BIO-BASED ADHESIVES FOR THE WOOD INDUSTRY – AN OPPORTUNITY FOR THE FUTURE?

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Abstract:
This paper reviews the use of some of the new technologies that may be implemented in bio-based adhesives, e.g. carbohydrate polymers, proteins, tannins, lignins, and vegetable oils.

In order to take a part of the market share, an adhesive should have low production costs, fulfil the environmental and health standards and give better properties than conventional synthetic adhesives. For large-volume wood products such as chipboard, it is essential to develop adhesives that enable the product to be cost competitive. Bio-based adhesives that are available and affordable for the wood industry suffer from three main problems: low moisture resistance, low reactivity and poor adhesive properties, and in several cases they are expensive compared to synthetic adhesives.

Keywords: *lignin; panels; protein; starch; sustainability; tannin; vegetable oils.*

INTRODUCTION

In order to work as a wood adhesive, a material has to be able to form bonds with the substrate surface. First the adhesive needs to form molecular-level contact with the surface, e.g. wet the surface, and after that it needs to be able to set by solidification or curing. The adhesive needs to be compatible with the bonding conditions used commercially and match the needs of the bonded assemble i.e. by having sufficient strength and tolerance towards water (Rowell 2012).

Adhesive bonding of wood has been the key factor for the efficient utilization of raw material in the wood industry over the past 150 years, and its significance will increase in the future with the development of new adhesive systems and wood products. The earliest evidence for the use of an adhesive in combination with wood comes from the Egyptian tomb findings and reliefs showing the production of intarsia 3500 years ago (Navi and Sandberg 2012). Until the 20th century, adhesives came from biological sources and poor moisture resistance was a significant weakness of these adhesives. As an example, the famous furniture maker Michael Thonét started his successful career using veneer and adhesive in his furniture production. As a consequence of the poor moisture resistance of the adhesives available in the 1830's, he developed the bending techniques for solid wood (without adhesive) that have been the basis of millions of pieces of furniture since then. In the 1940's, synthetic resins started to be dominant on the market because of their easier handling, adjustable viscosities and better moisture durability and finally a lower price (Müller *et al*. 2007). In recent years, formaldehyde emissions from wood products have been forcing many changes in the wood adhesive market (Frihart 2011).

The term "sustainability" in the context of adhesives refers to their environmental impact and cost. Today, adhesives are produced mostly from non-renewable resources. Both their production and their use result in a significant energy input and most are associated in some way with the emission of organic pollutants (Packham 2009). Sustainability in adhesive technology must consider the total environment impact, which means the full life-cycle. But current economic concepts mean that this technology will never become sustainable (Packman 2009). One way of approaching the sustainable concept might be to increase the use of natural binders in adhesive systems. The possible shortage of fossil raw materials and a higher environmental awareness, i.e. the need for adhesives with low formaldehyde emissions, seems to put bio-based binders into the focus of research (Krug and Tobisch 2010). The term bio-based adhesive is now used in a well-defined and narrow sense to only include those materials of natural, non-mineral origin which can be used after small modifications to replace synthetic adhesives (Pizzi 2006). The industrial use of such bio-based components is sometimes also a question of (regional) availability and of a specific quality (Fliedner *et al*. 2010).

OBJECTIVE

The purpose of this paper is to present an overview of the most common bio-based adhesives currently being used in the wood industry and their advantages and disadvantages compared to the most common synthetic adhesives. The potential for an increased use of adhesives from sustainable raw materials is also presented.

ADHESIVES

Currently, the adhesives most commonly used in the wood industry are synthetic condensation resins based on formaldehyde, reacted with various chemicals such as urea, melamine, phenol, resorcinol, or their combinations (Dunky 2003). The materials that fill the criteria of bio-based adhesives for wood with or without modification are carbohydrates, proteins, collagen, blood, tannins, lignins and unsaturated vegetable oils (Pizzi 2006). Wood can also be treated to provide adhesives using pyrolysis or liquefaction processes, but this is not discussed in detailed in this paper.

Carbohydrate polymers

Carbohydrates are plentiful and inexpensive, and they can, according to Pizzi (2006), be used as wood adhesives in three main ways:
- as modifiers for more expensive synthetic adhesives such as phenol formaldehyde and urea formaldehyde,
- as new adhesive building blocks, and
- directly as wood adhesives.

The major groups of carbohydrate polymers that are available in large volumes are cellulose, starch, sugars, and gums (Müller *et al*. 2007), but most research on the use of carbohydrates as adhesives is focused on cellulose and starch and their many modifications. Cellulose is the principal structural material in the cell wall of all plants. Starch is produced by plants as a way to store chemical energy, the most notable sources of starch being corn, wheat, rice, sage, and potatoes (Baumann and Conner 2003).

Characteristics

Cellulose is built up of blocks of β(1-4)-linked glucose molecules, and the hydrogen bonding between cellulose molecules gives it a strong crystalline structure that is not easily disturbed (Müller *et al.* 2007). Thus cellulose must be modified before it can be used as an adhesive (Baumann and Conner 2003).

Starch consists of amylose and amylopectin both of which are built up of α-D-glucose (Baumann and Conner 2003). The monomers in amylose have α (1-4) linkages that lead to a linear structure and amylopectin has a branched structure with both α(1-4) and α(1-6) linkages (Müller *at al.* 2007). The bonding capacity of starch is based on the large number of hydroxyl groups on each molecular chain (Nie *et al.* 2013).

The hydrogen bonds in both cellulose and starch are much weaker than chemical bonds, they are not strong enough to glue wood. The hydrogen groups also easily form hydrogen bonds with water molecules, which leads to a low water resistance. To solve these problems, modification of a chemical or physical nature is necessary (Nie *et al.* 2013).

Modification for adhesive

Cellulose can be activated by esterification or etherification. Esterification of cellulose is achieved using a mixture of sulphuric and nitric acids (Schönbein's method). Cellulose esters can also be prepared with organic substituents like acetate. Important cellulose esters are: cellulose propionate, cellulose butyrate, cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). If the hydrogen on the hydroxyl groups of the cellulose is replaced by an alkyl group, the result is etherification. Important cellulose ethers are: methyl -, ethyl -, carboxymethyl – (CMC), hydroxyethyl – (HEC), hydrozypropyl – (HPC) and benzylcellulose. HCE is actually used in the wood industry (Baumann and Conner 2003).

Starch adhesives tend to crystallize upon drying, and this means a loss of adhesion. To overcome this, starch can be modified by heating, alkali treatment, acid treatment, oxidation or enzyme treatment (Nwokocha 2011). The most typical modification to decrease the amount of hydroxyl groups and thus increase the water resistance of starch is to react it with a cross-linking agent such as sodium borate, isocyanate, or formaldehyde. These cross-linkers all have weaknesses that need to be solved. Sodium borate forms a hydrogen bonding complex with hydroxyl groups on the molecular chain instead of chemical bonds; isocyanate groups can react with water and much of it is wasted; and the use of formaldehyde is questionable due to health risks (Nie et al. 2013). Starch is modified by grafting synthetic polymers onto a starch backbone to create a copolymer with better adhesive properties, e.g. crafting starch with polyvinyl acetate can produce an adhesive suitable for the wood industry (Wang *et al.* 2012).

Use for wood industry

The disadvantages of both cellulose- and starch-based adhesives are their low water resistance and relatively slow curing rates that lead to long press times. Cellulosics also support the growth of microorganisms, but it is mainly because of their extremely low water resistance that cellulosics are currently not used as wood adhesives (Rowell *et al.* 2010, Rowell 2012). Starch and its derivates are mainly used in the paper and textile industries. By using formaldehyde-free starch/PVOH/crosslinker/latex mixtures it is possible to obtain an adhesive suitable for wood applications e.g. for use in plywood. However, of these four components only starch is sustainable (Haag *et al.* 2004, Baumann and Conner 2003).

Proteins

Both animal- and vegetable-based proteins with their wide variety of functional groups are well suited as a base for wood adhesives. The original wood adhesives were made of collagen extracted from animal bones and hides, casein (milk), blood, fish skins, and soybeans (Rowell 2012). Today, the focus is on proteins from *wheat gluten* and *soy flour* due to their low price, ready availability and easy handling. Wheat gluten is a by-product from wheat starch processing and bioethanol fuel production and soy flour a by-product of soy oil extraction (Wescott *et al.* 2006).

Adhesives based on proteins from marine fauna (MAPs), i.e. the mechanism by which mussels anchor themselves to the substrate, offer an interesting research area due to their strength and high water resistance. However, they are not readily available and also too expensive for most wood applications. Research has been carried out with success to mimic the properties of MAPs in other proteins, such as soy protein (Liu and Li 2004).

Characteristics

Unlike synthetic adhesives, protein-based adhesives have a secondary structure of a-helices and b-sheets, and a three-dimensional tertiary structure where a-helices and b-sheets fold into compact globules that interact with the surfaces of other globules forming a quaternary structure (Rowell *et al.* 2010). The physical and chemical properties of proteins are influenced by this complex structure as well as by the order and presence of amino acids. Amino acids are characterized by each having at least one carboxyl group (-

COOH) and an amino group (-NH$_2$) which makes them ampholytic, i.e. they can react as either acid or base, depending on their environment. This circumstance generally means that the pH-value is unimportant and makes it possible to combine the amino acid with a wide range of additives (Müller *et al.* 2007).

Modification for adhesive

To use a protein as an adhesive, denaturation is necessary to expose more polar groups for solubilisation and bonding via hydrogen bonds (Rowell 2012). Denaturation is a term for a modification, which changes the secondary, tertiary, or quaternary structure of the protein molecule without breaking covalent bonds. This process uncoils the protein and exposes the hydrophilic groups for modification reactions. Proteins can be denatured by exposure to heat, acid/alkali, organic solvents, detergents, or urea. Research on soy protein isolates has shown that both the detergent concentration and the pH-value have significant effects on the adhesive strength of modified soy protein isolate (Wang *et al.* 2005). It is possible to unfold protein complexes with urea, as its oxygen and hydrogen atoms interact with hydroxyl groups of the proteins and break down the hydrogen bonding in the protein body (Sun and Bian 1999). Too high a concentration of urea also breaks the secondary structure of the protein, and this can have a negative effect on the adhesive properties of the protein (Huang and Sun 2000). Proteins such as soy flours can also be treated with sodium dodecyl sulfonate (SDS), sodium docedyl benzene sulfonate (SDBS), and bio enzyme to break apart the quaternary protein structure while still retaining some secondary structure (Huang and Sun 2000). Similarly, enzymes are also used to achieve the desired binding and water resistance properties in wheat gluten (Nordqvist *et al.* 2012) and soy flour (Schmitz 2009).

Use for wood industry

Soy and wheat protein adhesives are sensitive to biological degradation, have high viscosities, low curing speeds, and low water resistance compared to conventional adhesives. Because of their to the low water resistance, they are currently used only for interior wood products (Rowell 2012). The simplest way to increase the water resistance of these adhesives is to cross-link them with synthetic resins such as phenol-formaldehyde (PF) or melamin-urea-formaldehyde (MUF). After denaturation, the protein is subjected to a stabilizer, such as formaldehyde, in order to prepare the protein for co-polymerization (Wescott *et al.* 2006). In these cases, the resin is not sustainable, but it makes it possible to lower the formaldehyde emission and the cost of resin by replacing phenol and formaldehyde (Wescott *et al.* 2006, Lin *et al.* 2012).

Tannins

Tannins are extracted from wood, leaves, and fruits and are more expensive, but some of them are also more reactive than phenols. There is a range of different tannins, depending on the source, which have different characteristics. Two of the best known condensed tannins are *epicatechin* and *catechin* from quebracho (e.g. *Mimosa tenuifolia*) and acacia (e.g. *Acacia mearnsii*) trees (Bedino 2012, Müller *et al.* 2007).

Characteristics

Tannins are polyphenols and can be divided into hydrolysable and condensed tannins. Hydrolysable tannins have partially esterified hydroxy groups (gallic and ellagic acid). The low reactivity of hydrolysable tannins towards formaldehyde and other electrophilic compounds limits their usage (Pizzi 2006). The condensed tannins consist of flavonoid units joint by C-C bonds which are highly resistant to hydrolysis (Müller *et al.* 2007). These multi-ring phenolics are more viscous and react in a manner similar to that of petroleum-based phenolics, and they are chemically and economically interesting for the preparation of adhesives.

Modification for adhesive

Tannins can be mixed with all types of synthetic binders without treatment. At pH values around 10, tannin and formaldehyde react to form high-molecular branched condensation products that are poorly hydrolysable. This binder component has a larger amount of pyrogallol-type B-rings that give low formaldehyde-emissions (Müller *et al.* 2007).

Use for wood industry

The problem with tannin-based adhesives is the limited availability of the raw material and their high price compared to synthetic resins (Dunky 2003, Rowell 2012). Condensed tannins can be used as the adhesive for the manufacture of particle board and medium density fibre boards of high quality and with low formaldehyde emission if cured properly (Valenzuela *et al.* 2012). The low emissions are the result of the high reactivity of condensed tannins with formaldehyde (Jahanshaei and Tabarsa 2012). The high reactivity also has a negative side since it can mean that the adhesive formulation has a short pot-life and a relatively high viscosity. Using dilute solutions to reduce the viscosity leads to additional steam in the hot pressing of the composite (Rowell 2012).

Tannin-based resins have shown a potential to replace UF-based resins in particle board applications due to their high moisture resistance and good mechanical properties (Bisanda *et al*. 2003). Valenzuela *et al*. (2012) have tested pine tannin without any correction of pH hardened with paraformaldehyde or hexamine in particle- and medium density fibre boards. The tannin adhesive was also mixed with isocyanates (pMDI 0-30%), and it was found that the dry internal bound strength decreased with decreasing amount of pMDI, but for boards with a thickness less than 12mm the strength fulfilled the norm EN312 even without hardener. Pressing times were between 13 and 16sec/mm (Valenzuela *et al*. 2012).

Lignins
Technical lignins are an inexpensive by-product from wood pulping. Lignin from the Kraft pulping process is today of limited use as an adhesive due to the inconsistency of the lignin product and the high cost of separating it from pulping chemicals. Lignosulfonates from sulphite pulping are on the other hand more useful for the production of reactive lignin (Rowell *et al*. 2012).

Characteristics
The chemical structure of lignin is complex and varying because the individual molecules are not fixed in any particular structure. Lignins are an amorphous and polyphenolic material that forms three-dimensional networks through co-polymerization of the phenylpropanoid monomers coniferyl, sinapyl and p-coumaryl alcohol (El Mansouri and Salvadó 2006). The low reactivity of lignin is due to the small number of reactive sites in the molecule (Dunky 2003).

Modification for adhesive
The cross-linked structure of lignins has to be partially degraded to achieve separation from the cellulose, and lignins need to be further polymerized to obtain useful adhesive properties. Their structural similarity to PF-resins make lignins interesting for mixing with these adhesives and also for auto-adhesion where lignin is activated by methods such as steam explosion, enzymatic activation, treatment with Fenton's reagent and irradiation with γ-radiation (Van Langenberg *et al*. 2010). For industrial uses, modification of the lignin adhesive or addition of synthetic resin necessary to increase the reactivity. Modifications include pyrolysis, in which pyrolytic lignins are created, or activation of the lignin by enzymes. Enzymes activate lignin either by polymerisation of lignosulphonate (oxidative enzymes) or by activation of the lignin present in the wood (Müller *et al*. 2007).

Use for wood industry
The main problem with lignin-based adhesives is their extremely low reactivity that leads to long press times and thus increases the production costs in for example board manufacture. The industrial success in using these materials has therefore been small, despite the fact that lignin has probably been the most intensely researched raw material for wood adhesive applications (Pizzi 2006).

If phenol-formaldehyde adhesive is mixed with up to 50% of lignin, an adhesive with better bending strength but lower thermo-stability and longer pressing times is obtained (Müller *et al*. 2007). Panels produced with lignin using glyoxal instead of formaldehyde as binder reached a strength required by international standards for exterior-grade panels (El Mansouri *et al*. 2006). Lignin from lignocellulosic ethanol residue (ER) differs from technical lignin in having a higher amount of hydroxyl groups that lead to higher reactivity (Zhang *et al*. 2013). Fibreboards of laccase-treated beech fibres (activation of the species' own lignin) showed the same strength properties as urea-formaldehyde-bonded boards, but wax treatment to increase the moisture resistance of the boards was not compatible with enzyme treatment (Felby *et al*. 2002). There are still economic and technological challenges to overcome before lignins are competitive as an adhesive. However, a true binder-less fibre-based product can be produced through enzymatic treatment with increased density (Widsten and Kandelbauer 2008).

Vegetable oils
Chashew nut shell liquid, castor, soy, and linseed oils are a few examples of vegetable oils that after modification are suitable for use as adhesives. The production of vegetable oils is steadily increasing throughout the world and various oils are now available at more acceptable prices (Kong *et al*. 2012). While the vegetable oils are biodegradable, the polymers for crosslinking are not biodegradable (Wallenberger and Weston 2004).

Characteristics
In general, vegetable oils occur as monodisperse low molecular weight substances, being a mixture of triglycerides with a small quantity of free fatty acids. Only castor and lesquerella oils naturally have hydroxyl groups (Wallenberger and Weston 2004). Most research is focused on oils that have at least some degree of unsaturation, which makes them suitable for a wide range of chemical transformations (Kong *et al*. 2012).

Modification for adhesive

Unsaturated vegetable oils can be modified in many ways. For example, the double bonds of an oil such as castor or linseed oil can be epoxidated and further cross-linked to produce high molecular weight polyols usable for adhesive purposes. The chemical modification of fatty acids which facilitates subsequent polymerization has a potential in the production of thermosetting resins (Kong *et al.* 2012).

Use for wood industry

Particle boards of coconut fibres were produced with caster-oil-polyurethane and compared to those produced with urea formaldehyde. Although the tensile strength was lower, the bending strength was higher in the caster-oil polyurethane boards (Fiorelli *et al.* 2012). Tannin in combination with N,N-bis(2-hydroxyethyl) fatty amides (HEFAs) from non-traditional oils (karanja and rice barn oils) was stronger than pure tannin (Patel *et al.* 2012).

Outlook

Adhesives from sustainable raw materials that are available and affordable for the wood industry suffer from three main problems: low moisture resistance, low reactivity and low adhesive properties, and in several cases they are expensive. Those with a sufficiently high water tolerance (e.g. tannins and MAPs) are expensive compared to synthetic resins. The low reactivity of the bio-based adhesives, with the exception of tannin with its high reactivity, caused problems in the industry by lengthening the press times. These problems must be the focus for further studies.

For lignin, the low reactivity is the main problem and, unless a totally new way of modifying or reacting lignin is invented, the market for lignin-based adhesives will remain low. For carbohydrates, the main problem is their poor adhesive properties. For example, starch has been modified in many ways to increase its moisture tolerance, reactivity, and adhesion (Nwokocha 2011). For proteins, the problem is to control the denaturation (Wang et al. 2005). If the availability of unsaturated vegetable oils increases, they offer an interesting base for wood adhesives. The tannin market will always be of limited volume because of the limited availability.

In order to take a part of the market share, an adhesive should have low production costs, fulfil the environmental and health standards and lead to better properties than the conventional synthetic resins. That is especially true in the board industry which is the single largest application of adhesives in the wood industry. Otherwise, products from sustainable materials will continue to be a niche market as customers connect wood with health and feeling good but not with ecological aspects, but are not in general willing to pay a higher price for such products (Knauf and Frühwald 2004). The development of sustainable adhesive systems has not proceeded sufficiently far and the only industrially viable options contain petrol-based chemicals, e.g. protein-PF glues by the company Dynea. However the research on sustainable adhesives is definitely expanding and, as further improvements arise, their industrial use will increase.

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