Review of existing bioresins and their applications

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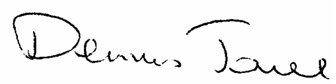
Signature 

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Executive Summary

This report represents the first output of the scoping study “Bioresins for re-engineered UK wood products” being conducted by BRE for the Forestry Commission under contract CFS 10/06. The intention is to critically appraise the current potential for bioresins in the UK and how they might contribute to an enhanced sustainability profile for future re-engineered wood products made from UK timber.

A new adhesive system in which all or part of the phenolic component is replaced by a bioresin is an attractive and real opportunity for the forest products industry. The need is to deliver this environmentally improved system without sacrificing high durability or ease of bonding. The movement away from synthetic resins made from petrochemicals, particularly in North America is happening and it is predicted for the UK that in 5 to 10 years the impact will be registering in UK markets and home production and manufacturer will have commenced.

The main conclusions from this initial review are:

- Synthetic resins are coming under increasing restrictions due to tightening environmental exposure regulations.
- Bioresins can now be used as natural, sustainable alternatives to traditional synthetic materials.
- A wide range of test adhesives has been derived from natural oils (bioresin) such as Cashew Nut Shell Liquid (CNSL) and vegetable oils (rapeseed, soybean, sunflower).
- Blends and part substitutions of petroleum based resins with bioresins are an increasing way of introducing the technologies into the wood industry.
- Fully bio-based composites boards in which the fibre component is made from hemp, flax or timber and a bioresin are viable and an attractive concept.
- High costs are a significant barrier to the development of bioresins, however, the production is becoming viable as technologies evolve, and economies of scale come on stream.
- Biofuel technology and green chemistry routes (the biorefinery concept) from production of chemical feedstocks is racing to meet demand for crop based fuels and other feedstock chemicals. This will present significant challenges and competition for use.
- Improvement in the performance of bioresin adhesives is a key focus for existing research.

The work within this project will continue to appraise the status of bioresins worldwide and the drivers and barriers dictating commercial growth, their fitness for purpose and viability for use in re-engineered wood products. The final phase of this study will:

- Consult with industry and other experts in the field in the UK
- Provide an updated version of this report to close the study (231-932 March 2008)
- Publish a BRE Information Paper on bioresins

The findings of this study will be developed into a series of recommendations and proposals, comprising a strategy for the further development of bioresins in re-engineered UK timber products.

Contents

1 Description of the project

The scoping study “Bioresins for re-engineered UK wood products” is being conducted by BRE for the Forestry Commission under contract CFS 10/06. The intention is to critically appraise the current potential for bioresins in the UK and how they might contribute to an enhanced sustainability profile for future re-engineered wood products made from UK timber.

DEFRA has been supportive in developing new polymer resins to create fully bio-based composites, such as boards in which the fibre component is made from hemp, flax or timber and the resin binder from rapeseed oil rather than the commonly used synthetic chemical resins. Considerable advances have been made over the past 5 years. A range of adhesives have been derived from natural oils such as Cashew Nut Shell Liquid (CNSL) and vegetable oils (rapeseed, soybean, sunflower). The cost was a significant barrier to the development of renewable materials, however, the production has become viable as technologies evolve, and economies of scale come on stream, along with price inflation of petroleum and increasing awareness relating to end of life disposal. Bioresins can now be used as natural, sustainable alternatives to traditional petro-chemical derived materials such as phenol-formaldehyde and iso-cyanate resins in the manufacture of composite products. Many of the synthetic resins are coming under increasing restrictions due to tightening environmental exposure regulations. The industry risk losing key familiar resins in the future; hence the need to critically assess the opportunity for bioresins. The development of a bioresin system for replacement of synthetic resin becomes important for the present and future ‘green’ credibility of re-engineered wood products.

This project aims to provide the platform upon which Forestry Commission can evaluate support for emerging bioresins and their application in timber re-engineering industry in UK.

2 Introduction

The idea of wood adhesives from renewable raw materials has been a topic of considerable interest for several decades. The level of interest and development has depended on demand and economic factors. The major thrust to date in bio-adhesives was the oil crisis of the early 1970's, though this interest waned as oil prices stabilised. However there is a new demand for bio-derived products, including adhesives, driven by consumer demand as well as environmental considerations. Consumer demand has been generated by a growing awareness of environmental issues and the desire to 'save the planet'. This has led to public opinion deeming petroleum-based products being harmful to the environment, with public perception dictated to by several environmental awareness groups. Whilst the aim of these groups is laudable, there is concern from industry in that a range of products cannot be removed from a marketplace without suitable replacements. In the case of adhesives for timber products, this could undermine public confidence in products using these adhesives, which could result in a move towards other products, often with worse overall environmental credentials. These public views are compounded by the increasingly strict government regulations being introduced to allay the environmental concerns of the public. Hence the desire to find new product ranges, based on bio-derived resources, represents a major step forward for most industries, but especially for the adhesives industry.

When considering bio-derived adhesives, it is necessary to establish the broadness of the definition. If considering the major component of the adhesive, the bio-derived material may be referred to as non-petroleum based. This definition would also include urea-formaldehyde (UF) resins. However this is not usually the case, for two reasons:

(i) the presence of formaldehyde is typically seen as synthetic-based; and

(ii) urea, whilst naturally derived, is considered under the general group of 'conventional adhesives'.

The term 'bio-derived adhesive' has come to be used in a very well-specified and narrow sense to only include those materials of natural, non-mineral or non-petroleum based, origin which can be used either in their natural state or after small modifications, capable of reproducing the behaviour and performance of synthetic resins. Such a definition limits the number of materials that can currently be included to tannins, lignins, carbohydrates, unsaturated oils, liquefied wood and wood welding by self-adhesion. Other materials have been identified, and work continues into adhesives manufactured using proteins, blood and collagen.

However, the aim of bio-derived wood adhesives is not to regress to the form of natural products adhesives as used up to the 1920s and 1930s (which were replaced by synthetic adhesives). The bio-based adhesives about which we are talking here are admittedly derived from natural materials, but using or requiring novel technologies, formulations and methods.

The renewed interest in bio-derived adhesives is occurring world-wide, with separate research projects all aiming to establish commercial opportunities for bio-derived adhesives. Work in the UK is currently ongoing in assessing opportunities for such adhesives through three separate concurrent studies by BRE (through this report), Jaako Poyry and the Biocomposites Centre. The fact that there are three separate studies demonstrates the increased interest in this subject at this present time.

The following sections will attempt to identify the main driving factors in the development and possible commercialisation of bio-derived adhesives, whilst later chapters will consider specific cases.

2.1 Synthetic resins and product demands

Adhesives have been used for millennia and have traditionally been based on naturally occurring materials that can bond, such as collagen and other fish, animal and plant based glues. In the history of material adhesion it is only relatively recently that synthetic glues have taken over and displaced natural adhesives. In doing so there is no doubt that the range and application of adhesives in construction has grown tremendously. Adhesives are used extensively in construction products from structural bonding of timber in glue laminated beams to floor and wall coverings and the resins that bind wood based panel products such as plywood and oriented strand board. Growth in offsite manufacture and closed panel systems has put greater emphasis on the role of adhesives. In all areas where wood is used adhesives are also used, including the following groups:

- Building, construction and civil engineering applications: sandwich panels (SIPS), wooden sub-flooring, factory assembled truss rafters, glulam, closed panels
- Woodworking and joinery: edge and face lamination, windows joints, doors, kitchens, furniture, staircases
- Primary wood bonding: plywood, chipboard, OSB, MDF
- Transport: marine plywood, panel products
- Do-It-Yourself: wood glues
- Assembly: sports equipment, toys

Adhesive product groups defined by FEICA are:

- Natural polymers: vegetable adhesives (dextrines, starches) and protein adhesives (casein, soyabean, albumen, animal glues)
- Polymer dispersions: natural rubber latex, polyurethanes (PUR), styrene butadiene rubbers (SBR), polyvinyl acrylates (PVA) and acrylics
- Hot melt adhesives: polyolefin, ethylene vinyl acetate (EVA), polyamide, PVC, polyurethane
- Solvent based adhesives
- Reactive adhesives
- Adhesives based on water soluble polymers

The Association of European Adhesive and Sealants Manufacturers (FEICA) estimate the total global value of adhesives business is €23,000 million. Adhesives are fundamental to the way we design and build and in Europe over an estimated 250,000 types of adhesive product with an annual production and use of 2.3 million tonnes per annum[1]. Adhesives bond material surfaces together and are either bond through a physical hardening or through a chemical curing via a polymerisation reaction. The great diversity of

[1] Bonding adhesives textbook (2004), pp88. Published by FEICA and download available from www.feica.com

products reveals the tailored nature of each system to meet the demands of the particular end use. Some are tailored to withstand humid environments such as exterior joinery joints.

Adhesives that rely on petroleum based feedstock are at risk from the volatility of the price of the raw materials and the chemical persistence. In addition adhesives in general are scrutinised for life cycle costs and must not have adverse effects on building occupants or the environment. The opportunity for bioresins is undeniably there but the adoption and development of this sector is yet to be assured as the technical performance needs to be rigorously demonstrated for consumers to accept the products, the cost value chain needs to be clarified and the advantages effectively communicated.

2.1.1 Synthetic resin adhesives

Man made polymers from petroleum feedstock have been tailored to the requirements of the wood working industry for the last 70 years. They dominate the market by displacing traditional natural adhesives of lesser performance in terms of wetting resistance and strength properties.

Table 1 presents the typical resins used in adhesives which broadly fall into two groups:

- Thermosetting resins: many rely on formaldehyde and cure by an irreversible condensation polymerisation reaction that eliminates water. The urea-formaldehyde resins are used extensively in the manufacture of plywood and particleboards products.
- Thermoplastic resins rely on evaporation of solvent to cure them and can be softened by heating. The pre-polymerised resin is dispersed in solvent. The polyvinyl acrylates are the most common form of these resins used in the wood furniture industries.

Type	Form	Characteristics	Application	Products
THERMOSETTING				
UF (urea formaldehyde)	Powder or liquid blended with melamine and other resins	High in wet and dry strength. Moderately durable under damp conditions	Applied at room temp and cured or some are hot pressed at high temperatures	Plywood and particleboard
MF (melamine formaldehyde)	Powder with or without catalyst	High in wet and dry strength. Very high resistance under damp conditions	Mix with water at room temp and cure at high temperature	Hardwood plywood, end jointing, edge laminating,
PF (phenol formaldehyde)	Aqueous alkaline dispersion for plywood and powder or liquid for OSB flakeboard	High in wet and dry strength. Very high resistance in damp conditions. More resistant than the wood to high temp and chemical.	Film form or powder and liquid at room temp. Most require hot pressing	Main adhesive for exterior softwood plywood and flakeboard
Resorcinol and phenol-resorcinol formaldehyde	Liquid with separate hardeners. Most expensive of the formaldehyde based adhesives	High in wet and dry strength. Very high resistance under damp conditions. More resistant than the wood to high temp and chemical.	Mix with hardener and apply and cure at room temp.	Laminated timber and joints that must withstand severe conditions e.g. I joists and glulam
Isocyanates	Liquid resins or water emulsions	Excellent adhesion to wood and high chemical and temp resistance	Very rapid cure on application of heat or in presence of moisture	Limited use in structural flakeboard, jointing - high cost
THERMOPLASTIC				
PVA thermoplastic	Liquids	High dry strength, low resistance to temp and moisture.	Liquid ready to use, room cure	Furniture, flush doors, plastic laminates
Hot melt adhesives (polyamides, polyurethane (PU), polyolefins etc.)	Solid	Gap filling, moisture resistance, lower strength	Melting or spread	Furniture, plastic overlays, patching, panel edging

Table 1 Synthetic resins and basic attributes summarised from Eckelman's published survey of wood adhesives[2].

2.2 Market drivers

As with other industrial sectors, the adhesives industry is under pressure through rising costs of feedstocks and oil price instability combined with the increased costs of compliance with environmental and safety legislation. REACH also poses concerns that some raw materials will no longer be produced. Many of the key market drivers for adhesives have stemmed from raw material costs and health and environmental concerns.

1. Health, Safety and Environment concerns with the resins: Some adhesives have issues associated with them due to the utilisation of particular chemicals, most notably formaldehyde, in their synthesis. Synthetic adhesive resins, such as phenol-formaldehyde and urea-formaldehyde, are largely used for bonding wood in the furniture making industry and also to bond wood based construction products. Human and environmental exposure of formaldehyde is of concern as it is a suspected carcinogen.

[2] Eckelman C.A. (1999) Brief survey of wood adhesives. Forestry and Natural Resources, Purdue University, West Lafayette, IN.

Bisphenol A is used in the manufacture of epoxy resins, which are widely used in many industries due to their strong bonding properties and are used in flooring, aircraft and car manufacture as well as DIY applications. Bisphenol A has received attention from regulating authorities and health organisations due to its alleged hormone disrupting effects.

2. Health, Safety and Environment concerns with other adhesive components: As well as the resin there may also be issues arising from other components in the adhesives. As the solvent used to disperse the resin and give it its working properties can comprise up to 80% of the final weight of the product it is the main focus of attention. The emission of organic solvents is detrimental to air quality and legislation in this area is becoming increasingly stringent. Total Volatile Organic Compounds (TVOC) limits for emission to indoor air from construction products limits emissions to safeguard health of occupants. The use of organic solvents in wood coatings has decreased rapidly in the last decade as the industry moved to water-borne systems. As a result of this an increasing amount of effort has been made by the adhesives industry to develop low-solvent and, where possible, solvent-free adhesives.

3. End of life concerns and recycling: Adhesives can potentially cause problems when it comes to the end of life of wood products. Adhesives (alongside paint and wood preservatives) are considered contaminants in reclaimed wood which impact on the ability to reuse, recycle or in some cases recover energy from the reclaimed wood resource. Recent research has focussed on wood preservative treated timber being reused in demonstration wood panel products blended with virgin wood. The emissions from such panels in a demonstration building were below the detection limits of the analytical methods. This suggest there may not be a technical issue with reusing treated timber in these end uses but the barrier of lack of industry confidence needs to be addressed. For adhesive bonded wood it is an attractive future prospect to consider the bioresin and wood being sent for composting, reuse or recovery of energy without any environmental or health and safety issue being compromised.

4. Chemical legislation: The REACH (Registration, Evaluation and Authorisation of Chemicals) Regulation entered into force on 1 June 2007. The Regulation aims to protect health and environment through better identifying the properties of chemical substances. In relation to this the Regulation gives greater responsibility to industry to manage the risks from chemicals and to provide safety information on the substances. Thus the adhesives industry will have to deal with a lot changes linked to the implementation of REACH for existing synthetic resins as well as new natural products such as bio-based resins. Natural products must be rigorously demonstrated to have an improved environmental profile than the substitute product – it is not simply enough to assume that a natural product will be better. Some of the most poisonous substances known to man are naturally occurring.

5. Standards and best practice: There are a high number of CEN standards for adhesive products and wood and performance aspects. New products must pas through the rigor of this process.

Adhesives are found in almost all consumer products; the development of environmentally improved bioresins based adhesives is an attractive option and has received considerable attention in the last decade. The volume of research into this field continues to grow.

Interest in, and commercialisation of, products from renewable resources is not well advanced despite the above drivers and governmental and societal requirements for sustainable development. The current market penetration is <1% for polymers and no more than 2% for lubricants and solvents, with only surfactants of the major classes of chemical products having high renewable resource usage (20%). The total market potential over the next 10-20 years is been estimated at typically ten times these values.

2.3 Biocomposites

This review is considering bioresins and their potential role in adhesives for wood and particularly re-engineered home-grown timber construction products. For completeness the review includes brief mention of biocomposites which have undergone considerable research alongside the bioresins as part of a whole biological composite solution. In the UK the focus of research is and has been for decades the Biocomposites Centre at the University of Wales, Bangor[3].

The concept is that a total composite of biological origin can be derived from crop residues, wood, fibres and crucially the bioresin to bind the product. The Biocomposites Centre have designed and engineered biocomposites from plant bio-fibres and a blend of unsaturated polyester resin and derivatized vegetable oil to replace existing glass fibre-polyester composites. These could transfer for use in housing applications. Natural fibre composites are an attractive goal as they could provide environmental gains, reduced energy consumption, lighter weight, insulation and sound absorption properties, thus providing many beneficial additions. Their success hangs on being able to deliver appropriate, matched to expectations based on synthetic composites, performance and durability.

Biocomposites were made using a non-woven fibre mat (90% Hemp fibre with 10% thermoplastic polyester binder) as reinforcement, and unsaturated polyester (UPE) resin as well as blends of UPE and functionalized vegetable oils as the polymer matrix. All composites were made with 30% volume fraction of fibre, which was optimized earlier. The structure–property relationships of this system as well as the thermo-mechanical properties of these composites were measured. The notched Izod impact strength of biocomposites from biobased resin blends of UPE and functionalized vegetable oil and industrial hemp fibre mat are enhanced by 90% as compared to that of the pure UPE-industrial hemp fibre mat composites. The initial tests also show an improvement in the tensile properties of the composite as a result of the incorporation of the derivatized vegetable oil. The morphological changes of the matrix and composites have been analyzed using electron microscopy by Mehta et al (2004).[4]

The Central Science Laboratory, York and the National Non-Food Crop Centre, York operate a European funded network for Industrial Crops and their Applications[5]. The application of bioresins and biocomposites for end uses in construction markets is part of the network which is dominated by biofuels, alternatives for petroleum based plastics in packaging and solutions for the automotive industry.

[3] www.bc.bangor.ac.uk

[4] Mehta G., Mohanty A.K., Misra M. & Drzal L.T. (2004) Biobased resin as a toughening agent for biocomposites. *Green Chem.*, 2004, 6, 254 - 258

[5] Interactive European Network for Industrial Crops and their Applications QLK5-CT-2000-00111 IENICA is a project funded under the Fifth Framework Programme of the European Commission Summary Report for the European Union 2000-2005 Prepared by: Caroline A Holmes, Agricultural and Rural Strategy Group, Central Science Laboratory, Sand Hutton, York YO41 1LZ.

2.4 Desired product profile

The production of bioresins must be sustainable. The factors that influence this include:

- Land use issues and competition with other needs such as agriculture for food, industrialisation, production of bio-fuels, conservation and building. Keen focus on renewable and green crop based fuels has seen market price rises in basic food stocks such as maize, soya bean other grains as these crops are simultaneously engaged in local and regional food markets as well as international fuel markets.
- Economic to produce to compete with less sustainable technologies
- Connected to regional supply chains and demands for the products to minimise transport impacts
- Be of a non-toxic and benign nature in production and in use to enhance the environmental profile of the products and to create incentive for their use as replacements for current technologies.
- They have to work. The bioresins as binders or adhesives must have equivalent long term performance to existing technologies and be as versatile and weather resistant. Robust test data must be available to enable comparison to market expectations for non-bioresin products.
- The products should present no compromises at the end of life of a product bound or glued with bioresins such that recycling is facilitated or energy can be recovered from the biocomposites without any detrimental emissions during combustion.

Replacement of synthetic resins with bio-based resins would improve the profile of reconstituted materials. To tackle the issue of poor water resistance the soya bean based resin was use din combination with PF resin to yield a water resistance adhesive. Protein adhesives, except blood proteins, are not durable enough to pass the water resistance tests typified by adhesive bonds. This study produced a soya bean flour adhesive that passed the tests for strand board manufacture.[6]

[6] Frihart C R & Westcott J M (2004) Improved water resistance of bio-based adhesives for bonding wood. In Proceedings of International Conference on Environmentally Compatible Forest Products, Oporto, Portugal, Sept 2004. p293-302.

3 Types of bio-derived adhesives

As noted in the previous section, there are several examples of compounds that may offer commercialisation prospects for new adhesive systems, these include:

- Tannins
- Lignins
- Cashew Nut Shell Liquid (CNSL)
- Carbohydrates
- Triglycerides
- Proteins
- Bioalkyds
- Waxes

Each of these will be considered in the following sections, outlining current knowledge and commercial prospects.

3.1 Tannin-based adhesives

Tannins consist mainly of gallic acid residues that are linked to glucose *via* glycosidic bonds, as shown in Figure 1.

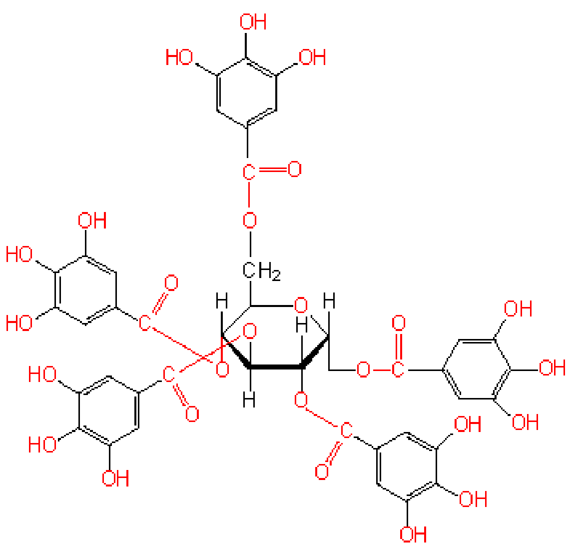

Figure 1 Basic chemical structure of tannin compounds

The word tannin can be used to define two different classes of chemical compounds mainly of phenolic nature: hydrolysable tannins and condensed tannins.

Hydrolysable tannins are mixtures of simple phenols, such as pyrogallol and ellagic acid, and of esters of a sugar, mainly glucose, with gallic and digallic acids (Pizzi[7]). Their simplicity affects their potential use, since there is a lack of macromolecular structure in their natural state. This is compounded by the low level of phenol substitution possible. Furthermore, this range of compounds is only produced on a limited level worldwide, and as such they demand high prices, which also limits their commercial applicability.

Condensed tannins, on the other hand, currently constitute more than 90% of the total world production of commercial tannins (200,000 tons per year), making this range of compounds more interesting for the preparation of adhesives and resins when considering both chemical reactivity and economic factors. The range of molecular possibilities may be judged from the simple schematic overview of oligomeric formation known to occur in nature from one of the simplest components of tannin, namely galloyl (Figure 2). Reproducing similar chemical linkages in adhesive systems could be achieved, for example through Ullmann reactions for the preparation of biphenyls or biaryl ethers.

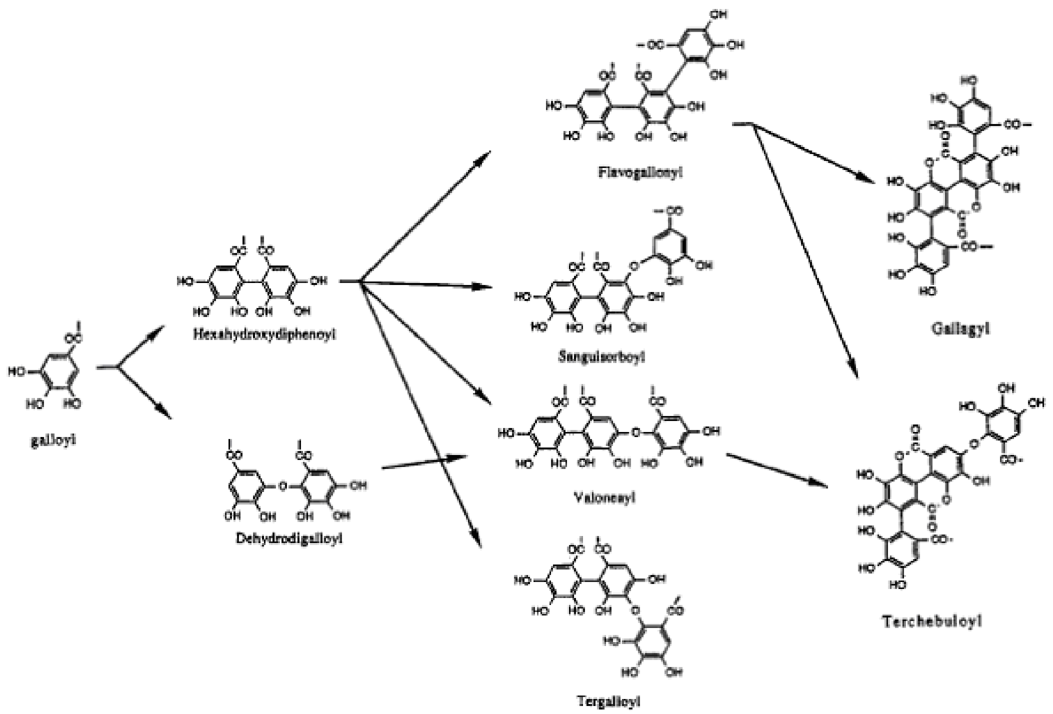

Figure 2 Chemical schematic showing oligomeric molecule formation from galloyl

Condensed tannins represent the formation cursors for flavonoids, and are widely distributed across nature re. Whilst the common consumer recognises the presence of tannins of red wine and tea, they are most widely distributed in nature in levels sufficient for commercial extraction in the bark of various trees. This opens up opportunities for the processing of timber bark resulting from primary processing procedures.

[7] Pizzi A (2003). in: Handbook of Adhesive Technology, 2nd edn, A. Pizzi and K. L. Mittal (Eds), Chapter 28. Marcel Dekker, New York, NY (2003).

Among the timber species recognised as providing high levels of these include various *Acacia* (wattle or mimosa bark extract), *Schinopsis* (quebracho wood extract) and *Rhus* (sumach extract). These represent species not available in the UK, and as such their use would represent a considerable financial cost.

There have been several projects funded through the European Commission considering the potential of tannins within adhesives. One of these ("Natural tannin-based adhesives for wood composite products of low or no formaldehyde emission"; FAIR-CT95-0137), looked to extend the commercial potential of tannins, which have been used in adhesive manufacture for some 30 years. However, there were three main obstacles to successful commercial activities within Europe:

1. tannins are sometime expensive due to the transport costs from far away producers
2. the quantity available for adhesives is not too great as only the production overflow from the leather market can be used
3. the established technology using high amounts of hardener yields panels of unacceptably high level of formaldehyde for at least a few months after panel manufacture due to the presence of unreacted hardener

This work contributed to identifying species of tree whose bark may be suited to use within adhesive manufacture. This led to demonstrating the potential of *Tsuga* (hemlock bark extract) and various *Pinus* bark extract species. This shows there is an opportunity for European and UK grown timbers to deliver into this emerging sector, though the supply of pine bark would need to be assured, given its current use in other market resource streams, such as garden mulch and bioenergy. There would need to be a continual assessment of the available resources, and competing markets, given the over-demand for UK timber resources at present.

In order to comply with emerging adhesive technology, the removal of formaldehyde from adhesive formulae is being considered, even though the majority of tannin (and phenolic) based adhesives having low formaldehyde emission levels already. This has led to two new avenues of investigation:

(i) the use of non-aldehyde containing or non-aldehyde releasing hardeners, and

(ii) the autocondensation process for tannins.

A fairly comprehensive overview of each of these has been reviewed by Pizzi[8], and is summarised below.

The use of non-aldehyde containing hardeners represents the closest approach to conventional technology, whereby the chemical action of the additive results in cross-linking reactions occurring between reactive sites present in the tannin-based molecules and the additive. This leads to an increase in the viscosity, and as the process continues, hardening finally occurs. The rate at which hardening is achieved depends on both the level of reactivity of the additive, and the extent of the three-dimensional polymerised network being produced. The main additive used in recent developments has been hexamine. Whilst technically a trimer of formaldehyde, hexamine is capable of undergoing rapid reaction for the formation of methylol bridges, and as such, will not result in much in the way of free formaldehyde

[8] Pizzi A (2006). "Recent developments in eco-efficient bio-based adhesives for wood bonding: opportunities and issues" *J. Adhesion Sci. Technol.*, Vol. 20, No. 8, pp. 829–846

3.2 Lignin

Lignin is an abundant polymer present in woody plants providing the glue that binds fibres such as cellulose together. Available as a by-product of pulping wood and with lignin contents of 5-50% as sulphonated lignins from Kraft pulping. Organosolv lignin is available from an alcoholic pulping process as the only non-sulphonated lignin.

Research into lignin based wood adhesives has had little practical success and offers no advantages over conventional adhesives. Chemically modified lignins have been studied extensively, mainly focussing on methlolation, epoxidation – the introduction of these cross linking sites still does not yield similar curing performance to a conventional PF resin. An issue that seems to have confounded the research is the characterisation of the lignin mixture itself and the lack of reproducibility of studies using lignins from different sources. This presents a barrier to commercial development if different blends and source of lignins are going to give different properties.

Lignin PF blends offer some opportunities and certainly the ability to use the lignin waste product is an attractive feature. If a process or technology could cope with a variety of lignins and produce the same performing product this would be a great step forward in the application of lignin based adhesives.

Etün & Zmen (2003) aimed to develop a phenolic resin for partially replacing phenol with modified organosolv lignin in phenol-formaldehyde (PF) resin production. Organosolv lignin-based resins showed comparatively good strength and stiffness. Test particleboards were produced and tested for their physical strength and dimensional stability. The particleboards bonded with Lignin-PF resins were comparable to those of the control-bonded particleboards. Organosolv lignin was concluded to be a feasible replacement for up to 30% of the phenol in particleboard-type PF resins.[9]

A German and Japanese combined research team[10] in 2002-2005 worked on lignin has been extracted from wood under High Pressure Hydrolysis (HPH)-subcritical condition, and mixtures of the HPH-lignin with natural fibres were prepared to obtain a granulate which could be processed on a small injection moulding machine. The mechanical properties of the test samples were measured and found to be comparable to those found for the wood-like thermoplastic with normal lignin from the current paper making process. The extraction conditions of lignin from wood were chosen as 5 MPa at 250□ and the separation condition of lignin from hot water was chosen as 0.3 MPa at 120□. In the case of the throughput of 1t-wood/h (160kg-lignin/h), the extraction cost of the lignin was estimated at 110 yen/kg-lignin. In summary, the wood-like thermoplastic by HPH-process has good mechanical properties, and HPH-process is feasible.

Akaranta & Wankasi (1999)[11] Peanut skin tannin extract-formaldehyde condensates were modified with resorcinol and cashew nut shell liquid. The copolymer resins formed were used as thermosetting and cold-setting exterior grade wood adhesives for sapele veneer panels. Results obtained showed that, on addition of para-formaldehyde, the resins modified with resorcinol cured at ambient temperatures while those modified with cashew nut shell liquid cured at higher temperatures. The bonded panels developed strength

[9] Etün N S & Zmen N I (2003) Studies on Lignin-Based Adhesives for Particleboard Panels Turk J Agric For 27 (2003) 183-189.

[10] G-02 (Registration number 2002GP008) Practical research of wood-like thermoplastic using lignin extracted by high pressure hydrolysis process. Research Coordinator Norbert Eisenreich (Fraunhofer Institute for Chemical Technology, GERMANY), Tsutomu Sakai (KRI,Inc., JAPAN), Wilhelm Eckl (Fraunhofer Institute for Chemical Technology, GERMANY), Michitaka Ota (Fraunhofer Institute for Chemical Technology, GERMANY), Emilia R. Inone-Kauffmann (Fraunhofer Institute for Chemical Technology, GERMANY), Helmut Naegele (TECNARO GmbH, GERMANY), Shiro Saka (Kyoto University, JAPAN), Mitsuru Kondo (KRI,Inc., JAPAN), Michiyuki Kono (Dai-ichi Kogyo Seiyaku Co.,Ltd., JAPAN) and Manabu Kikuta (Dai-ichi Kogyo Seiyaku Co.,Ltd., JAPAN)

[11] Akaranta O. & Wankasi D. (1999) Wood adhesives from peanut skin tannin-formaldehyde resins modified with phenols Pigment & Resin Technology Volume: 28 Issue: 5 Page: 293 - 296

and durability satisfying the requirements of International Standard Specification for phenolic resin adhesives.

3.3 Cashew Nut Shell Liquid (CNSL)

Cashew nut Shell Liquid (CNSL) is a phenolic-based range of compounds present as a protective barrier of the cashew nut, which grows outside the cashew apple, as shown in Figure 3.

Figure 3 The cashew apple, with nut growing from end of fruit.

The popularity of cashew nuts has led to considerable plantation areas being formed beyond the original growing regions in Brazil, with the Portuguese establishing several plantations in other regions of similar heat and humidity, to exploit the potential of the nut. This has resulted in cashews now being grown in more than 30 countries worldwide, with a nut crop of around 2.3 million tons per annum. Among the major raw cashew producing countries are Vietnam, India, Brazil and Nigeria, with India representing the major producer.

CNSL is meant to act as a deterrent against animals eating the exposed kernel and the nut inside. The phenolic nature of the CNSL is believed to leave an extremely bitter taste, as well a causing a mild burning sensation (due to the acidity of the phenols). It is this acidity that has been known to affect the skin of cashew nut pickers (through continual exposure). CNSL is actually a mixture of 4 main groups of compounds, which may vary in their composition through substitution of the aromatic phenolic ring (Figure 4).

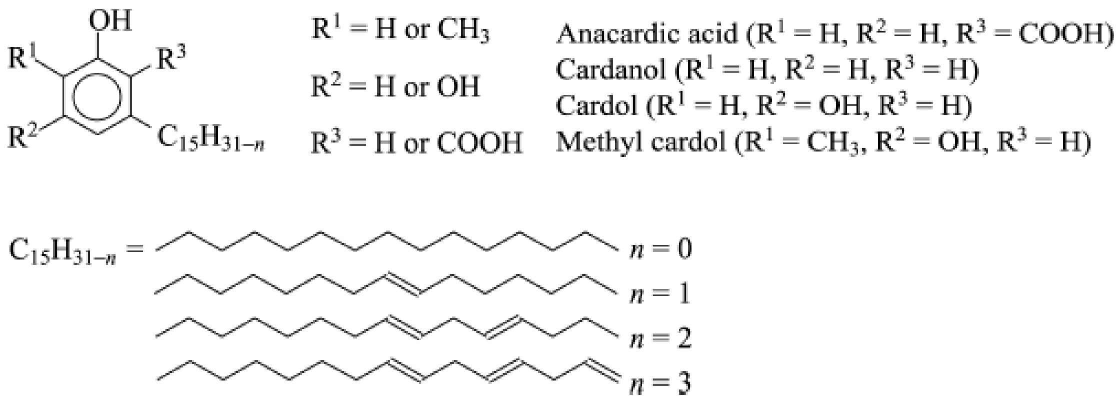

Figure 4 Components of CNSL.

The composition of CNSL can depend on the region of production, and may also vary from season to season. This variability may limit the commercial application since the chemistry may vary from batch to batch.

Warwick University, linked to the Warwick Manufacturing Group, have conducted research on advanced sustainable materials including alternative crop-based materials, the use of bioresin based products in the automotive industry, packaging and for innovative applications. Studies on the *Characterisation of cashew nut shell liquid for composite manufacture* were completed by Leonard Mwaikambo though the research has not been reviewed for this report.

3.4 Carbohydrate

Carbohydrates as gums, polysaccharides (cellulose, starch and hemicellulose) and sugars have been utilised in adhesives for centuries. They are readily available and very cost effective but no wood adhesive is available that is based on them. A variety of gums disperse in water and are used as adhesives in other sectors. Polysaccharides such as cellulose require cross linking agents to form adhesives and are employed as cellulose esters for example in gluing paper and to a limited extent wood. Cellulosic polymers with graft co-polymers according to Tomkinson[12] show potential for use in wood composite production.

The bonding of wood veneers, using phenolic resins in which part of the phenol-formaldehyde is replaced with carbohydrates have shown that the addition of non-reducing carbohydrates do not adversely affect the dry- or wet-shear strength of 2-ply Douglas fir bonded panels. This is encouraging but the extent of substitution without affecting key properties has yet to be established.

Conner and co-workers have shown the promise of a number of cellulosic and carbohydrate intermediates as possible glues for wood. The particular issues these adhesives face compared to classic petroleum derived wood adhesives has been extensively presented.[13]

[12] Tomkinson J (2002) COST Action E13 ‘Wood Adhesives’ Report of state of the art p46-65

[13] Conner A H, River B H, Lorenz L F (1986) Carbohydrate modified phenol-formaldehyde resins *Journal of Wood Chemistry Technology* 6 (4) p591-613 and Conner A H (2000) Proceedings of the 9th International Conference on jojoba and industrial crops and products p214.

3.5 Triglyceride

The research team led by Prof. Paul Wool in the Chemical Engineering Faculty at the University of Delaware, USA have conducted research into bioresins and natural fibre combinations. The team is behind ACRES (Affordable Composites from Renewable Sources) and are investigating the use of soybean triglycerides (Figure 5) as raw materials in the synthesis of new polymers. The ACRES programme includes research in genetic engineering, composite manufacturing and computer simulation in a drive to deliver commercially accessible technologies. “Soyoil” is being used to make affordable and renewable fibre-reinforced composites for high-volume applications. They have published extensively on production of composites and the modification of soyabean triglycerides to bring the technologies to commercial viability[14].

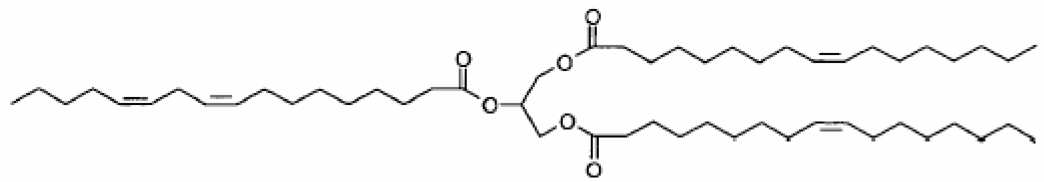

Figure 5 A triglyceride molecule. Triglycerides are the main component found in natural oils

They are exploring a broad range of conversion chemistry to modify soy products to composite resins. Several have been found to be potential candidates in terms of affordability and processing-property targets, and an optimal set is being explored. The target markets are the automotive industry and farm machinery for composite panels and the construction industry for lightweight panels.

Triglyceride oils derived from plants have been used to synthesize several different monomers for use in structural applications. These monomers have been found to be suitable to form polymers with a wide range of properties. Composite materials have been manufactured using these resins using glass fibres and natural fibres such as flax and hemp. It has been shown the properties exhibited by both the natural- and synthetic- fibre-reinforced composites can be combined through the production of hybrid composites.

These materials combine the low cost of natural fibres with the high performance of synthetic fibres. Their properties lie between those displayed by the all-glass and all-natural composites. Characterization of the polymer properties also presents opportunities for improvement through genetic engineering technology. Effort continues to optimize the properties of these materials and understand the fundamental issues that affect them.

[14] J. La Scala and R. P. Wool, "Rheology of chemically modified triglycerides", *JOURNAL OF APPLIED POLYMER SCIENCE* 95 (3), 774, (2005)

3.6 Plant based proteins

The most studied plant protein adhesive is based on soya, either the soybean meal or a protein isolated from the soybean. The glue is not water resistant and has moderate to low strength can be hot pressed and in the past has been used for interior Douglas fir plywood. They are also used in a blend with blood proteins.

Soy-protein-based wood adhesives have been used for centuries. Since World War II, they have been largely replaced by petroleum-based adhesives with superior performance and economics. Current research is focused on developing and commercializing four soy products:

1) a soy/phenol-resorcinol-formaldehyde (PRF) system for finger-jointing green lumber,

2) an improved waterproof product to replace phenol-formaldehyde (PF),

3) a foaming glue for plywood and

4) an improved water-resistant product to replace urea-formaldehyde (UF).

An epoxidized soybean oil (AESO) is a good cross link and is suitable for production of thermosetting adhesives. Åkesson et al[15] characterised the cross linking behaviour of this oil used with flax fibre mat and conclude it was promising for the production of thermoset resins. They noted that thermoset resins based on bio-based resins were few and not common. The advantage for the impregnation of fibres was noted and the ability to handle at room temperatures will be increasingly important – this all improves the matrix formed and the bonds between fibre and adhesive.

See Appendix A for information on soy-based wood adhesives from USB in the United States.

3.7 Animal based adhesives

Traditional animal glues are made from hide and bones and fish. For the wood industry these glues were not attractive as they had low moisture resistance, are difficult to apply, expensive and can be degraded by fungi and moulds. They were used in the furniture industry but have been displaced by the PVA type adhesives.

Animal protein glues (casein) from milk curds has been used in interior applications of timber adhesion and in laminating timber. They are very expensive as the raw material is costly; they were used for their superior moisture resistance compared to animal and plant protein glues. They had further drawbacks in that they stained timber with high tannin contents easily and were susceptible to moulds and fungal attack.

Blood albumin glues required hot pressing to cure them fully. They were a very important class of moisture resistant glue for softwood plywood manufacturer prior to the synthetic resins. They also displayed some temperature resistance and were less susceptible to attack by mould and fungi than the traditional animal glues and casein glues. They have been displaced by the phenolic resins.

[15] Åkesson D, Skrifvars M, Seppala J V and Walkenstrom P (2006) Preparation of natural fibre composites from bio-based thermoset resins. *In the Proceedings of the 27th Riso International Symposium on Materials Science, published by the Riso National Laboratory Roskilde Denmark* p365-370.

At the Agricultural University, Poznan, Poland research on blood plasma has shown that the products may have application in binding and fixing wood preservatives (copper sulphate) in timber[16].

Dried blood plasma has been used to fortify commercial formulations of PF resins with great success reducing hot press curing times by up to 30% compared with the pure PF resin[17]. Further to this the foamed blend is being trialled for bonding plywood to apply the adhesive by extrusion to the dry wood veneer. Initially data indicates a 25% reduction in adhesive application weights without loss of bond quality. Further work will establish if the bond properties are sufficient to enable this adhesive volume saving in addition to reduce curing times.

3.8 "Bio-alkyds"

The coatings industry in its diversity have embraced the use of resins of natural origin for centuries and indeed they are making a return from the 1960s influx of mass produced petroleum derived products as we see green consumer products marketed more openly. The focus of the natural resin paints are that they market on sustainable resource use (disconnection from oil), the coatings allow materials and buildings to breathe, minimised effects on occupant and user health and improved indoor air quality. Whilst a number of these issues may yet to be demonstrated by robust independent scientific scrutiny it is an example of a sector where bioresins are and can take market in replacement of conventional oil based products.

Many of the bioresins that are utilised in natural paints are in substitution from acrylic resins that also contain glycol ether as solvent. Some including casein, colophony (resinous sap of pine trees), saponified natural oils to produce soaps, tung oil, linseed oil, carbohydrates (cellulose and starch), shellac.

Aglaia natural paints produced by BEECK'sche Farbwerke in Germany use natural resins such as shellac and beeswax soap for indoor wall emulsions.

Auro[18] natural paint primers and interior and exterior gloss coatings for wood and wood-based products. Environmentally friendly and green markets in Germany water based coating using a plant based resin system (sunflower seed oil, ricinus oil, linseed stand oil, colophonium glycerine ester, partly as ammonium soaps) and surfactants made form rapeseed oil[19].

BioShield natural resin floor finish is available which is a hard wearing clear gloss or satin finish for interior floors of stone, tile, brick, concrete but is particularly well suited for solid wood and wood based floors. BioShield oil primer is used to pretreat the substrate for application of the resin. It is based on a linseed oil, a soy based alkyd resin, rosin and driers, oximes and silica.

Ansari and Goswami (2006)[20] have studied blends of shellac and acrylic resins revealed promising coatings products with good adhesion, flexibility and finish for cementicious materials. The esterification link between shellac and acrylic resins provides the coating capability; too much shellac can impair the coating performance. New opportunities for shellac in surface coating were demonstrated.

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16 I. Polus-Ratajczak and B. Mazela (2004) The use of blood protein in wood preservatives. *Holz Roh- und Werkstoff* v62 (3) 181-183.

17 Tracton A. A. (2005) Coatings Technology Handbook Third Edition. pp912. Published by CRC Press ISBN 1574446495

18 www.auro.de

19 http://www.naturaldeco.co.uk/info/datasheet.aspx

20 Ansari M F & Goswami D N (2006) Shellac-acrylic emulsion paints for cementations surfaces. *Pigment & Resin Technology* 35 (4) 183-187.

3.9 Wax based systems

Wax based systems are possible routes for enhancing the properties of wood treated with them. The concept of stabilisation of surfaces and bulk timber by using petroleum based waxes is exploited as part of a low moisture content and therefore more stable timber product. The use of natural wax based systems to stabilise wood, prevent moisture ingress and offer a degree of property (durability and dimensional stability) enhancement is being studied within a project funded by the BRE Trust “Natural products for enhancing wood durability”[21].

[21] www.bretrust.org.uk

4 Current prospects

Currently 145,000 tonnes of formaldehyde-based phenolic resins are used per year in Western Europe, with a similar amount used in the USA. The movement away from resins made with petrochemicals, particularly in North America is happening and it is predicted for the UK that in 5 to 10 years the impact will be registering in UK markets and home production and manufacturer.

4.1 United Kingdom

There are a number of producers of bioresins in the UK but they are characteristically small enterprises. The most prominent is Cambridge Biopolymers Ltd, Duxford[22]. They are developing cost effective, high performance materials using patent-protected technologies based upon sustainable and renewable resources, which deliver a positive environmental impact.

Cambridge Biopolymers Ltd have part of the company based in the United States which enables them to tap into the more developed markets and research in the USA on modified starch and soyabean oil bioresins. They can supply a range of adhesives derived from natural plant oils such as Cashew Nut Shell Liquid (CNSL) and vegetable oils (rapeseed, soybean, sunflower). Bioresins can be used as natural, sustainable alternatives to traditional petro-chemical materials such as phenol-formaldehyde and iso-cyanate resins in the manufacture of a wide range of composite products.

A project to develop a high performance eco-friendly adhesive resin derived from oilseed rape, the bioresin could be an alternative to the formaldehyde-based resins used in huge amounts in the building and furniture industries. The bioresin is as strong as high performance chemical resins but with several ecological advantages: it creates no toxic emissions; the raw material is sustainable and renewable; it is cost effective and the raw materials are widely grown; its products are recyclable and it is naturally water-resistant.

The Biocomposites Centre, Bangor are working with Cambridge Biopolymers Ltd on a what was DTI and industry funded project to commercialise novel thermosetting 'bioresins' derived from vegetable oils. It is hoped that these products will find use as replacements for formaldehyde-based resins, in applications such as wood-based panels and fibre reinforced composite applications.

Other reactive chemicals can be incorporated into the formulation to aid curing, such as tannins and resorcinols. These aromatic nucleophiles enhance the resin properties so that a rapid cure can be obtained in acid domains and, once polymerized, afford excellent bond strengths.

Water-resistant plant oils have been used as starting materials for a range of resin products currently under study at The Biocomposites Centre by Dr Paul Fowler and his team. Vegetable oils such as rapeseed (canola) soya, sunflower, and Cashew Nut Shell Liquid (CNSL) can be transformed to resin precursors that will polymerise when heated in the presence of acidic or basic catalysts. Typically, these resins can be used as formaldehyde-free alternatives to replace urea/phenol/ melamine formaldehydes in various applications.

[22] www.cambridge-biopolymers.com

Natural based waterborne adhesives such as starch and dextrin-based adhesives are widely used in the packaging industry due to their low cost, non-toxic nature and biodegradability. The concept designer JCID, of Colchester, is using bioresins - based on corn, soy, starch and cellulose originating from crops – to produce a plastic blow moulded container and film for cereal boxes.

The National Non-Food Crops Centre will continue to be an important focus for bioresin research networking and promoting technologies.

4.2 Europe

Foreco BV in the Netherlands used modified and activated linseed oils studied as part of the collaborative ECOTAN[23] project (*Increasing the durability, value and performance of European timbers by thermal treatments with reactive vegetable oils*) project to treat solid timber. The intention was to impregnate the wood to provide dimensional stability and durability and to polymerise the final outer oil using an activated linseed oil to provide a permanent moisture resistant protection to the timber. The polymerisation processes were developed at a laboratory scale, at pilot plant stage it was difficult to manage and needs considerable refinement as chemical engineering input. However, an experimental window treated with this oil system is on exposure at BRE and adding to the understanding of the long term stability of such a system.

4.3 International

The United States dominate the international research and application of bioresins and there is a considerable volume of information available. It would be impossible to generate an exhaustive account of all the research and development activity in the USA but a few key groups are mentioned in this section.

In 2004 Rohm and Haas Company received a $2million grant from the US Department of Energy and Department of Agriculture to develop novel bio-based adhesives and sealants derived from soybeans and other renewable materials.

Baxenden Chemicals Ltd have patented a technology for saturated polyester resins from oilseed rape using enzymes. Although this represents significant cost savings due to much lower processing temperatures, the final resin is still more expensive the traditional adhesives and is therefore currently only used in niche areas.

Although they have been around for a reasonably long time, interest in UV curable adhesives is growing as they often have favourable environmental profiles due to lower processing times, reduced emissions and their tendency to have better recycling qualities than other adhesives. UCB produce Ebecryl 860 as a UV

[23] http://cordis.europa.eu/data/PROJ_FP5/ACTIONeqDndSESSIONeq112482005919ndDOCeq1517ndTBLeqEN_PROJ.htm

curable coating which is based on an activated soybean oil working with the team at the University of Delaware[24].

Milliken & Co have been working towards eliminating the need for adhesives in their applications. They have developed a technology that allows carpet panels to be installed without the use of adhesives using a high friction bioresin coating (TractionBack) applied to carpet backings.

Cara plastics and the University of Delaware as mentioned in a previous section of this report have been working extensively on epoxidised soybean oils and their substitution for formaldehyde containing adhesives.

Cognis produce Tribest S531 an expoxyacrylate triglyceride oligimer which can be used in the formulation of adhesives.

The Worldwide Universities Network (WUN)[25] is an ambitious collaboration between Universities in the USA, the UK and the Netherlands (Illinois, Leeds, Manchester, Pennsylvania State, Southampton, Utrecht, Washington - Seattle, Wisconsin - Madison and York). WUN has acted as a catalyst to enable a multidisciplinary group of international researchers to come together under the theme of Green Chemistry. They express the overall Grand Challenge, as the need to prove the economic, environmental and social value of agricultural and forestry wastes for the manufacture of valuable chemical products at a local level. This is the biorefinery concept of green chemistry and has strong resonance with the provision of feedstock's for bioresins and adhesives.

The research presents a number of themes that will need collaborative funding including:

- Selective biotransformation of waste agricultural and forestry biomass to platform molecules
- Green chemical transformations of platform molecules to value added products
- Novel uses for biomaterials including starch, cellulose, silica and chitin (bioresins are a possibility here)

[24] Shrikant N. Khot , John J. Lascala et al (2001) Development and application of triglyceride-based polymers and composites Journal of Applied Polymer Science v82 (3)703-723.

[25] www.wun.ac.uk/greenchem/index.htm

5 Market potential

5.1 Costs

Where information was available it was scant and not suitable robust to reference. In general it appears that costs of bioresins as raw materials is more than their synthetic counterparts. This may be due to the scale of production of bioresins which is relatively small compared to synthetic adhesive resins.

As the environmental benefits are realised, the possible process efficiencies established and communicated and the long term technical performance built - a solid foundation for development and further application by building confidence in the market will occur. This combined with an increase in production will make the use of bioresins more cost competitive and increasingly an attractive solution for bonding wood based products.

5.2 Environmental factors

Recent legislative changes have placed greater emphasis on the environmental and health compatibility of products to which the general public are exposed. This is especially so with materials used in interior applications, and even more so where their used is in an enclosed area where there may be limited air flow or air exchange. Among compounds now recognised as causing problems in such uses are formaldehyde and volatile organic compounds (VOC's). There are two definitions of VOC, either in terms of reactivity (as often classified in the US), or in terms of volatility (as is more common in the EU and the UK). The presence of certain VOC's is believed to contribute to what is now commonly referred to as Sick Building Syndrome.

Traditional adhesive technology depended upon the use of formaldehyde to promote cross-linking polymerisation. The release of formaldehyde has been a major subject of research within the panel products industry in recent years. However it is important to note that any product incorporating wood will to some degree release formaldehyde, given its presence in nature.

Formaldehyde release will depend upon a range of factors (Table 2)

Factors external to the wood product	**Factors internal to the wood product**
Atmospheric moisture	Wood species
Temperature	Amount of waste material incorporated
Number of air exchanges	Type of resin used
	Manufacturing conditions
	Post treatments used on manufactured boards

Table 2 Factors affecting formaldehyde release in boards

One of the major issues facing the adhesives and panel products industries has been the reclassification of formaldehyde by the World Health Organisation, whereby formaldehyde was listed as carcinogenic to humans. This has led to the regulation of emissions from building products.

VOC is the collective term used for any volatile organic compound with a boiling point between 50^{o}C and 250^{o}C. An overview of VOC's was provided by Salthammer[26], whilst naturally occurring VOC's affecting panel product manufacture have been reported by Dix[27, 28]. There are two forms of emission that affect panel products – those during manufacture and those during service. It is the former that are the most significant, with considerable levels of release possible during the hot-pressing technologies used during the board manufacturing, either from formaldehyde or monomeric components within the adhesive mix. Thus components of urea, melamine, phenol, resorcinol or tannin may be released from traditional adhesive systems, whilst new adhesives will also experience a degree of loss of VOC's during hot pressing. Any hydrolysis reactions occurring during or after manufacture may also increase release of volatiles. The difference in hydrolytic release varies between different resin systems (for example aminoplastic and phenolplastic resins).

The resin industry currently is investigating several routes into improving the performance from formaldehyde based systems through:

- Better hydrolysis resistance of UF resins
- Reduction of the content of melamine in MUF resins
- Higher reactivity of the resins and hence shorter achievable press times
- Lower resin consumption necessary
- Reduction of formaldehyde emission

Whilst each topic is important, it is the reduction of formaldehyde that is seen by industry as the key driving factor.

Recently there has been in increase in the number of board classifications available, based on the level of emission from such boards. Table 3 provides an outline of these board classifications and the level of emissions permissible.

[26] Salthammer T (Ed.) (1999). Organic Indoor Air Pollutants – Occurrence, measurement, evaluation. Wiley-VCH, Weilhheim Germany.

[27] Dix B (2004). "Influence of VOC for strands made of pine heartwood and sapwood". WKI Short Report No. 6.

[28] Dix B (2004). "Influence of storage on the formation and emission of volatile organic compounds (VOC) from strands made of pine heartwood and sapwood". WKI Short Report No. 7.

Board quality	Standard	Test method	Upper limit of emission	Alternative upper limit (not listed in standard)
E2	EN 312 EN 622 EN 300	Perforator test EN120	30 mg/100 absolutely dry board	0.1 ppm in the Climate Chamber Test (EN 717-1)
E1	EN 312 EN 622 EN 300	Perforator test EN120	8 mg/100 (particleboard and OSB), 9 mg/100 (MDF)	0.1 ppm in the Climate Chamber Test (EN 717-1)
F**	JIS A 5905 JIS A 5908	Desiccator test JIS A 1460	≤ 1.5 mg/l	Perforator value (EN 120) 6.5 mg/100
F*** (E-Zero)	JIS A 5905 JIS A 5908	Desiccator test JIS A 1460	≤ 0.5 mg/l	Perforator value (EN 120) 2.5 mg/100
F**** (Super E-Zero)	JIS A 5905 JIS A 5908	Desiccator test JIS A 1460	≤ 0.3 mg/l	Perforator value (EN 120) 1.5 mg/100

Table 3 Overview on actual upper limits of formaldehyde release for different board qualities

The following methods have been employed to reduce formaldehyde emissions:

- Producing boards with low formaldehyde emission
- Using resins with low formaldehyde content
- Using additives in the resin
- Better molar ratio balances to reduce emission risks
- Improve processing parameters
- Age of the board in use and its influence on emissions in the short- and long-term
- Post treating manufactured boards

Further to the formaldehyde values indicated within Table 3, it is important to measure the levels of VOC's released from boards used for building products, and this must conform to levels outlined within pr EN 13419 and EN 717-1). At present limits vary between member countries across Europe. However, marketing strategies dictate that manufacturing is being centralised by many of the panel producers across Europe. Based on this, it makes sense to manufacture to the 'worst case scenario', in other words the most stringent limits. Applying such manufacturing practices will eventually standardise threshold limits at the lower levels across Europe.

There are a few cases of product labelling schemes in operation across Europe and North America, with Scandinavian countries having voluntarily introducing an Indoor Climate Labelling (ICL) scheme. Finland has a similar system, entitled “Classification of indoor climate, construction and finishing materials”, whilst Germany uses the ecological “blue-angel” label. This was created in 1977 by the Federal Environment Agency (UBA). Furthermore there are specific product quality assurance schemes, such as those for furniture.

The need for a comprehensive assessment scheme for VOC emissions for building products has led to a work programme being developed by the Committee for Health-related Evaluation of Building Products (AgBB). The AgBB test procedure[29] for building products in Germany represents a well-structured protocol that can be applied in other countries (Figure 6).

[29] AgBB (2004). “Ausschuss zur gegundheitlichen Bewertung von Bauprodukten” (Health-related evaluation procedure for volatile organic compound emissions (VOC and SVOC) from Building products”, downloadable document from www.uba.de.

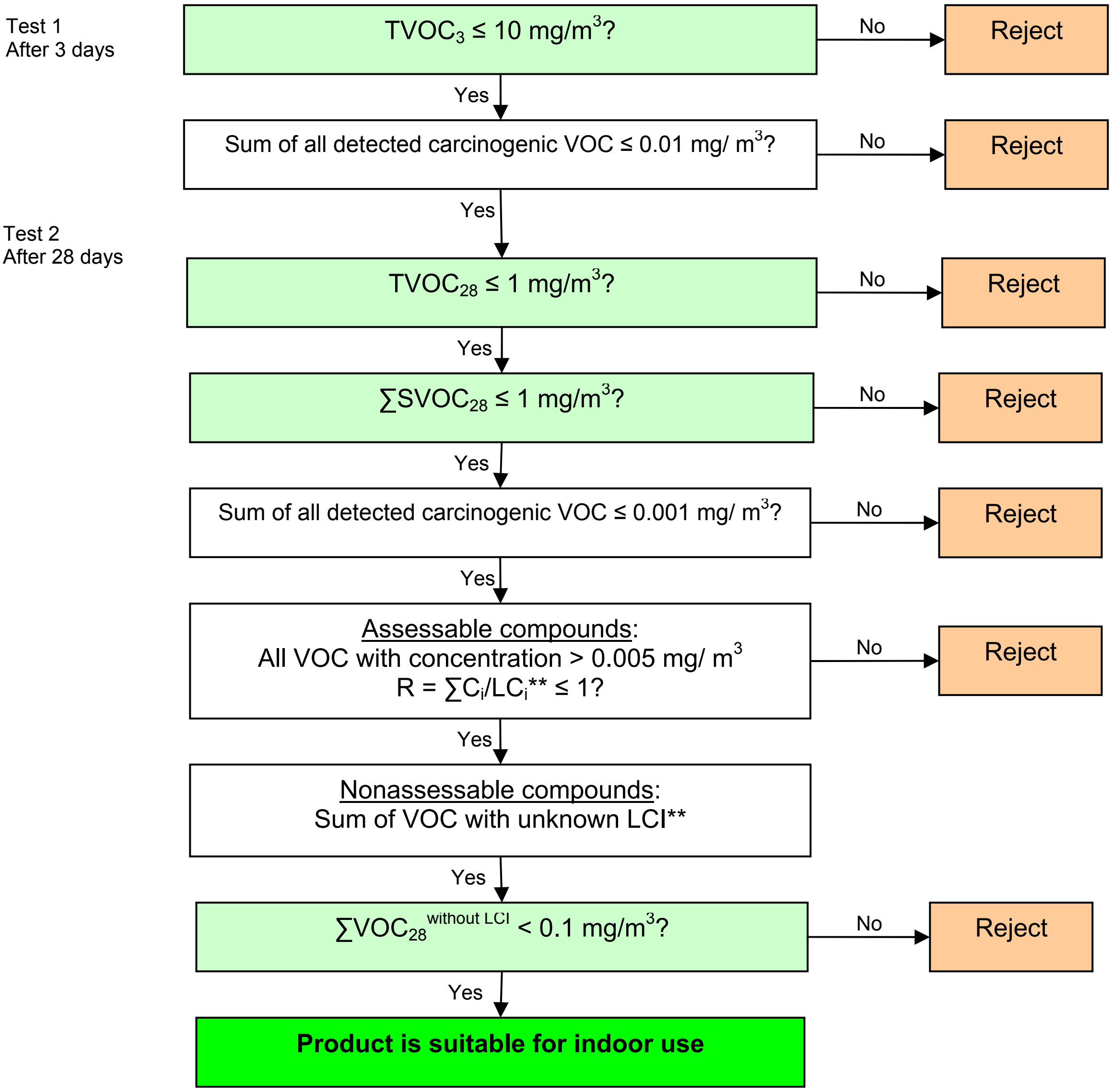

Figure 6 Schematic overview of German VOC testing procedure for building products

In the short to medium term future, the ramifications from the reclassification of formaldehyde as a carcinogen will continue, based on studies where it has been shown to be genotoxic in a variety of *in vitro* and *in vivo* systems (Blair et al[30]). Under conventional rules, genotoxic carcinogens usually have no assigned threshold levels. Due to the nature of the occurrence and reactivity of formaldehyde, the World Health Organization (WHO) have stated that "if the respiratory tract tissue is not repeatedly damaged, exposure to low, non-cytotoxic concentrations of formaldehyde can be assumed to be associated with a

[30] Blair A, Saracci R, Stewart PA, Hover RN, Hayes RB, Shy C. (1990). "Epidermiological evidence on the relationship between formaldehyde exposure and cancer". *Scandinavian J. of Work, Environment and Health*. **16**: 381-93

negligible cancer risk[31]. The recommended air quality guideline value of 0.1 mg/m3 as a 30-minute average is specified to be “over one order of magnitude lower than a presumed threshold for cytotoxic damage to the nasal mucosa”.

The trends in formaldehyde emission levels will tend towards other compounds such that there will be:

- a general reduction in allowable VOC emissions from building products
- an attempt to somehow ‘guarantee’ the right of everyone to breathe healthy indoor air
- an exclusion of odorous compounds from products used in indoor living areas.

These factors are complicated by the natural occurrence of formaldehyde. Whilst it should be noted that the use of wood to date in the construction industry has not been perceived as providing a health risk, it is the litigious nature of today’s society that drives manufacturing practices to restrict any perceivable risk. Wirth this in mind, the use of naturally derived resins would seem to offer the ideal opportunity for non-hazardous adhesive systems. This will be an area of considerable development over the next 10 years.

5.3 Renewability

Sources of raw materials for bio-derived or bioresins is highly diverse. An efficient and attractive proposal in terms of sustainability of the process and product would be to link the requirement for a bioresin to local sources of raw materials, oils or crop waste.

5.4 Whole Life Costs (WLC) and Life Cycle Assessment (LCA)

When developing and manufacturing new adhesives it is important to consider all stages in the lifecycle. Therefore it is essential that the composition of the adhesives, the product design, and the intended applications of the adhesives and recycling of the product at end-of-life must all be taken into consideration.

Construction products are increasingly being specified and differentiated in the UK market on the basis of environmental profile. This is an assessment of environmental impacts based on life cycle analysis (LCA) for a product from the raw materials, the transport, the processing, the distribution, installation, the service life in use (including maintenance) and at end of life the recycling, reuse or disposal. This whole chain can be assessed for a specific product (e.g. a specific wood composite using a CNSL derived bioresin) or by a trade body or consortium for a generic product (e.g. a composite of wood and resin). The profile is conducted by independent experts to generate an environmental profile declaration (EPD) for the product. This looks at everything going into (energy, water, and raw materials) the product and everything coming out (waste, water effluent, heat loss etc.) as well as the performance, service life and maintenance of the product. These aspects filter into Whole Life Costing (WLC) analysis that can be conducted to compare the cost effectiveness in cash terms of different solutions over the lifetime of the building.

The main push is in domestic housing market where ever tighter 'green' standards such as the Code for Sustainable Homes (in England) are driving step changes in the sector to improve the sustainability of

[31] WHO (1999). “Air quality guidelines for Europe”. WHO Regional publications, European Series, No. 91.

housing. The BRE Green Guide to Specification[32] is an easy-to-use publication, providing guidance for specifiers, designers and their clients on the relative environmental impacts of over 250 elemental specifications for roofs, walls, floors etc. The book compares and ranks building elements of the same functionality.

Environmental ratings of these specifications are based on Life Cycle Assessment using the Environmental Profiles methodology. This methodology was developed by BRE with funding from UK Government and support from a wide range of construction manufacturing trade associations. The Green Guide to Specification is currently being updated. In the 2008 forthcoming electronic edition of the Green Guide, individual company profiles will be shown alongside the generic profiles.

The expected sustainability impacts in a wide context of the uptake and development of bioresins in future in the UK and beyond can be grouped into the three pillars of sustainability.

Economic impact: bioresins would contribute to a competitive market sector and fosters innovation including new functionalities and new wood technologies. In addition new businesses and infrastructures are likely to be developed to deliver the new products and technologies. The objective here is to develop vibrant new businesses and grow traditional established businesses with new products.

Societal impact: bioresin development would contribute to jobs both by securing existing jobs in largely rural areas of the UK and Europe and create new jobs. There is also potential for societal impact through the improved health and safety of products both in manufacture and in long term use. Innovation within the new generation of wood products will improve the safety to the consumer by avoiding harmful products. Societal benefits on a large scale will also be won throughout the European Union if, as expected, the results lead to an increased share of wood and wood-based materials used in the construction sector. This will directly affect the sustainability of society by shifting towards a renewable resource which is neutral in the perspective of carbon dioxide release to the atmosphere.

Environmental impact: bioresins have significant impact here in minimising emissions from wood products. The new technologies and design solutions would offer no compromise at end of life so the products may be safely recycled and reused. In addition the technologies and principles of the work support the sustainable use of the renewable European forest resources by adding value. The European market is now facing increasing environmental regulations for construction products and bioresins appear to offer one solution for minimising environmental impact of glued wood products.

A project[33] funded by the Department for Environment, Food and Rural Affairs in 2005 investigated environmental assessment tools for biomaterials. The project team of North Energy Associates Ltd, Imperial College, and Springdale Crop Synergies Ltd had as its main objective the provision of companies engaged in the emerging biomaterials industry in the United Kingdom with ready access to the means and data to conduct comparative environmental assessments of their products in a format which gives confidence to their prospective customers about their claimed benefits.

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[32] Anderson J and Shiers D (2002) The Green Guide to Specification, 3rd edition. Oxford, Blackwell Publishing http://www.brebookshop.com/details.jsp?id=93716

[33] NF0614 under Programme CTD0402 "Supply Chain Assessment and Development for Industrial Materials from Crops", DEFRA.

The Work Programme consisted of the following tasks:

Task 1 Production of the Environmental Assessment Primer which describes the essential aspects of life cycle assessment, especially the preparation of life cycle inventories.

Task 2 Formulation of the Standard Reporting Format Spreadsheet

Task 3 Development of the Process Analysis Database focussing on primary energy requirements, water, greenhouse gas emissions and eutrophication

Task 4 Derivation of the Statistical Analysis Database

Task 5 Generation of Example Case Studies which illustrate the application of life cycle assessment. These are stated to include a bioresin derived from oilseed rape (compared with petrochemical resin) and a wood-plastic composite (compared with a petrochemical plastic alternative).

Task 6 Preparation of the Environmental Assessment Tool

The project was completed in March 2006 with outputs listed as an environmental assessment primer, a standard reporting format spreadsheet, a process analysis database, a statistical database and some example case studies. The conclusions of the work and the application of the environmental assessment standard format could not be found. Further investigation of the outcome of this study would be valuable if future profiling were to be considered a significant benefit for bioresin technologies.

6 Future developments

As with other industrial sectors, the adhesives industry is under pressure through rising costs of feedstocks and oil price instability combined with the increased costs of compliance with environmental and safety legislation. It is clear that the medium to long term future (5-20 years) that the substitution of less sustainable adhesives such as synthetic resins will occur with green chemistry adhesives derived from bioresin feedstocks. This report considered the drivers behind this which are considerable:

- Health, Safety and Environment concerns with the resins
- Health, Safety and Environment concerns with other adhesive components
- End of life concerns and recycling
- Increasing chemical legislation
- Standards and best practice

Interest in, and commercialisation of, products from renewable resources is not well advanced despite the above drivers and governmental and societal requirements for sustainable development. The current market penetration is <1% for polymers and no more than 2% for lubricants and solvents, with only surfactants of the major classes of chemical products having high renewable resource usage (20%). The total market potential over the next 10-20 years is been estimated at typically ten times these values.

Adhesives are found in many all construction products and especially those reengineered wood products and wood based panels. The development of environmentally improved bioresins based adhesives is an attractive option and the research need to deliver the technologies will continues to grow in the short term.

7 Conclusions

New adhesive systems in which all or part of the phenolic component is replaced by a renewable material without sacrificing high durability or ease of bonding is a need for the wood industry. The movement away from resins made with petrochemicals, particularly in North America is happening and it is predicted for the UK that in 5 to 10 years the impact will be registering in UK markets and home production and manufacturer.

The main conclusions from this initial review are:

- Synthetic resins are coming under increasing restrictions due to tightening environmental exposure regulations.
- Bioresins can now be used as natural, sustainable alternatives to traditional synthetic materials such as phenol-formaldehyde and isocyanate resins in the manufacture of composite products. Bioresins, which can biodegrade or be recycled are appearing in automotive components (car and truck parts), infrastructure (bridges and highway components) and the construction industry (formaldehyde- free wood based panels, engineered wood products).
- A wide range of test adhesives has been derived from natural oils (bioresin) such as Cashew Nut Shell Liquid (CNSL) and vegetable oils (rapeseed, soybean, sunflower). This diversity will be useful in matching feedstock resources to end use wood products as well as our ability to grow and produce bioresins in the UK. At present there is little evidence that the bond properties and permanence, water resistance, heat resistance, creep properties etc. are different based on the different bioresins and their original source oils.
- Blends and part substitutions of petroleum based resins with bioresins are an increasing way of introducing the technologies into the wood industry. This is likely the scenario for UK re-engineered wood products.
- Fully bio-based composites boards in which the fibre component is made from hemp, flax or timber and a bioresin are viable and an attractive concept. Considerable advances have been made over the past 5 years and more research is required to develop performance properties database. Confidence in the performance of the resins in the long-term is an issue that will grow with experience and as databases grow of properties
- High costs are a significant barrier to the development of bioresins, however, the production is becoming viable as technologies evolve, and economies of scale come on stream, along with price inflation of petroleum and increasing awareness relating to end of life disposal are likely to provide growing opportunity for bioresins.
- There is little evidence of bioresins and their application in UK re-engineered solid wood products.
- Advances in genetic engineering will be important for future bioresin feedstocks and the source plants.

- Biofuel technology and green chemistry routes (the biorefinery concept) from production of chemical feedstocks races away to meet demand for crop based fuels and other feedstock chemicals. This will present significant challenges for feedstocks proposed for use as bioresins for bonding wood and wood products. This will be influenced by land availability for production, worldwide prices of bio-oils (noting significant food price rises as more oil seeds are being considered for biofuel production) and competition for use in petroleum fuel substitution.
- Improvement in the performance of bioresin adhesives is a key focus for existing research. Bioresins and wood product technology requires an understanding of the balance between the improved health aspects and environmental profile and reduced performance properties (all bio adhesive) with poor health aspects and environmental profile and excellent performance properties (all synthetic adhesive). The aim is to match properties of the synthetic adhesive. This may not be possible in all circumstances which may lead to a need to engineer the wood product around the adhesive.

The work within this project will continue to appraise the status of bioresins worldwide and the drivers and barriers dictating commercial growth, their fitness for purpose and viability for use in re-engineered wood products.

The final phase of this study will:

- Consult with industry and other experts in the field in the UK
- Provide an updated version of this report (231-932 March 2008)
- Publish a BRE Information Paper on bioresins

The findings of this study will be developed into a series of recommendations and proposals, comprising a strategy for the further development of bioresins in re-engineered UK timber products.

Appendix A – Soy-based wood adhesives

Market Opportunity Summary

Soy-Based Wood Adhesives

January 2006

The Products

Soy-protein-based wood adhesives have been used for centuries. Since World War II, they have been largely replaced by petroleum-based adhesives with superior performance and economics. Current research is focused on developing and commercializing four soy products:

1) a soy/phenol-resorcinol-formaldehyde (PRF) system for finger-jointing green lumber,

2) an improved waterproof product to replace phenol-formaldehyde (PF),

3) a foaming glue for plywood and

4) an improved water-resistant product to replace urea-formaldehyde (UF).

Market Size and Value

Markets for these products include applications in panels, engineered wood products and new or emerging uses.

Long-Term Soybean Potential

Market Segment	Million Bushels
Panels:	
Particleboard	30
Medium-density fiberboard	12
Plywood	15
Oriented strand board	15
Other engineered lumber:	
Glue-laminated lumber	1
I-joists	1
Emerging markets:	
Framing lumber (green)	5
Pallets	1
Total Soy Bushels	**80**

The soy/PRF system for finger-jointing green lumber was introduced commercially in 1997 for framing lumber and qualified in 2000 for structural use. Other engineered wood products based on soy adhesive should grow out of this technology over the next two to three years. Oriented strand board (OSB) and face-gluing of pallets are considered medium-term opportunities (three to five years), and the others are considered long-term opportunities (more than five years).

Wood Panel Products

An estimated 230 North American mills produce approximately 40 billion square feet of combined particleboard, medium-density fiberboard (MDF), plywood and OSB annually.

Particleboard and MDF are composed of low-value wood byproducts, such as sawdust bound with UF resins. The replacement adhesive, a modified soy protein or a mixture of hydrolyzed soy protein and PF resins, is expected to result in a product with reduced formaldehyde emissions, improved water resistance and a longer life span. OSB is made of layered wood strands oriented at right angles to develop maximum strength and stability.

OSB competes with plywood and has seen significant growth due to its lower price and competitive performance in many uses. PF and, to a lesser extent, methyl diisocynate (MDI) are primary adhesives. Hydrolyzed soy proteins added to PF resins provide reduced costs, a faster cure rate and reduced emissions. Ongoing research sponsored by the United Soybean Board (USB) is investigating the substitution or partial substitution of hydrolyzed soy protein for PF resins.

Plywood is the largest of the panel products, but has seen market share decline since the introduction of OSB. PF is the principal adhesive used to bind thin wood veneers together or over products such as MDF. A soy-based extender for PF resins is being actively commercialized for use in plywood.

USB-sponsored research has resulted in the commercialization of soy protein to replace blood meal in making foamed glues for plywood production. Foamed glues expand adhesive volume to realize equal bond performance with a 20 percent to 30 percent reduction in adhesive use.

A soy-based formaldehyde-free resin has recently been developed for use in manufacturing hardwood plywood for interior use. USB-sponsored research is extending this new formaldehyde-free technology to provide an exterior grade resin for use in OSB and softwood plywood.

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Other Engineered Wood Segments

Two small segments offer limited potential, but rapid adoption, for soy wood adhesives. Both currently use either resorcinol-formaldehyde (RF) or PRF.

Glue-laminated lumber (glulam) consists of pieces of laminated lumber with a thickness of 2 inches or less. Combining hydrolyzed soy protein with the January 2004 currently used PRF will result in faster cure rates and improved economics.

I-joists are load-bearing structural members consisting of a top and bottom flange adhered to a vertical web made of OSB or plywood. Adhesives currently include melamines and resorcinals in finger-jointed flanges and resorcinals in web-butt joints. A hydrolyzed soy protein and PRF system will achieve faster cure rates and improved economics.

Emerging Markets

Additional market opportunities exist for soy-based wood adhesives in new or expanded markets. Two of these markets that show either short-term or medium-term potential are making dimensional lumber and pallets by finger-jointing green wood. Success in these markets should open additional ones in furniture, moldings and other related fields where external quality bonding is required.

PRF and polyvinyl acetate are currently used in finger-jointing short pieces of kiln-dried lumber to make usable studs at least 8 feet in length. These products are not suitable for joining green (high moisture content) lumber, and finger-jointing is not commonly practiced on green wood in North America. A two-part system of PRF and soy hydrolyzate has been shown to work effectively on green lumber before kiln-drying and will open a new market with competitive economics. The system offers three distinct advantages: increased value of shorts, increased productive lumber capacity through the kiln and decreased volatile organic compound (VOC) emissions. The primary source for VOCs comes from kiln-drying the knots in wood. Using the soy/PRF adhesive system to finger-joint allows sawmills to remove the knots prior to kiln drying, resulting in lower overall VOC emissions. The same soy technology can be used to face-glue deck boards to stringers to make pallets.

State of the Art

Most USB-sponsored research has concentrated on the use of hydrolyzed soy protein (soy hydrolyzate), which will be used either as a direct substitute or in a mixture with PF and UF. Soy hydrolyzate is made from soy isolate at a yield of 12 pounds of isolate per bushel.

In the short term, a two-part system of soy hydrolyzate and PRF will be commercialized in finger-jointing and other engineered wood uses. Ultimate formulations will depend on achieving both competitive performance and economics.

Relative Economics/Supplies

Phenol and urea wood adhesive pricing and availability are both subject to the vagaries of the petrochemical industry. Phenol demand is driven by bisphenol A and caprolactam (nylon 6 used in carpeting). Phenol capacity is expected to become very tight as demand in these areas grows.

Urea is derived from natural gas, with only about 5 percent of capacity going into adhesives.

Agricultural uses as fertilizer and feed additives utilize more than 90 percent of U.S. urea capacity. Urea prices fluctuate significantly with agricultural demand, and supply is tight seasonally.

Formaldehyde pricing is dependent on methanol supply and demand. Methanol prices were relatively stable for a number of years before spiking in 1994. The United States is a net methanol importer.

Soy adhesives, in contrast, are derived from a renewable domestic resource. Soybean prices fluctuate with world supplies of feed grains and oilseeds. The United States is the world's leading producer and exporter of soy, with annual production of about 3 billion bushels.

Advantages and the Path Forward

New soy adhesives promise both improved performance and economics to the wood products industry. They also should help to reduce emissions of VOCs and hazardous air pollutants.

USB is supporting research and testing to commercialize these products and ensure they meet industry standards. Working with industry partners, USB helps develop standard industry practices, an infrastructure to supply the products and acceptance of the resulting end products at all levels.

The United Soybean Board is made up of 64 farmer-directors who oversee the investments of the soybean checkoff on behalf of all U.S. soybean farmers. Checkoff funds are invested in the areas of animal utilization, human utilization, industrial utilization, industry relations, market access and supply. As stipulated in the Soybean Promotion, Research and Customer Information Act, USDA's Agricultural Marketing Service has oversight responsibilities for USB and the soybean checkoff.