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Green Adhesives: Options for the Australian industry – summary of recent research into green adhesives from renewable materials and identification of those that are closest to commercial uptake

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Green Adhesives: Options for the Australian industry – summary of recent research into green adhesives from renewable materials and identification of those that are closest to commercial uptake

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Executive Summary

The purpose of this project was to review the current state of the art in wood adhesives using renewable materials. A number of different sources of natural and renewable materials were investigated. These included

- Tannins
- Lignin
- Oils
- Proteins (in particular soy protein)
- Other sources

The use of these materials has been an active research area for a very long time. Many of the technologies are still at the pre-commercial, pilot or laboratory scale demonstration phase. There are a few technologies that are being touted as ready for full scale commercial use. These include the Dynea AsWood technology which incorporates a protein source with a phenol-formaldehyde resin and the Ashland/Hercules Soyad system which is a blend of a modified soy protein and a cross linking agent such as polyamide-epichlorohydrin (PAE). These two systems have been presented at a number of recent international conferences. A major driver for the introduction of these technologies appears to be changes in legislation that regulate the permissible level of formaldehyde emissions from composite wood products, in particular the CARB requirements in the USA. Many of these technologies still appear to be more expensive than urea-formaldehyde (UF) resin systems and are only finding a niche in the market where UF resins are not permitted.

The change away from petrochemical adhesives to those incorporating natural and renewable materials is currently underway in North America. It would be reasonable to expect that within the next 5 to 10 years, these changes will occur within the Australian and New Zealand marketplace, especially as the consumer becomes more environmentally aware. Given that these new technologies are still in the process of being introduced on an industrial scale, it is recommended that the Australian wood panels industry adopt a “wait and see” approach until these technologies have been “bedded down” and have several years of production history.

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Introduction

There has been increasing international attention given to the production and use of “green” adhesives for the manufacture and production of reconstituted and engineered wood products. This interest in these bio-based adhesives has arisen due to a number of drivers, the most important being recent government legislative changes to minimise the health effects relating to product emissions of volatile organic chemicals (VOCs), most notably formaldehyde, and the use of renewable materials as a cost effective replacement for petrochemical components of adhesives. This has been coupled with an increasing environmental awareness of the consumer and drive for sustainability. It is therefore timely to review the current state of the art in this area to help Australian manufacturers position themselves to capitalise on any technology advances being made.

The use of renewable natural materials as a major component of wood adhesives is not new. Adhesives using protein sources such as blood, casein and vegetable proteins such as soy and wheat were used extensively prior to the large scale uptake of synthetic adhesives such as phenol-formaldehyde and urea formaldehyde adhesives following World War II.

The definition of renewable wood adhesives is broad and has been interchangeable with other terms such as green and bio-derived adhesives. In a recent review (Jones, 2007); bio-derived adhesives were defined as “*materials of natural, non-mineral or non-petroleum based origin that can be used either in their natural state or after small modification, capable of reproducing the behaviour and performance of synthetic resins*”. In this review, the term “renewable adhesives” will be used and is defined as adhesives that contain a significant amount of a renewable and natural resource.

There have been a number of reviews on the historical development of wood adhesives based on renewable materials and the interested reader is directed to these for more information (see for example various chapters in Pizzi 1983, Pizzi 1989, Pizzi 1994). There has also been a recent review completed by BRE on the state of bio-derived adhesives for the UK wood industry.

In the past decade there has been resurgence in research carried out on wood adhesives focussed on finding alternatives to what may be termed the traditional formaldehyde based adhesives used in the composite wood panel industry. The question must be asked why?

The key drivers that have been seen in the building products sector for the most part are:

- Environmental concerns
- Voluntary codes and regulatory controls.
- Research driven technology seeking markets
- Price volatility

The background and answer to why is complicated but ultimately the drivers can be traced to issues relating to environmental sustainability and health.

The World Commission on Environment and Development definition suggests that sustainability is "*forms of progress that meets the needs of the present without compromising the ability of future generations to meet their needs*."

So in developed countries there has been an increased focus on ensuring that any development has a minimal impact on the current and future environment. This has translated into:

- Focus on renewable materials
- Reducing the reliance on fossil fuels
- Reducing indoor air quality impacts
- Reducing the use of energy and water.

Examples of this can be seen in the voluntary Green Building Councils Green Star building rating system and the Victorian Government's 5 Star energy rating system for commercial and domestic buildings. Both these voluntary codes have at their heart environmental sustainability with the ability to change the products and systems used in the building industry.

The issue of sustainability is not as simple as utilising renewable materials. There is now serious debate about the effect the utilisation of farm land for bio-fuels has on food prices and the down-side to the world's poor through these increased prices. In the USA corn prices have risen significantly due to the use of corn as a feedstock for ethanol production. The increased value of corn has a flow on effect as farmers convert plantings to corn to reap the financial benefits and as a result create shortages of other food commodities and consequently causing price increases in these areas as well. A similar debate has been seen in the timber industry over the purchase of farming land for conversion to forestry.

Formaldehyde Controls

In 2004 the International Agency for Research on Cancer (IARC) changed its classification of Formaldehyde to Category 1- known human carcinogen. In the past the health concerns relating to formaldehyde exposure had driven formaldehyde emission reduction. This reclassification and the desire to achieve environmental sustainability by many consumers have further driven the desire for alternative binders that do not contain formaldehyde.

As a result of the IARC reclassification the Californian Air Resources Board (CARB) in 2009 has introduced regulation in California which limits the emissions of certain wood composite products. To ensure compliance to the regulations manufacturers have to establish a third party certified quality assurance system that evaluates product emissions. In 2009 the US senate introduced a Bill to implement this regulation across all States of the USA.

Similarly in Japan a Building Law was established around 2005 to limit the use of high emission wood panels in the built environment. It should be noted that these limitations were restricted to products used in the construction of houses and not furniture. Compliance to the standard is primarily demonstrated through third party certification to the relevant JIS standard.

Additionally concerns about indoor air quality have driven labelling systems for VOC emissions and controls.

Price Volatility

In the last 25 years there have been various price changes in the price of oil. These changes have lead to swift changes in the price of petroleum products and their derivatives including constituents of formaldehyde based resins. The ability of manufacturers of wood products to recover these costs has been limited and so the desire to separate the price of the adhesive from this cycle has attractive benefits.

Research Push

Several research groups have driven a push for alternative binders. The push in part may be due to sustainability but also funding has come from organisations that have a financial stake in the supply of the alternative materials. Examples of groups that have been involved in research for alternatives are

- Resin Suppliers
- Soybean authorities
- Large Enzyme suppliers
- Entrepreneurs

It should be pointed out that wood adhesives prior to the Second World War were predominately based on natural raw materials and could be classified as renewable and green. In the past wood adhesives fell into five main categories (Lambuth 1989):

- Animal Glues
- Liquid Glues
- Casein & Vegetable protein glues
- Starch Glues and Blood Albumin glues

The primary reason for this was the lack of availability/know-how of synthetic adhesives and their relative cost. So the concept of natural adhesives has precedence in the past and potential relevance in the future. However, critical to their use the technology will have to:

- Perform in a similar way to current synthetic materials.
- Not impact on the environment in any significant way.
- Be available in quantities to supply the market.

Lambuth (1989) noted a number of consistent themes to the research that was being carried out at that time. These include:

- The recovery or production of today's synthetic resin raw materials from renewable resources or waste streams from renewable resources.
- Synthetic based on partial or total replacement of critical petrochemical constituents.
- Development of entirely new adhesives concepts.
- Enhancement of established natural adhesives.

What is apparent from previous writing is that the need for alternatives was driven by threats to supply of raw materials at a reasonable price. We have recently gone through a huge hump in raw material prices (2008) which has been weathered, all be it reluctantly, however recognition by users and a push to lower environmental impact and improved well-being is now becoming key to future developments.

In the following sections we consider the current state of research and commercialisation of Green Adhesives, particularly development activities over the last 10 years.

Adhesives from Renewable Materials

Enzyme Based Adhesives

A number of review articles have been published on the use of enzymes in the timber industry and in particular as wood adhesives (Mai et al (2004), Widsten et al (2004). Several authors have proposed the use of Enzymes from wood rot fungii as wood adhesives. (Kharazipour 1998a, Felby 1998) The main themes to this research are:

- Use of two component systems
- Use of single component systems
-

The two principal research groups are those of Kharazipour and Felby.

Mai (2004) observed the following: “Radical polymerisation of lignosulphonate instigated by oxidative enzymes (laccase, peroxidase) is an alternative way of cross-linking, with the positive side-effect that no carcinogenic formaldehyde is emitted during the service life of the boards (Kharazipour et al. 1998b). Spent liquor composed of lignosulphonate (component 1) combined with peroxidase or laccase (component 2) was proposed as a binder for particle boards (Nimz et al. 1972 ,1976). The required high quantities of cheap laccase can be obtained from the fungal fermentation of spent sulphite liquor that additionally contains easily accessible carbohydrates (Haars et al.1987).”

Two component systems

In this approach to bonding, polymerisation of materials high in lignin content is achieved by treatment with oxidative enzymes. Lignin containing material can be lignosulponates (Kharazipour et al 1998b, Nimz et al 1972, 1976). In a two component system the enzyme in addition to a high lignin content material are added to the wood.

One component systems

These systems rely on the activation of lignin present in the wood. This is particularly useful in the reactivation of lignin deposited on the wood fibres of MDF pulp. The process has been applied to both a wet process and a dry process. (Felby et al. 1997b, 1998, 2002; Kharazipour et al. 1997, 1998, 1998a)

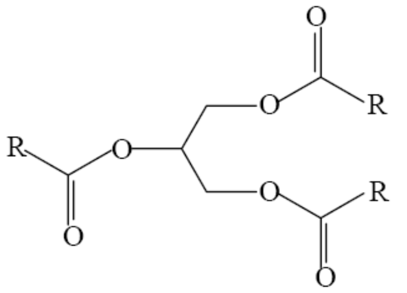
Key issues are:

- Performance is marginal and not particularly durable without addition of PF resin
- Cost of enzymes
- Time of incubation
- Slow cure time in press

A review of the patent literature revealed active patent applications from early to mid 1990’s to the early 2000’s. The patents are mainly assigned to Neste, Novo Nordisk and Pfleiderer and date from the mid to late 1990’s. Key patents related to these are US 6287708, US 5618482, and US 5505772 and their respective patent families. Further reading can also be found in *Enzyme applications in fiber processing*. (ACS symposium series 687) American Chemical Society, Washington, D.C.,pp 88–98

Modified Vegetable Oils

Several groups have reported the use of modified vegetable oils to manufacture thermoset resins suitable for wood composite manufacture. The approach in all cases appears to rely on the reactivity of the unsaturated bonds contained in the fatty acid of the triglyceride of the oil (see Figure 1 from Dunky et al 2002). Preform Polymerwerkstoff GmbH utilises epoxidised linseed oil and reports a material suitable for use as a wood adhesive. Further results have been reported by Adekunle (2007) of the use of modified soya bean oil as a composite binder.



Basic Triglyceride Sub-unit

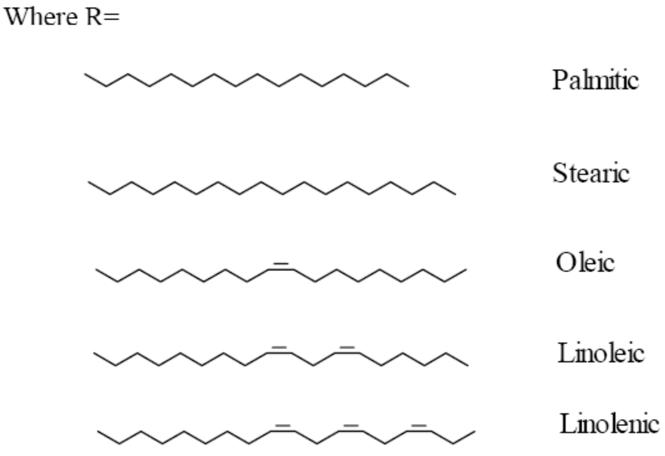


Figure 1

The scheme below (Figure 2) describes the process of oil modification and subsequent cross linking.

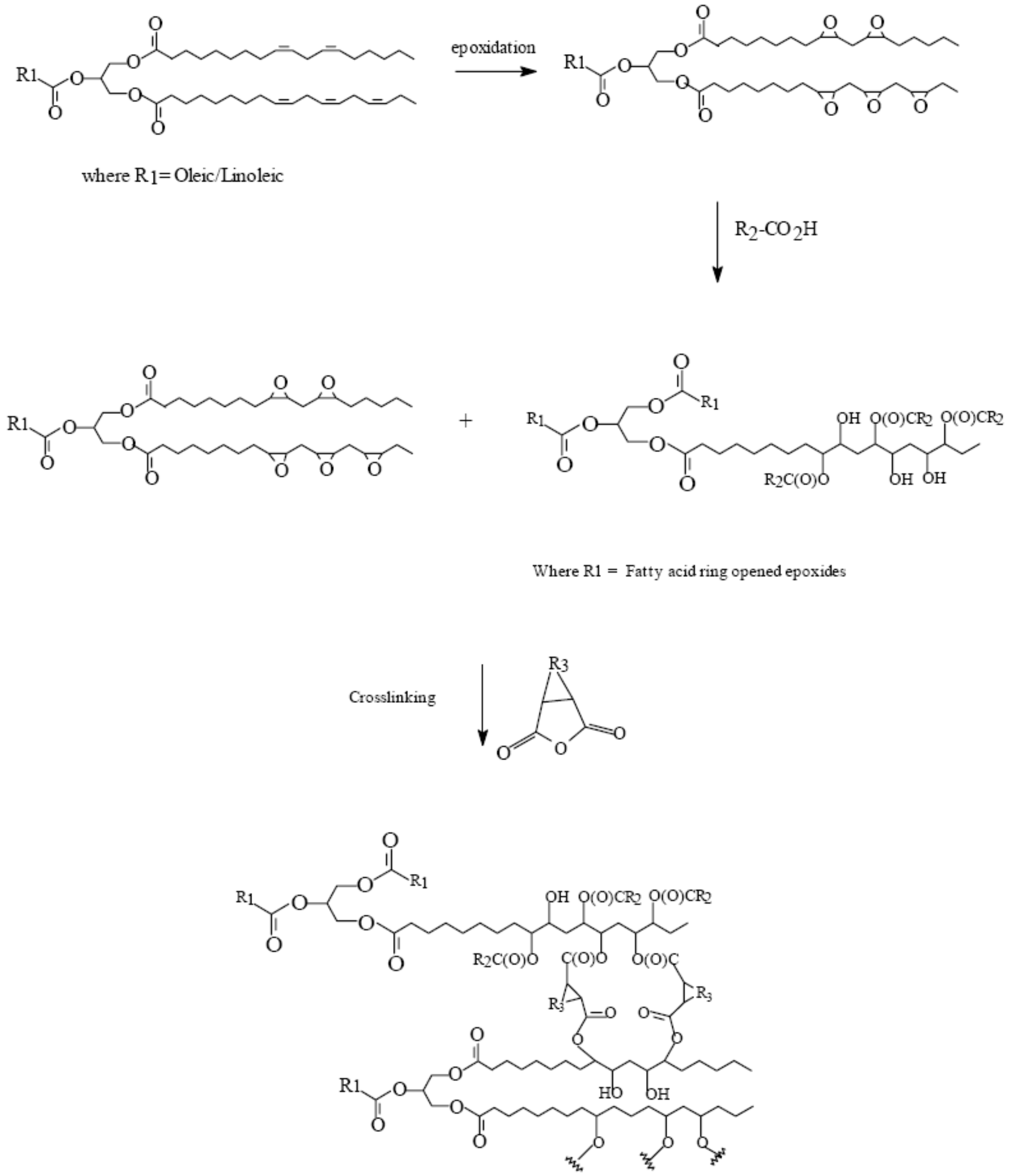


Figure 2

The Biocomposite Centre at the University of Wales, Bangor researched the use of modified Cashew Nut Shell (CNSL) which contains dual phenolic and fatty acid characteristics. See structure below (Figure 3 from Dunky et al 2002)

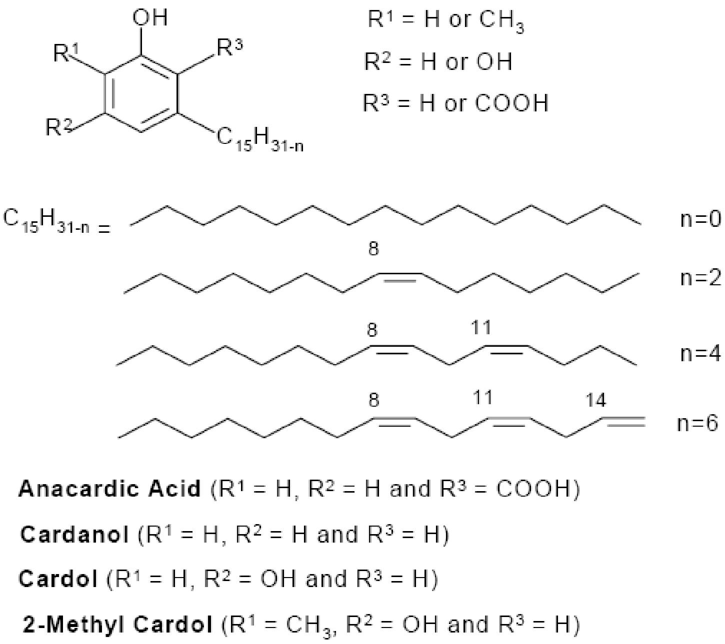


Figure 3

The work at the Bio-Composites Centre has focussed on producing various reactive groups on the oil. The work has been able to produce an aldehyde and this coupled with the phenolic group can lead to suitable crosslinking ability.

Example of CNSL aldehyde, Figure 4 from Dunky et al 2002)

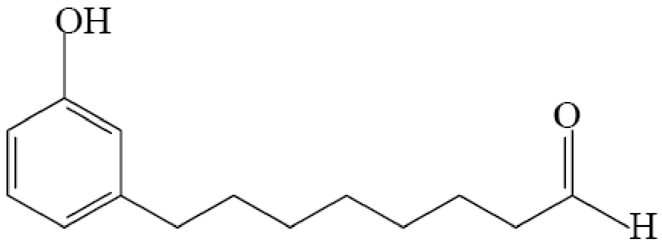


Figure 4.

Pilot scale production for commercial partners in the wood panels sector and full scale testing in other construction material applications has been undertaken. As an Example the following data is presented in Dunky et al (2002).

> "… a CNSL aldehyde resin at 10% application gave an IB of 1,05 N/mm^2 and an ABES value of 6,77 mPa compared to that of commercial PF resin that gave 0,69 N/mm^2 and an ABES value of 5,55 mPa. The resin also exhibited a good retained IB after soaking in water for 12 hrs and after immersion in boiling water for two hours, e.g., initial IB 1,05 N/mm^2 after 2 hrs boil 0,58 N/mm^2."

The technology has been licensed by Cambridge BioPolymers who continue to look for commercial opportunities.

Furans

The use of furfural, and furfuryl alcohol as adhesives has several benefits. Firstly, they can be derived from natural products through hydrolysis. Secondly, they readily condense with themselves and other chemicals such and Urea and Phenol making them suited to polymer manufacture.

The addition of furfuryl alcohol to Urea Formaldehyde resins is widely know in the production of binders for abrasives and is also commonly used in the manufacture of sand moulds for metal casting. The addition of these materials increases the temperature resistance of the finished article.

There are however issues with the use of these materials. The manufacture of furfural is not a particularly environmentally friendly one, relying on the acid hydrolysis and subsequent dehydration of hemicellulose resulting in large amounts of waste sulphuric acid and using large amounts of energy for manufacture. Secondly, furfural and furfuryl alcohol are known irritants (Safe Work Australia 2009).

A European consortium (Ecobinders 2009) recently researched the use of furans as a binder but according to their findings this part of the work didn't produce an economically viable adhesive system for wood panel products.

Casein

Casein has been used for many years as a wood adhesive. It is a natural protein material usually derived from cow's milk. The demise of casein as an adhesive began in the 1960's as with many other traditional adhesives when prices of synthetic materials began to drop and applications for wood adhesives began to grow.

The current research on renewable adhesives does not seem to include casein despite its good gap filling, cold setting and water resistant properties. The major issue appears to be the cost of the material which has been around € 9/kg. Additional concerns have been raised about the use of toxic chemicals in the glue-mix to prevent degradation by mould.

Despite these issues casein continues to be used in small quantities in speciality bonding situation in the packaging, door and allied industries.

Currently there are no known proposals for the use of these materials as alternative wood binders.

Carilite (polyketone)

Around the year 2000, the Shell Oil Company promoted a product with the trade name Carilite (2009). This product is not necessarily a green product in the sense that it made from renewable resources but it is an alternative binder that does not release formaldehyde.

The adhesive is based on a polyketone, cross-linked with a diamine. The resin is water-based, low-viscosity emulsion applied as a single component. Curing of the resin involves the reaction between the amine and the polyketone. The technology has not been commercialised but is still available for license from SRI International in the USA. SRI claims that the system is cost competitive and has several advantages including:

- High moisture gluing
- Water Resistance
- Faster Press times (40% faster)
- Long Pot-life (>12 months)

No data on panel performance was obtained.

Lignin

Lignin is a polyphenolic polymer composed of phenylpropenoid units and in nature has a primary role to bind cellulose chains within the ultra-structure of plant and wood fibre cell walls. Lignin is also an unwanted by-product of pulp and paper manufacture and can be removed by several methods during pulping. Several different types of technical lignins are commercially available and include Organosolv, Kraft and sulfite liquors. Typically, spent sulfite liquor (SSL) waste product from pulp mills has been the main source of lignin available for adhesives (Nimtz, 1983). However, with the current global interest in producing liquid biofuels from grasses and lignocellulosics, there is potential that biofuel production will be a source of lignin in the future.

The industrial application of recovered lignins has been an active research area for many decades. Adhesives represent one of many industrial applications where lignins have been trialled. SSL has been the main source of technical lignin investigated and has been the subject of many research articles and patents on its use as an adhesive, but none appears to have been furthered to commercial production. A review of articles using lignin in adhesive formulations finds relevant literature from the last 4 decades dominated by attempts to incorporate various lignins in native or modified form into phenolic resins for use in hot-pressed wood panels. While lignin-PF resin hybrids form the majority of published papers, there are reported uses with other resins or polymer systems as well as the oxidative coupling of lignin phenols. The use of lignin as an adhesive was reviewed by Nimtz in the early 1980s (Nimtz, 1983). While there are other literature reviews by prominent academic authors (Glasser, 1981a; Lewis, 1989; Roffael, 1991) which cover the 1970s and 1980s, there has been no substantial review of lignin in wood adhesives since this time other than those noted in broader reviews (Pizzi, 2006; Mueller, 2007).

Lignin Chemistry

Lignin is often described as a complex three-dimensional polymer comprised of various linked phenylpropenoid units as that given in Figure 1 (Uprichard, 1991). Additionally softwood and hardwood lignins may be distinguished by the presence of an additional methoxy group in the *ortho*-position of the phenyl ring. As a polyphenolic material, lignin has chemistry similar to phenol. It is this similarity and reactivity with formaldehyde which has made lignin attractive as a phenol replacement in wood adhesives.

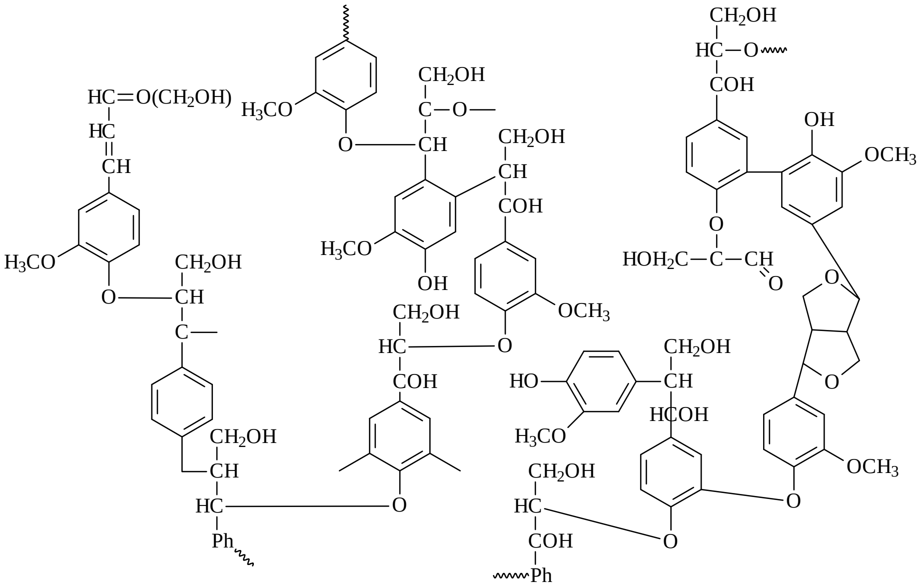


Figure 5. Some of the various structural units present in softwood lignin (from Uprichard, 1991)

Most lignin sourced and used in adhesives is described as the spent sulfite liquor (SSL) waste product from pulp mills (Nimtz, 1983). As a paper adhesive, lignosulfonates are dark and hygroscopic, but this is not considered a disadvantage in wood composite panels. Lignins can be cross-linked either intra- or inter-molecularly by either condensation or oxidative coupling. In both cases there are several patents for each process, but these require high temperatures at long cycle times. Reactivity will also vary depending on the lignosulfonate metal salt used (Na^+, Mg^{+2}, Ca^{+2} and NH_4^+). While reaction of lignin with formaldehyde is considered similar to phenol formaldehyde chemistry, the complexity of lignin reduces its reactivity. The presence of methoxy groups (adjacent to hydroxyls), steric hindrance and only 0.5 free positions per C9 unit (phenylpropyl group, Figure 1) lead to higher reaction temperatures and longer cross-linking times. This lignin-formaldehyde reaction chemistry has been investigated in detail (Truter, 1994). Furthermore, in a departure from more traditional adhesive condensation chemistries, lignin can also be cross-linked with itself on addition of sulphuric acid, hydrogen peroxide or via enzymatic means.

Formulating Lignin Adhesives and Resins

The reaction of lignin with formaldehyde resulting in methylolation and methylol condensation reactions is by far the greatest application of lignin in wood adhesives. The similarity to phenol reactivity has seen lignin sulfonates predominantly employed in phenol formaldehyde systems. While this chemistry is usually in combination with PF resin, there are examples of lignin combination with other resin or adhesive systems.

Phenolic resins

Substitution of lignin into PF resin appears the predominant application for lignin use in adhesives. The current review identified numerous authors reporting use of lignin in PF resins with research in this area active throughout the past 4 decades. Relevant papers include (Shen, 1976; Dolenko, 1978; Forss, 1979; Gamo, 1984; Muller, 1984; Gardner, 1986; Venter, 1987; Calve, 1988; Wooten, 1988; Olivares, 1988; Shroeder, 1990; Sefain, 1991; Lora, 1991; Zhao, 1994; Vazqeuz, 1995; Santana, 1996; Chen, 1996; Vazquez, 1997; Trosa, 1998; Kharade, 1998; Sarkar, 2000; Lisperguer, 2000; Parija, 2001; Zoumpoulakis, 2001; Wu, 2001; Cetin, 2002a; 2002b; Lee, 2002; Ruzinska, 2003; Alonso, 2005; Wang, 2006; Khan, 2006; Lora, 2007, Donmez Cavdae, 2008). While lignin integration into phenolic resin has utilised formaldehyde chemistry, other aldehydes including glyoxal (El Mansouri 2007a; 2007b, Lei,

2008) and furfural (Schneider, 2004) have also been described. Few authors describe total replacement of the PF resin component, most report partial phenol substitution of lignin into PF resin. Several papers also describe pH and chemical modifications to promote reaction or compatibility with PF resin during synthesis. Furthermore, there appears no current or significant past commercial uses of lignins in PF resins. This may be due to the lack of a ready supply of lignin, as much as the potential of lignin itself in wood adhesives.

As with the prevalence of coupling lignin in phenolic resin systems, various chemical modifications have been evaluated to change the reactivity and compatibility of lignins in PF resin or other systems, all with varying success. The main approaches have been phenolation (Vazquez, 1997; Cetin, 2002a; 2002b; Lee, 2002; Alonso, 2005; Liu, 2007), methylation (Young, 1987a; 1987b; Vazquez, 1997 Khan, 2004a; 2004b), demethylation (Shroeder, 1990; Wu, 2001) and methylolation or hydroxymethylation as it is also described (Zhao, 1994; Truter, 1994; Zoumpoulakis, 2001; Ruzinska, 2003). For the latter, Truter describes in detail the reaction chemistry of coupling formaldehyde with lignins (Truter, 1994). Other treatments include simple caustic treatment (Young, 1985a; 1985b), oxidation (Chen, 1994), plasticization (Bougila, 2005) and reaction with epoxy functionality (Hoffman, 1990; Kadota, 2005; 2006) to enhance phenolic resin incorporation.

A series of patents have been granted in the past decade which aligns to the typical approaches on lignin incorporation in phenolic resins. Several describe variations on the lignin incorporation and its chemistry during PF resin synthesis (US7,323,501; US7,064,175; CN1013588210; CN101348698; JP2007169491; KR930005520). This includes the use of lignin molecular weight segregation to give desired polymer weight and resin properties (CN101104782) and formulation of lignin-PF hybrids which can be spray dried (JP2003159703). Phenolation is described to achieve compatibility in the phenolic resin and adhesive performance (CN101260283; US7,276,591; JP2003159703). There are also patents on furfuryl alcohol cross-linking for use with phenolic systems (US6,747,076; US2002173564; WO02068507).

Other Traditional Wood Adhesive Systems

Incorporation of lignin into synthetic-based wood adhesive systems other than PF resin has generally been reported in the literature during the 1980s. Outside of PF resins, the next most reported adhesive system coupled with lignin is that employing isocyanate incorporation. Reactive coupling of lignin with isocyanates has been reported by several authors (Glasser, 1981b; Gamo, 1984; Gillespie, 1989, Pizzi, 1993a, b). Feldman similarly reports coupling with polyurethanes (Feldman, 1988). Lignin use in other adhesive systems includes examples with urea formaldehyde resin (Venter, 1987), epoxy functions (Hoffman, 1990) and poly(vinyl acetate) via enzymatic coupling (Sadowick, 1988). Co-reaction of resorcinol with lignin has led to the use of the modified lignin in a cold set adhesive for finger-jointing (van der Klashorst, 1989), but there are no other reports of lignin used in cold-set systems.

Evaluation of recent patent literature revealed lignin combined with various cross-linking resin systems including isocyanates, polyurethanes, epoxies and melamine systems. Lignin has been combined with a polyisocyanate with water used to control viscosity (KR840000612). Two patents describe combination of lignin with polyurethanes for use in foams and adhesive systems (JP2006326943; JP2005126515). A Japanese patent describes forming lignin bearing epoxy groups for part-substitution of bisphenol A and use as an adhesive (JP61215678). Lignin is also used as a hardener in combination with epoxidised vegetable oils (DE19741153). Melamine bearing methylol groups has been used to cross-link lignin (JP 2002146317). Polyvinyl alcohol has been coupled with lignin and polyamine phosphates to give an adhesive formulation which has reported fire-proof properties (CN1465646).

Non-Formaldehyde Adhesive Systems

Lignin has been used with several alternative cross-linking systems to yield hot-pressed adhesives for plywood. Raschip reports the coupling of epichlorohydrin to give lignin polymers capable of acting as adhesives (Raschip, 2007). However, several papers from the Li group (OSU) report lignin incorporation into systems through quinone coupling (of lignin) to yield durable adhesives. This approach utilises coupling with polyamines such as poly(ethyleneimine) (Li, 2005; Liu, 2006), chitosan (Peshkova, 2003a) or polyamineamide and polyamide-epichlorohydrin (Li, 2004). In each case, the base chemistry appears similar and is through generation of quinone species such as that described by this group for tannin (Li, 2004) and poly(4-vinylphenol) (Peshkova, 2003b). Several patents have appeared for this approach (US7,393,930; US7,265,169; US7,252,735; US7,060,798; US6,841,660; US6,790,271) variously describing the combination of lignin with polyamines, which can additionally include the presence of protein as a co-additive in the formulation. A second generation approach has been patented by Ashland-Hercules where lignin is described for use with soy-PAE (polyamine-epihalohydrin) adhesive systems (WO2008024444). An unrelated lignin-protein system has been described in recent patent literature in which these components are formulated in the presence of either zinc and calcium salts (US7,081,159) or through protein modification (CN101412898) to give hot-pressed wood adhesives.

Other non-formaldehyde approaches investigated to couple lignins have been through enzymatic means, with this elaborated on in the enzymatic coupling section. There are a number of papers related to the oxidative coupling of lignins with laccases or peroxidases, but this is usually through surface modification or coupling of wood fibre cell walls. The laccase systems have been reported by Felby (Felby, 1997; 1998) who has taken this coupling to pilot-scale (Felby, 2004) and by Huttermann (Haars, 1989) who has reported use at room temperature. This type of approach has been used to couple cinnamic acids (Widyorini, 2005) and *in situ* polymerisation (Huttermann, 2001). Of promise is the biografting of phenols by laccases described by Kandelbauer (Widsten, 2008). Laccase use has also been described for the coupling of chitosan with phenolics (Peshkova, 2003a). In a patent, the oxidative depolymerisation of lignin followed by demethylation and oxidative polymerisation gives a viable wood adhesive (KR930005520).

Tannins

The term “tannin” refers to a broad class of compounds which have varying and often complex chemistries compared to some of the other biomaterials discussed in this review. While historically tannins have been associated with the preservation of hides to leather, in the context of wood adhesives, it is only condensed tannins that are utilised in adhesives or resins. The attractiveness of using tannins in wood adhesives can be derived from their similar reactivity and cross linking chemistry with formaldehyde as that found for phenol- and resorcinol-formaldehyde systems. This commonality in reaction chemistry has been the main stay of tannin use in wood adhesives. Condensed tannins are polyphenolic materials and are generally comprised of the oligomeric flavonoid-type structures given in Figure 6. These tannins are predominantly sourced from either the heartwood or bark of a variety of tree species, but may also be present in the foliage and roots of plants and trees. For a long time, tannins have been commercially extracted in South Africa and South America from various

Acacia and Quebracho species with commercial-scale extraction of other species including hemlock, spruce and pine species also having been undertaken in other parts of the world.

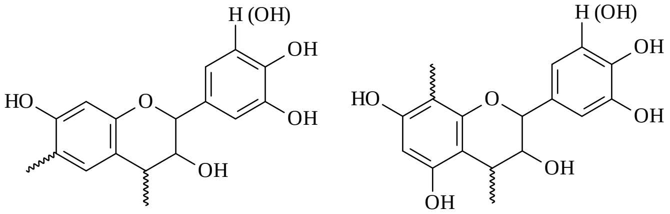


Figure 6. Chemical structures of resorcinolic type condensed tannins with 4-6 interflavanyl linkages present in quebracho extracts (left); and phloroglucinolic type condensed tannins typically present in pine species with 4-8 interflavanyl linkages (right).

The chemistry and use of tannins in wood adhesives has been reviewed well up to the mid 1980s by Pizzi. This provides a good introductory review of relevant tannin chemistry and its application to adhesive formulation (Pizzi, 1983). This early 1980's chapter gives examples of adhesive formulations which employ tannin chemistry and arguably, these preparations are still the basis of how most tannin-based adhesives are still formulated today. Furthermore, Tony Pizzi has been a dominant contributor to the tannin adhesive literature for more than three decades. Since the Pizzi review in the 1980s, there have been smaller reviews describing the use of tannins in adhesive formulations (Hergert, 1989; Sellers, 2001; Pizzi, 2000; Muller, 2007).

In summarising the primary literature over the last 30 years, it is evident the publishing of tannin adhesive research has generally been clustered into broadly similar themes during this period. The general categories of research areas include:

i. historical use of tannin with formaldehyde producing an adhesive used in plywood and particleboard manufacture.
ii. use of tannin-formaldehyde adhesives in particleboard and plywood in the mid 1980s and more recently.
iii. evaluation of tannin substitution in phenol-resorcinol-formaldehyde adhesives;
    - from the mid 1980s other EWP applications were investigated with formaldehyde chemistry contributing to tannin incorporation into PRF resins.
iv. reaction of tannins with urea-formaldehyde methylol species; and
v. the emergence of research on tannin reactions using non-formaldehyde systems
    - these include the use of formaldehyde "donors" or non-formaldehyde crosslinkers.

In the main, the majority of this work is reported for plywood and particleboard applications, but other reconstituted wood products such as MDF and OSB are now being assessed for use with tannin-based adhesives, as these panel board products emerge as mature wood products.

TANNIN CHEMISTRY

Some understanding of tannin chemistry and reactivity is required to successfully formulate tannins into adhesive formulations (formaldehyde or non-formaldehyde based approaches) and, ultimately, for the longevity and performance of the adhesive. The explanations of tannin chemistry featured in two references (Pizzi, 1983 and Hemingway, 1989) collectively provide a comprehensive review of basic tannin chemistry aspects and a basis for how tannins may be formulated into traditional adhesives or considerations required for non-formaldehyde systems.

Of primary importance is to understand the variable reactivity of condensed tannins toward aldehydes (Pizzi, 1983). This is primarily derived from the hydroxyl substitution patterns of different tannin extracts and has been attributable to the differences in reactivity of the phenolic A & B rings as well as between resorcinolic- and phloroglucinolic-tannin structures, for example Figure 6. While this reactivity has been defined for formaldehyde, its basis is also relevant to other aldehydes (furfural, acetaldehyde, propionaldehyde), particularly given current legislative changes and trends in adhesive formulation. Complexation with various metal ions has also been demonstrated to accelerate or retard tannin coupling with aldehydes. Furthermore, given condensed tannins are usually crude extracts without refinement, the presence of alcohols or sugars can also impair reactivity. This impact on adhesive formulation and performance is important as tannin extracts may be composed of only 70-80% active phenolics. One historic consideration for the use of tannin adhesives, particularly in batch formulation, has been the issue of molecular weight build. As tannins react, the molecular growth can be great with each increasing molecular linkage which has practical implications such as short pot life (Pizzi, 1983) and the often overlooked vitrification of the adhesive through incomplete cross-linking and cure.

In examining tannin cross-linking, this chemistry has historically been dominated by formaldehyde, but reactivity with other aldehydes has been reported, as well as use with other cross-linker systems.

The reaction between tannin and formaldehyde has been the main stay of tannin use in wood adhesives. This tannin-formaldehyde reaction has been evaluated by several different authors analysing reaction products, the promotion of reactivity by bivalent metal ions (Pizzi 1979b) and the impact of differing tannin structures (Roux, 1980). In later papers there was a more analytical approach to the tannin-formaldehyde reaction with Sowunmi looking at caustic or ester treatments (Sowunmi, 1996), use of mechanical analysis to predict adhesive strength (Garnier, 2001; 2002) or reaction processes (Osman, 2002; Simon, 2002).

While furfural (Pizzi, 1978a; 1978b) is an aldehyde which has been coupled with tannins to form an adhesive, more recently glyoxal (Lei, 2008; Ballerini, 2005) has been promoted to cross-link tannins due to its reactivity. The use of hexamine (hexamethylenetetramine) as a formaldehyde donor in tannin resin formulation has been used to good effect in hot-pressing situations (Pizzi, 1983). Other formaldehyde donors such as oxazolidines (US7,319,115; WO9909083) and the cross-linker tris-nitromethane (Trosa, 2001; Kim, 2003) have been employed to provide room temperature cure of tannin adhesives. The affinity of tannins toward methylol groups is the basis for chemical coupling of tannins in PF and M/UF systems for which there is extensively published work. Here, the condensation reaction of tannins with methylol groups present on phenolic or UF resin species is the mechanism for tannin coupling (synthesis) and cross-linking (cure) with these substrates.

Outside of traditional adhesive condensation chemistries, other approaches to formulating tannin adhesives have been undertaken. Promoting tannin autocondensation (Pizzi, 1995) reportedly gives a satisfactory adhesive bond. This approach uses a unique facet of condensed tannin chemistry in which the tannin oligomers are promoted to self-polymerise forming a cross-linked polyphenolic network. While this has been demonstrated in the patent literature (Pizzi, 1995), there is no report of further refinement or current commercial uptake of this technology. In another approach which utilises inherent tannin chemistry, the affinity of tannins for amine-based compounds has been used by researchers to give adhesives in which the tannins are reacted into cross-linked networks on coupling polyamines (Li, 2004; Nakanishi, 2008). Tannin coupling with polyamine has been reported to give plywood bonds (Li, 2004), but the absence of any follow up work suggests this may not be a practical application for tannin cross-linking. Related is a paper by Nakanishi combining tannin with poly(N-methylolacrylamide) to use in place of PF resin (Nakanishi, 2008).

FORMULATING TANNIN ADHESIVES AND RESINS

Over the last few decades tannin incorporation has been evaluated with most wood adhesive systems. The reasons for using tannins have been varied and include material replacement, cost reduction, increased cross-linking or adhesive reinforcement, promoting cure and efforts to improve water resistance. As noted above, the commonality of polyphenolic tannins with phenol and resorcinol chemistry and the tannin reactivity toward formaldehyde have made tannins ideal candidates to be substituted into wood adhesives. However, by and large, and for a variety of reasons, this published research has not led to widespread uptake of tannin-based adhesive technologies in EWPs. However, conversely, there are current examples of product runs which do utilise tannins in their manufacture.

Recent patents exist for the varied combination of tannins with formaldehyde to produce various wood panels. One patent describes the addition of both powdered and liquid tannin to furnish followed by formaldehyde to bond fibre- and chip-boards (DE19704525). A second utilises alkaline pH adjustment and the presence of a tertiary amine to gain tannin reactivity with formaldehyde for use in particleboard production (JP2006348271).

In returning to the 1980s review by Pizzi, several example formulations of general tannin-based adhesive systems were given which encompass common wood adhesives (Pizzi, 1983). While these formulations were typical of the late 1970s/early 1980s literature, they still form the basis for more recent approaches to tannin systems where to maintain performance, tannins invariably required incorporation with synthetic components (Pizzi, 1983). Pizzi described adhesive systems comprising mixtures of UF and PF resin components with tannin; cold-setting adhesive compositions; tannin-formaldehyde combined with an isocyanate resin and tannin reacted with UF resin and starch (Pizzi, 1983).

Tannins with Phenolic Resins

Tannins have been used in phenolic resin applications, substituting or replacing phenol and resorcinol in typical wood adhesives. Typically this use has been with Acacia and Wattle tannins, but not exclusively as the use of condensed tannins from pine, spruce and quebracho species as well as other sources have been described. Almost exclusively tannin formaldehyde and methylol coupling chemistry is used, though there are more recent examples of differing aldehydes substituting for formaldehyde.

As noted above, tannin-formaldehyde chemistry has contributed to tannins either being substituted into phenol-formaldehyde or as a replacement for this resin. Kulvik (Kulvik, 1976) reported use of tannin in PF resin as well as Saayman (Saayman, 1976) using tannins for fortification of PF and RF resins. Such examples are covered in the Pizzi review (Pizzi, 1983). Between the mid 1980s and until the mid 1990s there appears a gap in the literature which describes tannins with PF resin. However, in the past decade several papers have appeared ranging from tannins cross-linking PF resins (Zhao, 1995; Souwunmi, 1996; 2000), bark liquefaction (Santana, 1996), through to a very recent report on tannin substituting phenol (Stefani, 2008). In the case of direct liquefaction of bark with phenol, this reportedly gives better plywood bonding than the corresponding bark without tannin present (Santana, 1996). Furthermore, recent literature reports the use of various analytical techniques to evaluate cure characteristics of tannin-PF formulations and include the use of rheology (Vazquez, 2002a; 2005a), differential scanning calorimetry (Vazquez, 2002b; 2005b; 2005c; 2006), and the use of automated bond evaluation (ABES) (Lecourt, 2003). Vazquez et al. also report wettability characteristics of Tannin/PF systems (Vazquez, 2003).

Several patents in the past decade outline the use of various tannins with phenolic resin. The source of tannin varies and includes larch (CN1120572), persimmon (CN101328252) and phlobaphene containing tannins such as mimosa and quebracho (CA569169). All have been variously added to cross-link or minimise the phenol content in the PF resin-based systems. While application has generally been in liquid form, there is also a patent for application of the adhesive in powdered form for OSB production (CA2323765). Mixed resin systems of tannin containing PF resin with either isocyanate (US7,064,175) or UF resin (CN1422928) have also been published.

Tannins with Amino- Resins

Historically, tannins have been described as cross-linkers in urea- and melamine-based resins to provide water resistance. Pizzi reports the incorporation of tannins with UF resin through coupling methylol species (Pizzi, 1977, 1978a; 1978b; 1979a) with the addition of furfural to aid cross-linking (Pizzi, 1978a; 1978b). More recently, there are a few papers specifically reporting tannin incorporation into to UF systems. A recent patent describes the reaction of tannin with urea methylols to provide cross-linking (WO2004058843) and a caustic tannin extract is described as reacting with urea resins (KR900005401). In a variation to tannin combination with UF resin, there is a patent describing the bonding of hydrolysed, reconstituted panelboards by addition of tannin (DE10025812). This approach utilises the coupling of tannin with hydrolysed UF species to effect bonding of the panel. In another approach to minimise formaldehyde emissions, tannins have been combined with carbamide resins (DE20313424).

Hybrid amino-based resins such as phenol melamine urea formaldehyde (PMUF) resins have been examined with tannin providing additional cross-linking (Cremonini, 1996). It was also reported the presence of the tannin with PMUF imparts fire resistance to the bonded product. In phenol urea formaldehyde (PUF) resin systems Vazquez has examined the rheology and thermomechanical analysis on tannin addition and cure (Vazquez, 2005a; 2005b; 2005c). More recently, tannin in melamine formaldehyde (MF) and PVAc/UF systems have been evaluated as a means of reducing formaldehyde emissions from the glued wood products (Kim, 2006; 2007; 2008).

Tannins in structural bonding adhesives

The use of tannins in structural gluing of glulam and fingerjointing emerged in the 1980's with two distinct tannin-based technologies evolving to displace resorcinol formaldehyde-based systems. So called Honeymoon systems were reported by Pizzi (Pizzi, 1985) and Hemmingway (Krebich 1989), where tannin-formaldehyde chemistry was mated with PRF resin. The second approach was to include tannin in PRF resin synthesis (Krebich, 1985, Paridah, 2006). Both approaches involve tannin substitution for resorcinol, however neither technology was a complete replacement for this chemical in the above cold-set systems.

The mimicry of resorcinol by tannins was first mooted by Roux where tannin A-ring chemistry (Figure 1) could be paired with the reactivity of resorcinol (Roux, 1972; 1975). However, in reviewing the literature on tannin-resorcinol systems, it was not until the mid 1980s that papers appeared describing general use of tannins in cold setting applications. Krebich reported use of pine bark tannins in the synthesis of PRF resin (Krebich, 1985, 1989a; 1989b; Hemingway, 1985). Around this time, Pizzi also reported variations on his tannin-based Honeymoon system (Pizzi, 1985). A gap then develops in the literature before reports by other researchers regarding modification of tannins with resorcinol (Akaranta, 1999; Wankasi, 2002) and alternatives to formaldehyde in the form of tris nitromethane (Trosa, 2001) or oxazolidines (WO9909083) for cold-setting tannin adhesives. Chemically blending tannins post-PRF synthesis is the basis of a patent for high tannin content PRF systems (US7,319,115). The chemistry used in this system is similar to that reported by Hemingway (Hemingway, 1986), where alkaline pH or use of ammonia is the basis for cross-linking of tannin or tannin/PRF systems (Grigsby, 2004; Paridah, 2006; Panamgama, 2007). The combination of radiata pine bark and the chemical approaches used in the PRF/tannin adhesive system make this applicable to EWP practises in Australia. This gluing technology fulfils JAS, ISO and ASTM standards as well as the challenging durability and creep components of the CA0112.9 structural adhesive standard. However, like many of the renewables featured in this review, the technology requires the radiata pine bark tannin be available in commercial quantity for technology uptake (US7,319,115).

Non-Formaldehyde Tannin Systems

A range of non-formaldehyde cross-linkers are known for tannins. The use of other aldehydes, tris nitromethane (Trosa, 2001; Kim, 2003), methylene “donors” such as hexamine (Pizzi, 1983) and oxazolidines (WO9909083; US7,319,115) and tannin-polyamine coupling (Li, 2004; Nakanishi, 2008) have already been discussed above. The reaction chemistry between tannins and either isocyanates or epoxy functions has been modelled by Sakai et al. (Ge, 1996) and Baeza et al. (Soto, 2005), respectively. However, in the context of EWP applications, it is only the combination of tannins with isocyanates or urethane systems which have been described in recent patents. As an example, tannin in powdered form can be combined with PF resin and an isocyanate resin for OSB applications (US7,064,175; CA2392876). Similarly, this approach has also been described for plywood production (GR3018245) and for other composites (CA2392876). Combination of tannin with polyurethanes is well known for forming foams (Tondi, 2009; Ge 2003), but only one patent details tannin-polyurethane use in composites, where tannin inclusion in the polyurethane assists in bonding (DE10333958).

Tannins Blended with Other Biocomponents

Few, relevant articles exist on tannin-based adhesive systems prepared with other biobased components. However, tannin has been formulated or cross-linked with proteins, lignins and starches to provide “greener” approaches to adhesive systems. Generally those systems identified still use aldehydes to couple tannins and mirror the common approaches in synthetic wood adhesive systems using either phenolic or amino chemistry.

Tannin-Protein Systems

In combining tannin with proteins, Triboulot describes the presence of tannins improving the performance of protein-based glues (Triboulot, 1996). Pizzi uses glyoxylated soy flours as a means to react proteins with tannins (Amaral-Labat, 2008). This likely uses amino-methylol chemistry analogous to that used in amino-based systems or reaction of N-hydroxymethylacrylamide with tannin (Nakanishi, 2008). Included with the above is the example of tannin reacting with polyamines (Li, 2004). In this example quinine tannin mechanisms formed through dihydroxyphenylalanine groups (Jensen, 1988) are likely exploited for amine coupling with tannins, but this approach (Li, 2004) does not appear to be extensively reported as for lignin (Liu, 2006; Li, 2005; Peshkova, 2003a; 2003b;Geng, 2006).

Tannin-Starch Systems

Those few papers describing the direct coupling of tannins with starches utilise aldehyde chemistry to reportedly impart tannin-starch cross-linking. Saayman describes coupling tannin, starch and formaldehyde as a means of “water proofing” starch-based adhesives (Saayman, 1977). Related to this approach is that described for bonding wood furnish using the combination of water soluble carbohydrates and tannin-formaldehyde (WO9837148). However, in a more direct approach to combining starch with tannin, the inherent dialdehydes present in oxidised starches are used to react with tannins, but this formulation has only been used in "re-tanning" leathers (Srinivasan, 1986).

Tannin-Lignin Systems

Only one paper reports the coupling of tannin with lignin to enhance adhesive performance (Lei, 2008). This was achieved by glyoxylation of lignin and subsequent coupling with tannin. This is akin to the reactions of PF resin and tannin and was reported as a non-formaldehyde approach.

Soy Protein Adhesives

Wood adhesives utilising soy protein were first used in the 1920's and continued to be used until after World War 2, when the use of adhesives based on petrochemical materials became all pervasive. In the last decade, research into the use of soy protein as an adhesive to manufacture wood products has seen a huge resurgence in North America. This has been largely driven by the allocation of research grants by the American United Soybean Board.

The soy protein is derived from the residual soy meal remaining after the removal of the oil. The soy meal is further refined into three different "grades" of product with varying protein levels (Table 1).

Table 1. The 3 grades of soy protein and their protein content.

Soy Product	Protein content (%)
Soy flour	48
Soy protein concentrate	65-80
Soy protein isolate	90+

Soy protein is rich in amino acids that have reactive groups which can potentially react with other cross-linking additives. The typical amino acid composition of soy protein is given in Table 2 (Porter and Jones, 2003).

Table 2. Typical protein analysis of soy protein taken from Porter and Jones and sorted into reactive and unreactive amino acids as presented by Wescott et al.

Reactive Amino acid	%	Unreactive Amino acid	%
Histidine	1.37	Alanine	2.12
Tyrosine	1.68	Proline	2.90
Arginine	3.71	Valine	2.30
Lysine	3.30	Tryptophan	0.62
Cysteine	0.74	Leucine	3.94
Methione	0.71	Isoleucine	2.20
Threonine	2.05	Phenylalanine	2.51
Serine	2.76	Glycine	2.17
Aspartic acid/Asparagine	6.02		
Glutamic acid/Glutamine	8.97		
Total reactive amino acids	***31.31***	***Total unreactive amino acids***	***18.76***

Much of the early work focused on chemically modifying the soy protein to add different functionality such as maleic anhydride, thiols or other functionality (Rogers 2004, Huang 2008, Liu 2007, Liu 2004, Li 2004, Liu 2002, Schwarzkopf 2009). Research then appeared to focus on using the reactivity of the amino acids of soy protein to cross-link with other crosslinking resins such as PAE.

Over this past decade, two major research groups appear to be actively developing the soy-based adhesives. These are the Oregon State University group led by Professor Kaichang Li and the USDA Forest Products Laboratory (FPL)/Heartland Resource Technologies collaboration.

Li's work is embodies a patent portfolio of 4 US patents. These are

1. US 7060798 "Modified protein adhesives and lignocellulosic composites made from the adhesives"
2. US 7252735 "Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives"
3. US 7265169 "Adhesive compositions and methods of using and making the same"
4. US 7393930 "Modified protein adhesives and lignocellulosic composites made from the adhesives"

There are a number of patent applications based on this portfolio, including Australian patent applications (see Table 3).

US 7060798 describe chemically modifying the soy protein to introduce additional phenolic, amine and thiol functional groups that can form cross-links to form adhesive bonds. This idea is continued in a more recent patent (US 7393930).

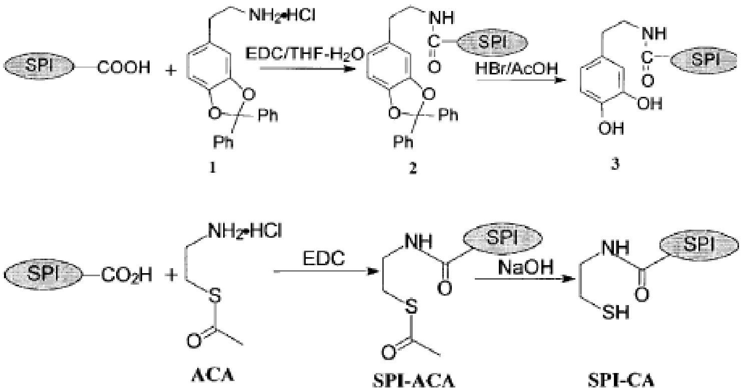


Figure 7. Examples from US 7060798 of chemically modifying the soy protein for use as a wood adhesive by introducing an additional phenolic moity (top) or thiol (bottom).

US 7252735 describes the use of soy protein (or lignin) and a cross-linking agent that contains at least one nitrogen containing crosslinker such as an amide, amine, imine, imide or nitrogen containing heterocycle. Particular reference was made to aminopolyamide-epichlorohydrin (PAE) resins that contain a nitrogen heterocycle, as given in Figure 8, as the cross linker

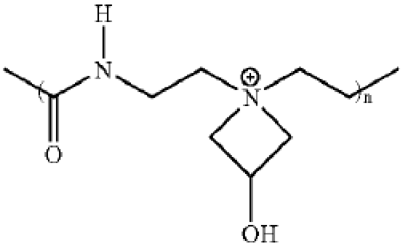


Figure 8. Aminopolyamide-epichlorohydrin (PAE).

US 7265169 describes the preparation of an adhesive suitable for bonding wood that consists of a lignin component, a boron compound and an amine material. A further claim is made for extracting the lignin component from decayed wood and using it in combination with a polyamine.

The other major research activity was undertaken by the USDA FPL and/or Heartland Resource Technologies collaboration. The research activity appears to be based around the US patent US 7345136 and European patent EP 1268702.

There are also a number of patent applications that further extend the base technologies, particularly around the denaturing of the protein to reduce the viscosity. These are listed in Table 4.

Both of these technologies have been licensed to Hercules Chemical Company (which has recently been acquired by Ashland Chemicals) and is marketed under the Soyad® tradename. This system has been presented at several recent industry conferences and uses modified soy flour and either of two different classes of cross linkers. These cross linkers are either formaldehyde resins (such as UF, PF, MUF) or non-formaldehyde resins (such as MDI or PAE). Particular emphasis has been around the use of the PAE resin with the functional azetidium group (Figure 8) which is capable of reacting with many of the reactive amino acid groups found in the soy protein to give a water resistant adhesive with covalent and non-covalent bonds.

This system has evolved and is now onto its third generation. A brief description of these three systems was recently presented by Hercules and is given below (Foong, 2008).
1st generation – high viscosity (>100,000 cps) system that required specialised equipment to mix and pump
2nd generation – used modified soy flours and higher PAE/soy ratios to give lower viscosity (5,000-50,000 cps) systems with solids content limited to less than 34%. This system involved the use of in-line mixing of the two components prior to application.
3rd generation – single component system with a solids content of ca 40-50% and a lower viscosity (500-2,000 cps).

Hercules has advertised that these adhesives are suitable for producing particleboard and medium density fibreboard as well as hardwood plywood (non-structural). Whilst no exact cost of these adhesives is readily available, Hercules has claimed that these systems are equivalent in cost to other low formaldehyde emission adhesives systems such as PF, MUF and pMDI. Hercules has also published some trials on using the soy flour blended with formaldehyde-based resins (PF and MF).

Table 3. The patent portfolio based around the research by Li *et al*.

Patent No	Title	Published
AU 2005/208786 A1 patent application	Formaldehyde-free adhesives and lignocellulosic composites made from the adhesives	Aug 11, 2005
AU 2004/319912 A1 patent application	Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives	Dec 1, 2005
US 2004/0089418 A1 patent application	Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives	May 13, 2004
US 2005/0282988 A1 patent application	Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives	Dec 22, 2005
US 2007/0218307 A1 patent application	Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives	Sep 20, 2007
US 2008/0213597 A1 patent application	Formaldehyde-Free Adhesives and Lignocellulosic Composites Made from the Adhesives	Sep 4, 2008
US 7252735 granted patent	Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives	Aug 7, 2007
US 2004/0037906 A1 patent application	Modified protein adhesives and lignocellulosic composites made from the adhesives	Feb 26, 2004
US 2004/0220368 A1 patent application	Adhesive compositions and methods of using and making the same	Nov 4, 2004
US 2006/0156954 A1 patent application	Modified protein adhesives and lignocellulosic composites made from the adhesives	Jul 20, 2006
US 7060798 granted patent	Modified protein adhesives and lignocellulosic composites made from the adhesives	Jun 13, 2006
US 7265169 granted patent	Adhesive compositions and methods of using and making the same	Sep 4, 2007
US 7393930 granted patent	Modified protein adhesives and lignocellulosic composites made from the adhesives	Jul 1, 2008
WO 2005/072260 A2 patent application	Formaldehyde-free adhesives and lignocellulosic composites made from the adhesives	Aug 11, 2005
WO 2005/113700 A1 patent application	Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives	Dec 1, 2005
WO 2005/072260 A3R4 patent application	Formaldehyde-free adhesives and lignocellulosic composites made from the adhesives	Aug 11, 2005

Table 4. The patent portfolio based around the research by Heartland Resource Technologies.

Patent No	Title	Published
WO 2005/100451 A2 patent application	Water-resistant vegetable protein adhesive compositions	Oct 27, 2005
US 2008/0255333 A1 patent application	Vegetable Protein Adhesive Compostions	Oct 16, 2008
EP 1268702/B1 granted patent	Vegetable Protein Adhesive Compostions	Sep 14, 2005
EP 1268702/B2 granted patent	Vegetable Protein Adhesive Compostions	Sep 23, 2009
WO 2005/100451 A3R4 patent application	Water-resistant vegetable protein adhesive compositions	Jan 25, 2007
WO 2007/064970 A1 patent application	Water-resistant vegetable protein powder adhesive compositions	Jun 7, 2007
AU 2007/275303 A1 patent application	Stable adhesives from urea-denatured soy flour	Jan 24, 2008
US 2008/0202684 A1 patent application	Wood adhesives containing solid residues of biomass fermentations	Aug 28, 2008
AU 2001/038164 A1 patent application	Vegetable protein adhesive compositions	Nov 1, 2001
WO 2008/011455 A1 patent application	Stable adhesives from urea-denatured soy flour	Jan 24, 2008
WO 2005/099477 A2 patent application	WATER-RESISTANT VEGETABLE PROTEIN ADHESIVE DISPERSION COMPOSITIONS	Oct 27, 2005
US 7345136 granted patent	Water-resistant vegetable protein adhesive dispersion compositions	Mar 18, 2008
WO 2001/059026 A3R4 patent application	Vegetable protein adhesive compositions	Aug 16, 2001
WO 2001/059026 A2 patent application	Vegetable protein adhesive compositions	Aug 16, 2001
WO 2005/099477 A3R4 patent application	Water-resistant vegetable protein adhesive dispersion compositions	Apr 26, 2007

Other Proteins

Whilst most of the current work on vegetable protein based adhesives for wood adhesives appears to focus on soy as the protein source in the past and to a limited extent currently other proteins sources have been considered. A number of references detail the potential of wheat and other vegetable proteins as adhesives and or polymer films but little published details appear to be available for application in Wood Composites.

In recent research Yang et al (2006) published work that examined the addition of blood and peanut based proteins to PF resin. In this work the comparison was also made to soy protein.

The results of panel properties showed a reduction in performance compared to the straight PF resin apart from with the blood/PF blend but performance was acceptable. It should be noted that the blend comparisons were performed at 70% protein solids replacement and with simple blending of the protein with the PF resin. It would be reasonable to expect some improvement with appropriate formulation of the product.

In research carried out by Nahla et al (2007) wheat gluten was modified with NaOH and Urea and partially substituted in a UF glue mix to make Reed-based Particleboard. The best performing adhesive was a glue mix with 20 % UF resin and 80% wheat gluten. The wheat gluten had been modified with 3% NaOH and 1.5M Urea on gluten solids. This mixture produced boards that exceeded the requirements of the European Standards as well as those obtained with pure UF resin. It should be noted that press time was 12 minutes and the board thickness was not revealed.

Recently Nordqvist (2009) presented details of the performance of wood adhesives made from Wheat Gluten (WG) compared to Soy Protein Isolate (SPI) for use in furniture applications. In this work the SPI performed better than the WG. Although in both cases the European standard was achieved for dry bonds.

Dynea “AsWood” technology in part appears to be based on PCT application WO 2008/026056 A2 and its patent family. This application exemplifies the use of cornmon or wheat protein. Further reading on the application of this technology can be found in the Appendix.

Based on these limited examples it would appear that other protein sources apart from soy can provide suitable materials for use as wood adhesives. An important factor determining performance will be the protein content.

Recommendations

It appears that the use of wood adhesives based on renewable materials is close to coming full circle. Protein and other natural adhesives were used extensively before the advent of the petrochemical derived adhesives such as phenol-formaldehyde and urea formaldehyde. Like then, any new biologically derived adhesives will have to overcome the advantages of the current adhesive systems, namely cost and quality consistency.

Much of the technology surveyed still appears to be at the pre-commercial, pilot or laboratory scale demonstration stage. The major driver for the development of the new technology, at least in the North American market, is the introduction of the CARB formaldehyde emissions regulations and other so-called “Green” building initiatives. The issue for these initiatives appears to be the reduction of volatile organic chemicals (VOCs) and formaldehyde in particular. It is foreseeable that similar market drivers will become more important in the Australian and New Zealand markets.

Most, if not all, of the current adhesive suppliers to the wood composites industry are responding to these drivers and developing technologies to reduce formaldehyde emissions. These technologies are still based on formaldehyde-based adhesives that have been blended or reacted with other materials, some of which include renewable materials. The newest non-traditional adhesive supplier appears to be the Ashland/Hercules Company with the introduction of their soy protein based Soyad resins. This technology has been trialled at plywood, MDF and particleboard mills. It is unclear whether this technology is currently being used on a full time production basis. Whilst no definitive pricing data could be found, these adhesives still appear to be more expensive than urea-formaldehyde adhesives and are only cost competitive against the more expensive PF and MDI-based adhesives. As such, they are finding niche opportunities for products that require low formaldehyde emission levels or where the use of urea formaldehyde adhesives is prohibited.

It is important to note that all of the technologies that are considered “green” still have a large component that is petrochemically derived or the renewable material has been chemically modified with petrochemicals.

The change away from petrochemical adhesives to those incorporating natural and renewable materials is currently underway in North America. It would be reasonable to expect that within the next 5 to 10 years, these changes will occur within the Australian and New Zealand marketplace, especially as the consumer becomes more environmentally aware and the requirement of export markets change. Given that these new technologies are still in the process of being introduced on an industrial scale, it is recommended that the Australian wood panels industry adopt a “wait and see” approach until these technologies have been “bedded down” and have several years of production history.

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US7,060,798	Modified protein adhesives and lignocellulosic composites made from the adhesives
US7,064,175	Adhesive system containing tannin for binding lignocellulosic materials
US7,081,159	Soy protein based adhesive and particleboard
US7,252,735	Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives
US7,265,169	Adhesive compositions and methods of using and making the same
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PATENTS

CA 2323765	SPRAY DRIED TANNIN/SPRAY DRIED PHENOLIC DRY MIXTURES TO PRODUCE OSB BINDERS
CA2392876	ADHESIVE SYSTEM CONTAINING TANNIN FOR BINDING LIGNOCELLULOSIC MATERIALS
CA569169	ADHESIVE-TANNIN MODIFIED PHENOL FORMALDEHYDE
CN 1120572 (A)	Larch tannin adhesive
CN 1422928	Additive of applying condensed tannin extracts as adhesive for thermosetting wood
CN101328252	Preparation of low free monomer, degradable persimmon tannin modified phenolic resin
DE 10025812	Production of tannin-containing binder, for use in manufacture of timber products, e.g. chipboard, involves extracting tannin-containing bark with hot water and heating used amino resin-bonded chipboard with extract
DE 19704525	Method of manufacture of low-formaldehyde wood fibre or chip board bonded with tannin formaldehyde resin
DE 20313424	Method for producing fibre board with a reduced emission of formaldehyde with thermal stabilisers added to the resin prior to

	pressing and heating especially products such as tannin or resorcin or phenol or melamine
DE10333958	A single- or multicomponent polyurethane composition containing polyisocyanate and tannin as contact adhesive useful as a surface coating material and as a contact adhesive in a polyurethane-containing surface coating material
GR3018245	An adhesive composition comprising isocyanate, phenol-formaldehyde and tannin, useful for manufacturing plywoods for exterior application.
JP2006348271 (A)	Tannin adhesive, woody composite material using the same, and method for producing the woody composite material
KR900005401	Process for the preparation of adhesive for wood
US7,064,175	Adhesive system containing tannin for binding lignocellulosic materials
US7,319,115	Adhesives
WO 9837148	Adhesive composition and its use
WO2004058843	A tannin, aldehyde, amino compound based resin composition and its use as a binding agent for composite wood products
WO9909083	Oxazolidine hardeners for bonding wood articles with resorcinol resins

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