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SUSTAINABLE BIO-BASED ADHESIVES FOR ECO-FRIENDLY WOOD COMPOSITES. A REVIEW

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ABSTRACT

The aim of the present review is to summarize the current state of research in the field of sustainable bio-based adhesives used for production of eco-friendly wood composite materials. The article is focused mainly on the use of lignin, starch and tannins as raw materials and alternatives to the existing conventional adhesives. It is expected that increased amounts of bio-based adhesives will be used in the production of wood composites in order to meet the current needs for development of sustainable and innovative materials which will make the wood-based panel industry more sustainable and lower its dependence on fossil fuels. However, there are still substantial challenges for the complete replacement of petroleum-based wood adhesives with bio-based adhesives, mainly because of their relatively poor water resistance, low bonding strength and large natural variations due to different growing conditions. In this respect, fundamental research is still need in order to determine the factors for formulating bio-based adhesives with optimal properties and broaden their application in wood-based panel industry.

KEYWORDS: Bio-based adhesives; lignin, tannins, starch, wood-based composites.

INTRODUCTION

The bioeconomy strategy, launched by the European Commission, and the transition to a stronger, circular and low-carbon economy have posed new actions and requirements towards a greater and more sustainable use of natural resources by sustainably increasing the primary production and conversion of waste into value-added products, enhanced production and resource efficiency. The extended use of bio-based products, defined as "products, wholly or partly derived from materials of biological origin, excluding materials embedded in geological formations and/or fossilized" can make the economy more sustainable and lower its dependence on fossil fuels (European Biomass Industry Association 2019). As they are derived from renewable raw materials such as plants, bio-based products can help reduce CO_2 and have other advantages such as lower toxicity or innovative product characteristics. For this reason, the European Union has declared the bio-based products sector to be a priority area with high potential for future growth, reindustrialization, and addressing societal challenges (European Commission 2018).

The conventional adhesives for production of wood composites are made mainly from fossil-derived polymers, based on phenol, urea, melamine, formaldehyde, isocyanate, etc. (Youngquist 1999, Frihart 2012, Ferdosian et al. 2017). These fossil-derived adhesives are cost-effective and perform very well regarding bonding performance, mechanical properties, thermal stability and water resistance (Jin et al. 2010, Zhang et al. 2013, Jivkov et al. 2013a, Jivkov et al. 2013b, Yang et al. 2015). Most of the industrially used wood adhesives comprise formaldehyde which is a highly reactive compound, making it well suited for its intended use. However, formaldehyde has been identified as a hazardous and toxic compound and in 2004 was re-classified from "probable human carcinogen" to "known human carcinogen" by the International Agency for Research on Cancer (IARC 2004, EPA 2017). There is sufficient evidence that long-term formaldehyde exposure can cause cancer of the nasopharynx and leukaemia. Also, a positive association has been observed between exposure to formaldehyde and sinonasal cancer (IARC 2006). Thus, the concern about free formaldehyde emissions from wood composites, especially in indoor applications, along with the increased environmental consciousness related to the sustainability of raw materials and final products, as well as the new stricter environmental legislation, are the main driving factors for shifting the scientific and industrial interest from the traditional formaldehyde-based synthetic resins to the new bio-based adhesives for production of eco-friendly wood composites (Dunky 2004, Frihart 2005, Kües 2007, Pizzi 2006, Navarrete et al. 2013, Valyova et al. 2017). It should be noted that nowadays there are only a few bio-based adhesives for production of wood composites and they are not economically feasible to mainstream the production of wood composites. For these adhesives and for the ones still in development, a synthetic cross-linker is usually required to reach the required properties at reasonable cost (Hemmilä et al. 2017).

Different biomass resources such as lignin (Klasnja and Kopitovic 1992, Pizzi 2006, Kunaver et al. 2010, Li et al. 2018, Gadhave et al. 2019), starch (Wang et al. 2015, Li et al. 2015), tannins (Trosa and Pizzi 2001, Santos et al. 2017, Ndiwe et al. 2019), etc. have been used as renewable raw materials for production of bio-based adhesives. The aim of the present review is to summarize the current state of research in the field of natural, bio-based adhesives used for production of eco-friendly wood composite materials. The article is focused mainly on the use of lignin, starch and tannins as raw materials.

Wood-based composite production in Europe

Following the European economic recovery, European wood-based composite production increased by 2.8% in 2016, to 74.7 million m^3, despite lower production of wet process hardboard and stagnant particleboard production (European Panel Federation 2017, UNECE/FAO 2017). Particleboard comprised more than half of total wood-based composite production in Europe in 2016, fibreboard accounted for 30% and OSB for almost 9% of the total production. The particleboard production increased by 0.5% in 2016, to 37.8 million m^3, still far below the peak of 44.4 million m^3 in 2007. The production of fibreboard increased by 739 000 m^3 (+3.2%) in Europe in 2016, to 23.7 million m^3. The top five producing countries were, in descending order, Germany, Turkey, Poland, Spain and France, together accounting for about 75% of production in the subregion. MDF production in European Panel Federation member countries increased by 2% in 2016, to 12 million m^3. Turkey contributed a substantial 5.1 million m^3 to total production in the European subregion and had the largest growth in volume (292 000 m^3 + 6.1%). Despite four years of growth, Europe's MDF production is still significantly lower than the achieved peak of 21.6 million m^3 in 2007. OSB production increased in Europe by 9.6% in 2016, to 6.7 million m^3, as Romania and Germany are the two largest OSB producers in Europe. Poland became the third-largest following an expansion in 2015 (European Panel Federation 2017). European plywood production increased by 5.3% in 2016, to just less than 4.9 million m^3. Finland is the most important producer in the subregion, accounting for more than 23% of total production. The rest four top producers - Slovakia, Poland, Romania and Spain (in descending order, by volume) reported positive trends in production, with an average growth of 5.4% (European Panel Federation 2017).

Bio-based adhesives

Lignin

After cellulose, lignin is the second most important component of plant biomass with an estimated 300 billion total tons in the biosphere and an annually resynthesis of about 20 billion tons (Glasser and Kelly 1987). It is present in lignocellulosics including wood, grass, agricultural residues, and other plants (Fu et al. 2010). Worldwide, more than 50 million tons of lignin accumulate annually as by-product of pulp production (lignosulfonate from sulfite pulping processes and kraft lignin from sulfate pulping processes) (Kües et al. 2007). About 10% of the technical lignins are exploited industrially whilst the rest is combusted or not utilized at all (Kharazipour et al. 1991, Gargulak and Lebo 2000, Chakar and Ragauskas 2004, Gosselink et al. 2004). The possibilities for use of lignin in adhesive applications have been extensively studied by many authors (Hemmilä et al. 2017, Ferdosian et al. 2017, Ghaffar et al. 2014, Pizzi, 2010, 2016). The main interest in lignin is due to its phenolic structure with several favourable properties for formulation of wood adhesives such as high hydrophobicity and low polydispersity. However, the chemical structure of lignin lowers the reactivity of the resin, which is a disadvantage in applications where fast curing times are needed.

Lignin-based adhesives can be classified into two groups - lignin-based phenol-formaldehyde adhesives, where lignin is used as a partial replacement of phenol, and formaldehyde-free lignin-based adhesives. In different studies lignin is often combined with synthetic resins such as phenol-formaldehyde (Cetin et al. 2002, 2003, Ghaffar and Fan 2014, Olivares et al. 1995, Guo et al. 2015, Pizzi 2016) or urea-formaldehyde resins (Podschun et al. 2016) to decrease the cost (Shimatani et al. 1994) or free formaldehyde emissions (Yang et al. 2015). Certain interest in this field represent the laboratory studies for manufacturing MDF by adding lignin as a binder (Zouh et al. 2011, Nasir et al. 2014) which allow the production of ecological low-toxic panels. Another studies in the MDF field considered adding laccase enzyme-activated lignin to the fibres or activating the lignin in the fibres by enzyme treatment (Kharazipour et al. 1991, 1998) but this needed the addition of 1% isocyanate to the panel to press at acceptably short press times or significantly extending the pressing time (Felby et al. 1997). There are also a number of successful attempts to produce MDF in laboratory conditions on the basis of lignosulfonates (Yotov et al. 2017, Savov and Mihajlova 2017a, Savov and Mihajlova 2017b, Savov et al. 2019, Antov et al. 2019).

Akhtar et al. (2011) used lignosulfonate as a replacement of phenol in the synthesis of phenol-formaldehyde resin at a relatively high replacement level (up to 50 wt %). Phenol-formaldehyde resin composed of 50% lignosulfonate had better strength properties in comparison with the commercial adhesives with a great economic effect. The highest values of shear strength in both wet and dry conditions were achieved at twenty percent substitution of phenol by lignosulfonate.

Another study was focused on the application of Kraft lignin-based phenol-formaldehyde resin (50 wt % Kraft lignin) as an adhesive for production of oriented strand board panels (Donmez Cavdar et al. 2008). In hardboards, addition of 3 - 8% kraft lignin made a post-heat-treatment unnecessary for reduction of swelling, regardless of when lignin was added - prior or after fibre production (Westin et al. 2001). In another study, water stability (swelling in thickness and water absorption), internal bond strength, and mechanical properties were reported to be improved in panels made from fibres of softwood residues defibrated in presence of extra lignin (Anglès et al. 2001).

Application of enzymatic hydrolysis lignin in the production of phenol-formaldehyde resin has also been studied (Jin et al. 2010, Qiao et al. 2014).

The number of studies on the synthesis of formaldehyde-free lignin-based adhesives is relatively low. Geng and Li (2006) prepared a formaldehyde-free wood adhesive using Kraft lignin and polyethylenimine for production of plywood. Yuan et al. studied the physical and mechanical properties of a modified ammonium lignosulfonate/ polyethylenimine mixture as a green adhesive for MDF production (Yuan et al. 2014). El Mansouri et al. (2007) developed a novel process to substitute formaldehyde in wood adhesive for particleboard production. The prepared formulation met the requirement of the international standard EN 312 for exterior-grade panels and demonstrated comparable reactivity to formaldehyde-based adhesives. Navarrete et al. (2010) prepared a novel bio-based adhesive derived from a low molecular mass lignin and tannin without incorporating any synthetic resin. The obtained adhesive classified as an effective zero formaldehyde emission based on the desiccator method. A novel bio-adhesive for wood using kenaf core lignin and glyoxal was developed and tested (Hazwan et al. 2019).

Starch

Starch is a natural polymer and has attracted much attention in applications including food, papermaking, additives and adhesives, mainly because of its renewability, abundance, good adhesion and low price (Imam et al. 1999, Qiao et al. 2016, Norström et al. 2018, Zhao et al. 2018, Gu et al. 2019). Starch is the admixture of two distinct polysaccharide fractions: amylose and amylopectin; both are composed of glucose with different sizes and shapes (Tester et al. 2004). The proportion of amylose to amylopectin varies in accordance with the botanical origin of the starch and affects the properties of the wood adhesive (Norström et al. 2018).

Starch-based adhesives rely on hydrogen bonding forces, which are much weaker than chemical bonds. They also easily form hydrogen bonds with water molecules, leading to poor water resistance. Therefore, it is necessary to modify starch in order to increase its performance for adhesive applications. Higher bonding strength and better water resistance can be achieved by combining starch with another component, for example polyvinyl alcohol, formaldehyde, isocyanates, and tannins (Qiao et al. 2016). There are several studies about starch-based adhesives prepared by grafting vinyl acetate onto starch using ammonium persulfate as the initiator (Wang et al. 2011, Wang et al. 2012). It was demonstrated that the graft efficiency was important and had a large effect on the bonding performance of the starch adhesive (Wang et al. 2015). A typical chemical modification of starch by converting hydroxyl groups into esters in order to improve the hydrophobic properties of starch is esterification. Qiao et al. (2016) obtained esterified corn starch by reacting with maleic anhydride and then crosslinking with a polyisocyanate pre-polymer. The optimal amount of pre-polymer was determined to be 10 wt %, resulting in the dry and wet shear strengths of 12 and 4 MPa, respectively. Other researches (Tan et al. 2011) modified a starch-based adhesive by addition of blocked isocyanate and auxiliary agent. Gu et al. (2019) synthesized an environmentally friendly starch-based adhesive for wood-based panels by grafting polymerization of vinyl acetate monomer onto corn starch and crosslinking polymerization with N-methylol acrylamide. The water resistance of the obtained adhesive was significantly improved to more than 1 MPa. The authors found that the improved performance is due to increased crosslinking density and formation of complex network structure.

Another universal synthetic adhesive that can be used as a crosslinker of starch and other bio-based adhesives is epoxy resin. Epoxy resins have been tested mainly for veneer gluing, e.g. in combination with polyvinyl acetate grafted starch adhesives. Epoxy groups form three-dimensional networks that provide good shear strength in both dry and humid conditions (Nie et al. 2013).

Protein-starch composite (Anderson et al. 2011, Gadhave et al. 2017) and tannin-starch composite (Moubrik et al. 2010) can also be used for wood and wood composites adhesives which is eco-friendly system with zero formaldehyde emissions. Moubarik et al. (2009) reported a partial substitution of phenol-formaldehyde with corn starch-quebarcho tannin-based resin in the production of plywood. The optimal replacement value was determined to be 20% (15% cornstarch and 5% quebracho tannin). The addition of this resin improved the water resistant properties and reduced the formaldehyde emissions. The same authors developed a non-volatile and non-toxic cornstarch-tannin adhesive for interior plywood (Moubarik et al. 2010). The mechanical properties of the produced plywood were greater in comparison with the conventional phenol-formaldehyde resin. The addition of tannin made the starch-based wood adhesive less toxic and more environmentally-friendly; it also shortened the reaction time.

In some other studied urea-formaldehyde resin was reactively blended with various concentration of starch (Dimas et al. 2013), esterified starch (Liu 2013, Zhu 2014) and oxidized starch (Ni 2014, Sun et al. 2016) as wood and wood composite adhesive. It was found that new system with urea starch blending has lower brittleness and formaldehyde emission. Oxidized starch blended urea-formaldehyde resin adhesive has good chemical stability, insulating properties, temperature resistance, aging resistance, and oil resistance and can be applied to wood adhesion (Dunkey 1997, Bloembergen et al. 2005).

Another strategy to improve the performance of starch-based adhesives is to incorporate fillers or additives into the formulated adhesives. Wang et al. (Wang et al. 2011) demonstrated that the bonding strength, water resistance as well as thermal stability of the starch-based adhesive were improved significantly by silica nanoparticles. An addition of 10% silica led to the shear strength values of 5.12 MPa and 2.98 MPa in dry and wet condition, respectively.

Tannins

Tannins are natural polyphenols divided into two classes of chemical compounds of mainly phenolic nature: hydrolysable tannins and condensed tannins (Kües et al. 2007). Tannins occur naturally in bark, wood, leaves and fruits of different plant species but only a few plants have high enough concentration to make their extractions worthwhile. Tannins can be extracted from pine, oak, chestnut, wattle, eucalyptus, myrtle, maple, birch, willow, etc. Different extraction methods exist and they have a significant impact on the adhesive properties of tannin extracts. Extraction of the plant material and subsequent purification of the isolates, followed by spray drying, yield powdered tannins (Pizzi 2003). Other components of the extraction include sugars, pectins and other polymeric carbohydrates, amino acids, as well as other substances (Dunky 2003).

Hydrolysable tannins have been successfully used as partial substitutes (up to 50%) of phenol in the manufacture of phenol-formaldehyde resins (Kulvik 1976, 1977). However, the naturally low macromolecular structure, the low level of phenol substitution they allow, limited worldwide production, and relative high price makes them less interesting compared to the condensed tannins (Pizzi 2003, 2006). Condensed tannins with a yearly production of 200 000 tons make up more than 90% of the world´s commercial production (Pizzi 2003, 2006).

The application of tannins as adhesives for wood-based panels depends mainly on the content of reactive polyphenols and the reactivity of these components towards formaldehyde. Tannins can be used as adhesives alone (with a formaldehyde component as crosslinker) or in combination with aminoplastic or phenolic resins. MDF produced with tannins replacing parts of phenol in phenol-ureaformaldehyde resins or even with 100% tannin resin can meet interior grade requirements but usually not exterior grade specifications (Roffael et al. 2000, López-Suevos and Riedl 2003). Different tannin sources and time of tannin addition in the process chain of MDF production (e.g. before or after defibration of wood chips) have been shown to influence of the characteristics of resulting boards (Dix and Schneider 2006). Adhesive formulations for wood applications, prepared using different hardeners and tannin powder from Turkish red pine bark, have been developed and tested by Gonultas (2018) and Uçar et al. (2013). A thermosetting tannin-based wood adhesive system from formaldehyde reaction with both condensed and hydrolysable tannin has been studied by Özacar et al. 2006.

Some studies focused on developing resins totally free of formaldehyde by combining tannins with other bio-based material, e.g. protein (Li et al. 2004). Santos et al. 2017 have studied the possibility of completely removing formaldehyde from adhesive formulations by developing particleboard adhesive based on tannins, extracted from rom industrial lignocellulosic wastes, namely chestnut shell, chestnut bur and eucalyptus bark. Nath et al. (2018) have studied the properties and possibilities for production of particleboard with tannin-based adhesive from mangrove species. Cui et al. (2015) added cellulose nanofibers into tannin-based adhesives for particleboard production and reported significant increase of the mechanical properties of the produced panels.

Tannins have been used as adhesives for production of wood-based panels in South Africa, Australia, Zimbabwe, Chile, Argentina, Brazil, and New Zealand (Li and Maplesden 1998, Dunky and Pizzi 2002). The application in Europe is rather limited, only for special products with specific properties.

CONCLUSIONS

Bio-based adhesives provide an eco-friendly and sustainable alternative to the conventional adhesive systems used in wood-based panel industry. All natural adhesive raw materials, presented above, can significantly reduce the negative environmental impact of harmful formaldehyde and volatile organic compound emissions from wood-based panels. At the same time, bio-based adhesives can enhance the transition to circular economy by meeting the current needs for development of sustainable and innovative materials which will make the wood-based panel industry more sustainable and lower its dependence on fossil fuels.

However, there are still substantial challenges for the complete replacement of petroleum-based wood adhesives with bio-based adhesives, mainly because of their relatively poor water resistance, low bonding strength and large natural variations due to different growing conditions. There are successful solutions how to overcome these drawbacks, but most of them have been tested in laboratory conditions and not in large-scale industrial production. In this respect, fundamental research is still need in order to determine the factors for formulating bio-based adhesives with optimal properties and broaden their application in wood-based panel industry.

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