier stage of fossil fuel resource depletion. Despite hundreds of years of experience in the pulping of biomass, technically feasible processes for separation of biomass into its main components still lie mostly below the threshold of economic viability. The present treatment strategies, whether thermal, thermochemical or thermomechanical, still require considerably energy input. Thus an important future research direction is the cost-effective fractionation of lignocellulosic biomass. Specifically, the processes involved in lignin recovery from black liquor (such as acid precipitation and membrane filtration) need to be improved so that better separation, decreased losses during washing of the precipitated lignin, and improved purity can be achieved. Research into the use of flocculants, surfactants and ions for effective lignin isolation from black liquor produced from various fraction strategies would also be worthwhile.

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