



Technological performance of formaldehyde-free adhesive alternatives for particleboard industry



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ABSTRACT

Due to their high reactivity, chemical versatility and economic competitiveness, formaldehyde-based polycondensation adhesives are used in huge amounts - in 2010 in the order of 20 million metric tons - around the globe, primarily in the wood-processing industry. Since the 1970s formaldehyde emissions from products made thereof came under pressure and were reduced continuously. The discussion intensified again initiated by the latest European CLP (classification, labelling and packaging) regulation, which came into force in 2016, classifying formaldehyde as a Carcinogen Category 1B compound. In view of potential and even stronger future restrictions of formaldehyde use, appropriate alternatives to substitute formaldehyde-based adhesive systems such as urea formaldehyde would have to be developed and implemented in the wood processing industry. The present review represents a critical appraisal of formaldehyde-free adhesive systems for particulate wood composites production proposed in literature so far. Adhesive systems analyzed here include both synthetic and renewable-based adhesives. The core of the review is an assessment of the individual adhesive systems based on selected technological (product and process) parameters relevant for wood-particleboard production. Based on this data we evaluated their potential to identify suitable alternative adhesives having a certain probability to meet the requirements of a large-scale processing industry sector. As an overall conclusion, there are still many challenges to overcome to replace formaldehyde. Except for pMDI-based systems, most of the alternative adhesives are considerably less reactive, which would result in dramatically higher production costs. Furthermore, the availability of most components proposed to produce alternative adhesives are currently not available in the necessary quantities. Moreover, toxicological investigations on alternative systems are still missing. As several components replacing formaldehyde are also toxic or hazardous to different extents, it cannot be guaranteed that the individual proposed alternative adhesives are safer during processing and service life compared to conventional systems. Due to the nature of the organic material wood, particleboards will always release a certain amount of formaldehyde, even when produced with formaldehyde-free adhesives.

1. Introduction

Adhesives have played and will continuously play an important role in the efficient utilization of wood resources and in the development and growth of the forest products industry [1,2]. Adhesive bonding of solid wood and wood particles of various sizes is the key factor for the production of modern, functional wood products, whether they are used for construction, furniture, or other applications [3,4].

For centuries, wood was bonded using bio-based adhesives until synthetic adhesives, mainly thermosetting ones, gradually took over in the 20th century, as they were typically regarded as more effective, better cost efficient [1] and more stable for the use in humid conditions. Today the main classes of thermosetting adhesives are amino-based, phenolic and isocyanate resins. The utilization of these thermosetting adhesives, are considered as more economical and reactive adhesives with quick curing behavior, and versatile in range of properties in cured

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state. These adhesives have been dominating the field of wood composites industry for many decades [5]. Within this group, urea-formaldehyde (UF) resins are the most important adhesives in terms of quantity [6]. Due to their low cost raw materials, their rapid curing, their high dry bond strength, and a colorless glue line, UF-based adhesives are almost exclusively used for producing wood-based materials, such as particleboard or medium density fiber (MDF) boards for interior applications [7]. When products are utilized in conditions exhibiting higher humidity, UF resins are usually modified with significantly more expensive compounds such as melamine, phenol or resorcinol [5].

The final adhesive composition in use depends on the requirements of the wood-based material such as the required strength properties, the expected moisture resistance, the desired formaldehyde emission class and the production cost of the finished product. For the dominating cases of PBs and MDF boards, both products require adhesives that possess relatively high dry strength, dimensional stability, moderate temperature and moisture resistance and, for processing considerations, fast curing and preferably water solubility for facilitating adjustment of viscosity.

Almost two thirds of amino resins produced in Europe (6.6×10^6 t/a in 2004 [6]) were consumed by particleboard production, about one third by the production of MDF, the remaining 5% is used by all other end applications [8]. More recently other panel types increased in relative importance, but European wood-based panel production is still dominated by particleboards amounting to more than 50% of the production volume, followed by fiber based panels (30%), oriented strand boards (OSB, 7%), and plywood (11%) [9]. Regarding the issue of the cost of the final panel the materials involved amount to 40–60% [10,11] of the total product costs (compare discussion on various adhesive scenarios (→ 7, Fig. 7). Therefore, the cost for the resin amounts to approx. 30%–50% of the material costs, whereby the products contain only 2–14% of resin in terms of quantity related to the wood dry mass. Thus, small changes in resin quantity or resin cost significantly affect the total product price [12]. The other principle material costs are the ones for the wood raw material (86–98% of the product mass), and with minor contribution additives and other chemicals. Expenses for energy (approx. 15–20%), manpower (approx. 5–20%), and the processing cost (depreciation, maintenance, etc.) of the panel (approx. 25% [10] to 30%) are the other main cost components. Due to the high investments needed for a typically continuous panel production the productivity of a plant is essential. In principal the processing speed which is composed by the time needed to heat up the panel during hot pressing and to sufficiently cure the adhesive for further processing is the main driving factor for the processing cost. Consequently, fast

curing amino resins are preferred by the particleboard industry. Because particleboard is primary used for indoor applications, it is of less importance that these resins are hydrolytically unstable, even though this could negatively influence formaldehyde emissions. Wood panels used in outdoor applications, like plywood and oriented strand boards (OSB), are produced with hydrolytically stable resins like PF (Plywood, OSB) and pMDI (OSB). In wood based panel industry, the required hot pressing time is typically indicated by a so called *press factor*, which is the time in seconds needed to cure 1 mm of panel thickness. Reported values on industrially achieved press factors depend obviously on the adhesive system and hot pressing temperature used and may be in the order of 3–7 s/mm panel thickness [13,14]. Typical hot pressing temperature in industry ranges from 180 to 240 °C, whereby this temperature mainly influences the heating up rate of the panel in the hot press. The temperature available for curing the core layer of a panel is typically limited by approx. 110–120 °C (e.g. for standard thickness of 19 mm). This temperature limitation is based on the presence of water vapor and gas pressure within the panel, and the corresponding short residence time in the hot press being the product of press factor times thickness [compare these to the discussion on temperature development within particleboards (→ 6.12, Fig. 6)].

When it comes to emissions from wood based composites, the discussion about formaldehyde started already in the mid-1960s as reviewed by Roffael et al. [15,16] or Salthammer et al. [17], and achieved various stages of reduced emissions in the 1970s and intensified in 1980 when the carcinogenicity of formaldehyde in rats and mice after long-term inhalation exposure was reported. Since the late 1980s building ecology-oriented institutes claim a continuous limitation of formaldehyde emissions for wood-based materials throughout Europe [18]. In 2004 a study of Hauptmann et al. [19] based on a cancer risk model reported that the standard mortality rate of workers exposed to high formaldehyde concentration would be increased. The topic of formaldehyde in indoor environment including the before mentioned study were intensively and controversially discussed by various authors as reviewed by Salthammer et al. [17]. Basically referring to the mentioned risk model of Hauptmann et al. [19] the International Agency for Research on Cancer (IARC) reclassified formaldehyde as carcinogen category 1 in 2004 [18]. Recently the discussion in the European Union peaked in the latest European Chemicals Agency (ECHA), Classification, Labelling and Packaging (CLP) regulation, which came into force in January 2016, classifying formaldehyde as a Carcinogen Category 1B compound. Driven by the standard requirements specified by the local authorities in e.g. Europe, Japan, USA, formaldehyde content and emissions from wood based composites have been continuously reduced over decades. In Table 1 a selection of former and current recommendations and standard requirements applicable for wood based composites are indicated. It is evident that the individual regulations of the different authorities are difficult to compare [20], as they are based on very different testing methodologies (i.e. chamber-, desiccator-, flask-, gas analysis-, or perforator method), they use different testing conditions (e.g. temperature, air exchange rate, humidity, time of measurement), and they may also refer to different parameters such as formaldehyde emission in contrast to formaldehyde content [21]. All standards are based upon the analysis of the composite and not the adhesive.

During the last decades industry made great effort and many innovations in amino resins technology to gradually reduce formaldehyde emissions in order to fulfill the individual product- and standard requirements for each type of composite. This has changed over time (Fig. 1): initially the formaldehyde content in an adhesive mixture was chosen to be sufficiently high to guarantee a rapid curing of the resin to a polymer network during hot pressing. This formaldehyde content is typically indicated by the molar ratio formaldehyde to urea (F/U, for an urea-formaldehyde adhesive example) which developed from 1.6 to 1.8 (indicating a significant formaldehyde excess) in the 1970s, to molar ratios in the range of 1.02–1.08 [5] for standard E1 adhesives to values

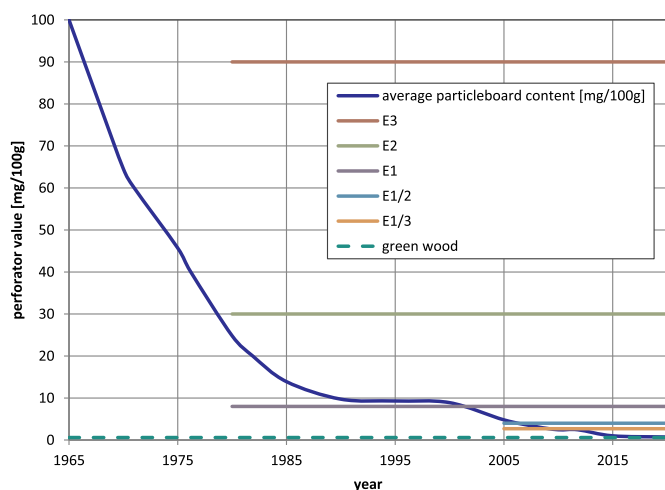


Fig. 1. Development of formaldehyde content of industrially produced particleboards in Europe, redrawn from Refs. [32–34].

as low as 0.94 for current industrially available UF or even 0.90 for industrially available melamine containing adhesives to fulfill even highest European EPF-S, Japanese F****, US CARB 2 standards or the internal IKEA company (IKEA IOS-MAT-0003) requirements. In general it is expected that a lower molar ratio of resins results in Ref. [29] lower formaldehyde emission during the hot-pressing process [30,31] and later on in service. Wolcott et al. [30] showed that the amount of the formaldehyde emissions additionally depend on the type of bonding of formaldehyde within the polymer network. Here formaldehyde bonded in form of methylol groups may be released more easily compared to formaldehyde incorporated in more stable methylene bridges.

Related to processing behavior and product properties the available amount of formaldehyde in the adhesive may directly influence a variety of process and product parameters. As discussed already before, the curing velocity of the adhesive is typically decreased for lower molar ratios, evident by an increased press factor. Consequently low-emission resins require longer hot-pressing times and the production throughput is reduced. As a consequence, product costs are typically increased, along with adhesive cost. The effect is discussed later for different adhesive scenarios ($\rightarrow$ 7) in more detail. Moreover, a reduced F/U molar ratio is expected to also result in higher crystallinity of the cured UF [29], lower mechanical properties (e.g. internal bond strength) when comparing similar adhesive quantity, a lower degree of crosslinking and therefore more pronounced thermoplastic behavior of the products (noticeable by a higher tendency to creep) as well as higher thickness swelling, higher water uptake, and adhesives are more prone to hydrolytic degradation as summarized by Dunky and Niemz [4].

Current adhesive systems fulfilling low formaldehyde emission standards (e.g. F****, Japanese JIS A 5905 or the JAS SE 9 standard) are called Ultra Low Emitting Formaldehyde (ULEF) resins, which are UF based resins with a low melamine content, to still reach a stable network despite of the low formaldehyde content. Additionally, scavenger technology is a developing field to reduce formaldehyde emissions during life time [e.g. 35–37]. Another option is the reduction of formaldehyde emissions by condensing proteinous renewable materials in phenol-formaldehyde resins [33,38,39], which are available on the market (Prefer Resins, Erkner, Germany). Here, the much more hydrolytically stable bonds of phenol to formaldehyde (compared to hydrolytically unstable ones of urea to formaldehyde) together with the addition of proteins to the thermosetting system leads to a reduction of the formaldehyde emissions of the wood-based panel to a level as low as the ones of untreated solid wood [33,40]. Although conventional phenolic resins are hydrolytically stable and emit therefore less formaldehyde, the resins have much slower curing than UF resins and are therefore less popular in particleboard industry. Formaldehyde emissions from bonded boards are released by different mechanisms [41].

Until now, we mainly discussed formaldehyde artificially added to wood-based composites originating in the usage of adhesives. Emissions can originate from 1) synthetic free formaldehyde that is not polymerized into the network, and which will emit during or quickly after panel production; 2) formaldehyde can be released due to adhesive hydrolysis, which will emit over the life time of the panel depending on moisture and temperature; 3) biogenic sources. Formaldehyde is also ubiquitous in living organisms (humans, animals) and it is naturally occurring in many plants and thus also in wood [42,43]. From the latter biogenic formaldehyde can be formed and emitted from the main wood components (cellulose, hemicellulose, and lignin) [44] as well as from its extractives [24]. Among the structural polymers present in plant tissues, lignin was identified to generate most formaldehyde [42,43]. Long-term measurements in European monitoring sites were carried out in several studies [26,45] and have shown that formaldehyde is released from solid wood (Table 1). Consequently wood-based products will never be free of formaldehyde or without formaldehyde emission, even when no additional formaldehyde is introduced by adhesives. Natural formaldehyde emissions caused by the untreated wood itself

may be in the range of 0.002–0.009 ppm (based on chamber tests) and may be increased by a factor of 10 when industrially dried at high temperature. Thus, the emissions caused by industrially processed wood itself are already close to the values required to fulfill e.g. Japanese F**** standard (Table 1). Especially for the case of particleboards another formaldehyde source is gaining importance. The amount of recovered wood used in such boards is continuously increasing. Himmel et al. [46] investigated the effect of use of recovered wood and measured formaldehyde emissions of 0.013 ppm using pMDI to bond native wood particles, but they reached also values of up to 0.1 ppm again for pMDI bonded particleboards, but this time by using 100% of recovered particles previously bonded with an E1 fulfilling adhesive. Some particleboard mills depend up to 100% on recovered wood due to the need for recycling or lack of native material, which is more and more used in competing process streams such as for generating thermal energy. With the need of using such recovered wood an additional, rather undefined formaldehyde containing and emitting source is added to wood based panels.

Despite substantial activities over the last decades to significantly reduce formaldehyde emissions from wood-based composites, potential and highly probable even stronger future restrictions, such as a hypothetical complete ban of added formaldehyde for indoor applications, may be a future scenario together with a trend to substitute conventional adhesives with bio-based ones as recently reviewed by Hemmälä et al. [21] or Ferdosian et al. [47]. As a consequence, appropriate alternatives to substitute conventional formaldehyde-based adhesive systems have to be developed to be implemented in the wood processing industry within a reasonable time span.

The aim of the present review is in giving an overview of currently proposed or available alternative adhesive systems with the constraint of being “formaldehyde-free”, a term further defined in the following section. The core of the present review is an assessment of individual adhesive systems based on selected technological (product and process related) parameters crucial for wood-particle processing. This database should allow getting an introduction to an overview of the substantial research activities which have been taking place during the last decades to develop formaldehyde-free adhesives. The juxtaposition of process and product parameters should furthermore help to evaluate their potential and identify suitable adhesives having a certain probability to meet the requirements of a large-scale processing industry sector. For understandable reasons it is not possible to summarize all relevant parameters for a thorough assessment in such a review, as not all relevant data is available in the studies included.

The adhesive systems analyzed here include both synthetic and renewable-based adhesives.

At the beginning, it seems to be necessary to define “formaldehyde-free” for the present study. Obviously, “formaldehyde-free” adhesives do not contain formaldehyde incorporated in the network. Here, “formaldehyde-free” adhesives are defined as being adhesives that furthermore do not comprise components that are made out of formaldehyde and are also capable to release formaldehyde. The definition is graphically depicted in Table 2. Adhesives containing and emitting formaldehyde, like aminoplastic resins, are not formaldehyde-free. Phenolic resins are, contrary to aminoplastic resins, hydrolytically stable and boards made using PF resins emit formaldehyde at considerably lower rates than boards produced with UF resins [48]. Nevertheless, the cured resole comprises dimethylene ether bridges that can hydrolyze and release formaldehyde [49]. Therefore, also resoles are not regarded to be formaldehyde-free adhesives. Furthermore, adhesives comprising formaldehyde-releasing and formaldehyde-made derivatives like paraformaldehyde, hexamethylenetetramine (“hexamine”), hexamethoxymethylmelamine (“HMMM”) and the like are not considered formaldehyde-free in this work, although several publications are available claiming that adhesives made of such components are formaldehyde-free. The field in the lower right corner of Table 2 lists components not made using formaldehyde and not capable to

release formaldehyde and are therefore formaldehyde-free without doubt. Furthermore, also adhesives containing chemicals produced out of formaldehyde but are, to current knowledge, completely unable to release it, like the group of polymeric methylenediphenyl diisocyanate (pMDI), are defined as “formaldehyde-free” adhesives. Even adhesives comprising chemicals that, in theory, can release formaldehyde during decomposition reactions, but are not produced out of formaldehyde or its derivatives, like various polysaccharides or wood compounds are claimed to be “formaldehyde-free” adhesives within the frame of this review. This seems to be misleading, but such adhesives can be classified as “no added formaldehyde” products [50].

In the following, adhesive groups which are already in commercial use or have been used in related scientific studies on wood based composites are mentioned. This includes studies on adhesives for wood based particleboards as well as studies using related methodologies typically used to access adhesives properties for before mentioned purposes such as studies testing adhesives with the help of thin wood veneers strips according to ASTM D7998-15 [51] (e.g. by using an automated bonding evaluation systems ABES [52]). Corresponding main components are briefly introduced in the following (→ 2, → 4) and resulting adhesive groups including their associated main properties are described and discussed (→ 6).

Adhesives or studies aiming for bonding solid wood only, as for glue laminated timber or the like, are not considered in the present study. Thus, there is no claim for the following list to completely represent adhesives for bonding wood of any shape and type, but for adhesives intended for the production of wood particle-based panel products typically produced in large scale continuous productions an extensive literature review was performed.

2. Crosslinking agents

“Crosslinking agents” are substances that cause, promote or regulate the formation of intermolecular, covalent or ionic bonds between polymer chains resulting in a three dimension network EN 923 [53]. The conversion of pre-polymers and/or polymers into polymers of higher molar mass and then into a network is called curing [54]. The adhesive turns from a liquid into a solid substance forming a stable glue line that connects wood. Similar to formaldehyde, some of the substances listed are also reactive monomers. During polymerization with other monomers, oligomers and/or polymers bearing reactive groups are formed. Residual monomers might remain as crosslinking agent in the resulting adhesive, or additional monomers might be post added as crosslinking agents.

In the following, most crosslinking agents mentioned in the present study are briefly introduced in order to provide a basis for the final discussion at the end of the present review. Also current production volumes are listed so the reader can estimate the implications of replacing the vast amounts of formaldehyde currently used. Many of these chemicals bear several trivial and trade names beside their preferred IUPAC name and variations of these names are also used in the cited publications. In our review, we use only the names in the following captions. Furthermore, also the CAS registry numbers are listed between square brackets to support the “non-chemist” readers by unambiguously assigning the mentioned chemicals. An overview of the chemical structure of crosslinking agents is compiled in Table 3.

2.1. Formaldehyde [50-00-0]

Formaldehyde is a very reactive molecule. It is a dipole with a lower electron density on the carbon atom so it readily reacts with atoms with a higher electron density. The resulting methylol group can form a crosslink to another molecule by the loss of water.

Monomeric formaldehyde is a colorless gas at room temperature but is obtained and normally applied as an aqueous solution called formalin. In solution, it is in fact present in the form of methylene glycol

[463-57-0] and its oligomers. In industry, concentrated formalin (> 50%) is used, whereas in laboratory more stable concentrations of 35–37% are used. The largest share of formaldehyde is used for the production of resins. Formaldehyde is produced by oxidation of methanol. The worldwide capacity for producing formalin is approx. 18×10^6 t/a (2011) based on 100% formaldehyde, whereby the global consumption was estimated to be 13.1×10^6 t/a (2011) based on 100% formaldehyde [55].

2.2. Alternative Aldehydes

One approach to produce formaldehyde free adhesives is to replace formaldehyde, the “simplest” and cheapest of all aldehydes, with alternative aldehydes, and ideally similar reaction mechanisms. Here, aldehydes which are inexpensive and available on a large scale are preferred.

2.2.1. Glyoxal [177-22-2]

Glyoxal (Ethanedial) is the simplest possible and commercial most important dialdehyde [56]. Anhydrous glyoxal is a liquid at ambient temperature, but polymerizes rapidly when traces of water are added. Thus, glyoxal is normally applied in an aqueous solution at a concentration between 30% and 50% [57]. In solution, glyoxal exists mainly as hydrated monomer (“1,1,2,2,ethantetraol”), dimers, and trimers [58]. Urea-glyoxal resins (also comprising formaldehyde) have been known for more than half a century, however not as a wood adhesive, but for the textile finishing market for use as wrinkle-recovery, wash-and-wear, and durable press agents [59]. A formaldehyde-free urea-glyoxal resin to produce particleboard was proposed later [60]. Furthermore, due to its bi-functionality, glyoxal is an efficient crosslinking agent and therefore an interesting candidate for the production of formaldehyde-free resins. Among the many processes to produce glyoxal, only those based on the oxidation of acetaldehyde or ethylene glycol are industrially relevant. The world production volume of glyoxal is about $120\text{--}170 \times 10^3$ t/a (2002) [57].

2.2.2. Dimethoxyethanal [51673-84-8]

As a “masked” glyoxal dimethoxyethanal is the monoacetal of glyoxal with methanol (glyoxal dimethyl acetal) [61] and can be commercially obtained as an aqueous solution. Reactions can occur with the free aldehyde group and with the second one after hydrolysis of the acetal.

2.2.3. Glyoxylic acid [298-12-4]

Glyoxylic acid is produced industrially by oxidation of glyoxal in aqueous solution [57]. It is sold as solution or as the solid monohydrate [563-96-2], which is hygroscopic and easily soluble in water. Glyoxylic acid bears an aldehyde group on one side of the molecule and a carboxyl group on the other side. When used as replacement for formaldehyde in a melamine resin, the aldehyde reacts with the melamine, but for full crosslinking, the acidic group needs to be esterified with a polyol [62].

2.2.4. Glutaraldehyde [111-30-8]

Glutaraldehyde (1,5 Pentandialdehyde) is produced by oxidizing cyclopentene or by a Diels-Alder reaction of acrolein with methyl vinyl ether, and is sold as a 25% or 50% aqueous solution [56]. In solution, it exists as a mixture of monomeric and oligomeric hydrated forms. Glutaraldehyde can react with several functional groups of proteins and is one of the most effective crosslinking agent for proteins [63]. It is used for leather tanning, as a disinfectant and sterilizer, and as a biocide in oil recovery. Glutaraldehyde can also crosslink cellulose [64] and is therefore also used in paper and textile industry to improve wet strength and dimensional stability of fibers. It is considered as the second most important dialdehyde after glyoxal [56].

2.2.5. Glycolaldehyde [141-46-8]

Glycolaldehyde can be obtained by the oxidation of ethylene glycol [65]. Furthermore, using a special catalyst, glycolaldehyde can be produced in high yields out of formaldehyde as a mixture containing also glyceraldehyde [367-47-5] and higher sugar derivatives [66].

2.2.6. Vanillin [121-33-5]

Vanillin is a phenolic mono-aldehyde which also contains one methylether group (4-hydroxy-3-methoxy benzaldehyde). Because of its good aroma, it is an important flavor and fragrance. The aldehyde is the main component of the extract of the vanilla bean, but can also be produced synthetically. About 20 t/a originate from natural sources, whereas 12×10^3 t/a are synthesized. Corresponding prices for both sources are indicated elsewhere [67].

2.3. Isocyanate

Isocyanates are highly reactive organic compounds containing isocyanate functional groups ($R-N=C=O$). Isocyanates are electrophiles, and as such they are reactive towards a variety of nucleophiles including alcohols, amines, and water. Molecules bearing two or more isocyanate groups can be excellent crosslinking agents.

The main application of isocyanates is in the production of polyurethanes, which represented a world market of almost 20×10^6 t/a (2004) [68]. Polyurethanes form upon the reaction of isocyanates with (a mixture of) polyols. Often, also water has been added to the polyol mixture. The reaction of the isocyanate group with water leads to the splitting off of CO_2 -gas and the formation of amines, which can again react with isocyanates. Because of the gas formation, polymerized foams in a variety of density and stiffness can be formed. In the case of one component isocyanate adhesives there is in fact a reaction with a “hidden” second component: water from the air or from wet surfaces as typically present in wood. Polyurethane foams are typically used as insulation materials, mattresses, cleaning sponges, shoe soles, or skateboard wheels. Furthermore, this polymer class is used as fibers, coating, and adhesives [69].

Isocyanates are industrially produced by reacting the corresponding amines with phosgene. The synthesis is carried out in two steps via the intermediacy of a carbamoyl chloride ($RNHC(O)Cl$) [70]. The production processes relevant for wood adhesives are very well described in literature [5,71].

2.3.1. 4,4'-Methylene diphenyl diisocyanate (MDI) [101-68-8]

Monomeric MDI is produced out of pMDI. It bears two isocyanate groups and is an important crosslinking agent. Pure MDI is a white solid with a melting point of only $40^\circ C$. The worldwide capacity for MDI amounted for approx. 3.4×10^6 t/a (2004) [72].

2.3.2. Polymeric methylene diphenyl diisocyanate (pMDI) [9016-87-9]

An isocyanate produced in large industrial scale is pMDI (polymeric methylene diphenyl diisocyanate). Other than the name suggests, pMDI is often not a real polymer, but a mixture of the homologues and isomers of MDI [73]. pMDI is produced by the condensation of aniline with formaldehyde and the subsequent phosgenation without purification. Monomeric MDI is obtained as high quality product by distillation of the result, whereas the residual mixture is sold as pMDI [70]. The composition of pMDI varies, the main component being 40–60% 4,4-MDI; the rest is composed of other isomers of MDI, triisocyanates, and higher molecular mass oligomers. Thus, numerous types of pMDI exist, which are available as yellowish-brownish liquids of different viscosity. As pMDI cannot be diluted with water, pMDI was reacted with polyglycols to form EMDI, an emulsion of pMDI in water [74]. Although formaldehyde is used to produce pMDI, the aldehyde cannot be set free afterwards anymore. Therefore, pMDI is considered as a formaldehyde free adhesive according to our definition.

The major consumption of pMDI is in the production of

polyurethanes. Furthermore, pMDI has been in use in the particleboard industry since 1973 [75] and is the most common isocyanate based adhesive in the wood panels industry [5,71].

2.3.3. 2,4-Toluenediisocyanate (TDI) [584-84-9]

Toluenediisocyanate is a crosslinking agent bearing 2 isocyanate groups. TDI is liquid and one of the most important industrial isocyanates. Generally the 2,4 isomer or mixtures of 2,4-TDI with 2,6-TDI are used. TDI is mainly used for foams and coatings [76]. TDI is, however, not common in wood adhesives. NMR investigations of one-component PUR wood adhesives, some commercial and some experimental, all from different industrial manufacturers, showed that TDI is either present in a very small proportion or is completely absent [77,78]. The worldwide TDI production capacity was estimated to be 1.9×10^6 t/a (2004) [72].

2.3.4. Emulsion polymer isocyanates (EPI)

“Emulsion polymer isocyanates” are two component adhesive systems. One component, called “hardener” is isocyanate, usually pMDI ($\rightarrow$ 2.3.2). The second component is an emulsion latex containing hydroxyl groups. This latex is based on styrene-butadiene rubber (SBR), and ethylene-vinyl acetate (EVA) [7]. As the components are emulsions, high molecular molecules can be used while keeping the viscosity low. Both components are mixed prior to use. The isocyanate reacts with the hydroxyl groups of the latex forming polyurethane groups. EPI is used for panel bonding, bonding of plastics to wood surfaces, and for bonding OSB web in I-joist production [71,79].

2.4. Sugar-based

“Sugars” is the chemical name for all nutritive mono- and disaccharides. They bear both primary and secondary alcohol groups, which theoretically could be used for crosslinking reactions. Furthermore, upon heating, many reactions can take place converting the sugars into numerous more or less reactive compounds. The controlled reaction of sugars into furan compounds is well known. Although the incorporation of such heterocycles into (not necessarily formaldehyde free) wood adhesive formulations has been investigated, the industrial application is still modest [80].

2.4.1. Glucose [50-99-7]

Glucose or “grape sugar” is an abundant hexose sugar as it is also the monomer of the biopolymers starch and cellulose. Glucose bears four secondary and one primary alcohol groups. In aqueous solution, it exists as a mixture of α - and β -chairs that mutarotate from the one form to the other through the open chain form which is an aldehyde. Glucose is used in numerous food and nonfood applications. Furthermore, it is fermented to produce products like lactic acid, citric acid, and bio-ethanol [81]. Glucose is produced via the enzymatic hydrolysis of starch and can become even more important when production methods starting with cellulose as feedstock become industrially available [82]. The production is estimated to be 30×10^6 t/a (2007/2008) [73].

2.4.2. Sucrose [57-55-6]

The common and legal name for sucrose is just “sugar”. It is the dimer of glucose and fructose (“fruit sugar”) and bears 3 primary and 5 secondary alcohols. The main application is in food sector. However, it can also be used as a polyol in the production of polyurethanes [83]. Sucrose is extracted and refined from sugar cane and sugar beet with a combined worldwide production of 155×10^6 t/a (2004) [84].

2.4.3. Furfural [98-01-1]

Furfural is a colorless liquid and is the aldehyde of furan. It is produced by acid-catalyzed digestion of hemicellulose-rich agricultural waste [85]. The oligomers are hydrolyzed by an acid catalyst to monosaccharide pentoses, which are dehydrated to furfural. Therefore,

furfural is a renewable compound. In 2005, a global production about 250×10^3 t/a was published [86].

2.4.4. Furfuryl alcohol [98-00-0]

Furfuryl alcohol is a colorless to yellowish liquid. It consists of a furan ring bearing a methylol group. Furfuryl alcohol can be polymerized by the addition of a strong acid. As such, furfuryl alcohol is important for its use as a foundry sand binder, where it crosslinks with itself and other monomers [87]. Of the world production of furfural, 60–70% is converted to furfuryl alcohol by catalytic hydrogenation.

2.4.5. 5-Hydroxymethylfurfural (HMF) [67-47-0]

Hexose sugars can be converted into 5-hydroxymethylfurfural. The furan ring bears both a methylol and an aldehyde group. HMF is very reactive, however therefore also unstable and hard to synthesize [88]. AVA Biochem (Switzerland) operates the world's first industrial plant for HMF and claims to be able to produce 300 t/a in aqueous solution at a concentration of 10–20% (wt/wt) at a purity of greater than 90% [89].

2.5. Epichlorohydrin [106-89-8]

Epichlorohydrin is both an epoxide as an organochlorine compound. It is produced starting from propylene via the route of allylchloride and hypochlorous acid or via the route of allyl acetate and chlorine [83]. It can also be produced out of renewable glycerol using hydrogen chloride [90]. Epichlorohydrin is extremely reactive and is used to produce reactive prepolymers like PAE resins ($\rightarrow$ 2.6.1) and epoxide resins ($\rightarrow$ 2.7). The epichlorohydrin market is estimated to grow to 1.9×10^6 t/a by 2017 [91].

2.6. Reactive polymers derived from the paper industry

Some papers can only fulfill their purpose when having sufficient wet strength. For this reason, the paper industry is using wet strength resins. Beside MF and UF resins, also formaldehyde-free resins are used for this purpose [92]. These wet strength resins are reactive polymers used as crosslinking agents for several formaldehyde-free adhesives.

2.6.1. Polyamidoamine-epichlorohydrin (PAE) [25212-19-5]

PAE resins are produced by reacting polyamidoamines with epichlorohydrin, cationic four-membered ring structures (hydroxy-azetidum) are formed, which are the functional groups involved in wet-strength development in paper [93]. Aqueous solutions of PAE resins are used for making tissue paper, paper towels, base paper for liquid packaging [94]. PAE resins have been developed and commercialized starting from the end of the 1950s and represent nowadays above 90% of the market of wet strength agents in neutral to alkaline pH paper furnishes [95].

2.6.2. Polyethylenimin (PEI) [9002-98-6]

Polyethylenimin is a linear or branched polymer of its monomer ethylenimine (aziridine) and consists of repeating amine groups and ethylene spacers. PEI was the first effective wet strength resin used under neutral to alkaline pH conditions [92], but is less effective and more expensive than formaldehyde based wet strength resins [96]. Polyethylenimin is often abbreviated as PEI but should not be confused with polyetherimide, which officially bears this abbreviation [97].

2.6.3. Polyvinylamine [26336-38-9]

Polyvinylamine is a thermoplastic polymer bearing amino side groups. These primary amine groups are water compatible and can act in many ways as crosslinking agent. Polyvinylamine is in use as relatively new wet strength resin as well as retention aid and fixing agent in the paper industry [92]. It has only been produced industrially since 2002 by the polymerization of N-vinylformamide to

polyvinylformamide with subsequent alkaline hydrolysis in a plant with a designed capacity of 4.5×10^3 t/a [98].

2.7. Epoxy resins

The very reactive epichlorohydrin reacts already during resin synthesis with monomers bearing an alcohol group to form pre-polymers with epoxide functional groups. Nowadays, almost 90% of the world production of epoxy resins is based on the reaction of bisphenol A (2,2-bis(4-hydroxyphenyl)propane) and epichlorohydrin, yielding diglycidyl ether of bisphenol A (DGEBA) [99]. Crosslinking agents, such as polyamines, are used to cure these resins [100]. These epoxies are used in repair and low-bonding pressure applications [101]. Because of the high price and limited durability in wood bonding, epoxy resins do not play a significant role in the production of wood products [71], although they are used for some applications involving solid wood such as in repair of construction timber [102]. To our knowledge, epoxide resins have never been used to produce particleboards.

2.8. Polyacids

Polyacids are molecules bearing more than one acid group. By esterification reactions, they could crosslink chains bearing alcohol groups. Furthermore, because of their acidity, they can also catalyze numerous reactions.

2.8.1. Citric acid [77–92]

Citric acid is an organic polycarboxylic acid containing three carboxyl groups and one alcohol group. The water-soluble crystalline white solid naturally occurs in citrus fruits. Its main application, with about 70% of the total volume, is in the food and beverages industry. Nowadays, all industrially produced citric acid is obtained by several fermentation processes in a global yield of 1.6×10^6 t/a (2012) [103].

2.8.2. Maleic anhydride [108-31-6]

Maleic anhydride is a white crystalline solid. Although it is not a polyacid itself, it rapidly converts into maleic acid [110-16-7] when dissolved in water. Both carboxyl groups of maleic acid as well as its double bond are very reactive [104]. The main usage of maleic anhydride (40–60%) is in the manufacture of unsaturated polyester resins [72]. Maleic anhydride is produced by catalytic oxidation of suitable hydrocarbons, mainly benzene [72,104]. The world production of maleic anhydride is about 1.3×10^5 t/a (2004) [72].

3. Toxicological information

The ability of reactive molecules to interact with biological systems, implies a “hazard” in toxicology according to definitions [105], whereas the potential to come into contact with biological systems is defined “exposure”. Although the purpose of this review is to make a technological evaluation, we feel that also a short evaluation of the toxicological effects of crosslinking agents involved in adhesive alternatives is needed, as the main driver for replacing formaldehyde is its suspected carcinogenicity. Hereby we limit ourselves to “hazards” and quote information according to the international commission Regulation (EC) No 1272/2008 of 16 December 2008 “Global Harmonized System of classification and labelling of chemicals” (GHS) out of the most recent safety data sheets. Table 3 lists the crosslinking agents, the GHS hazard pictograms for “toxic” (GHS06) and “health hazard” (GHS08), as well as the GHS hazard statements H 350 “may cause cancer” and H 351 “suspected of cancer causing”. Please note that this information is only on free compounds, and not on any substance that is formed out of their reactions. Furthermore, the risk of exposure is not evaluated here as it would need numerous experiments to determine free crosslinking agents in adhesive and boards, as well as the corresponding emissions. Table 3 shows that several alternatives for

formaldehyde are also toxic and even (suspected) carcinogenic, however it might be that there is less exposure from particleboards in use as a result of these chemicals. In addition, possible emissions different to formaldehyde might occur using alternative adhesives. As most of the alternatives described here have not been evaluated for their potential health risk, it could happen that a proposed alternative becomes even more hazardous than current technology.

4. Components

Beside crosslinking agents, adhesives often have additional components. The component that is primarily responsible for adhesion and cohesion is defined as “binder” EN 923 [53]. Furthermore, monomers that are used to produce binders but have no additional function as crosslinking agents, are listed here. However, some of these components might act as crosslinking agent to some extent in other applications. Currently, the largest groups of these components are of synthetic character and based on fossil resources, but there is a desire to increase the share of renewable materials, as can be seen at the increasing amount of scientific studies in this field.

4.1. Monomers for amino-based adhesives

Currently, amino resins are by far the largest group of adhesives used to produce particleboards. The reactive pre-polymers are produced out of the crosslinking agent formaldehyde and synthetic monomers as compiled in the following.

4.1.1. Urea [57-13-6]

Urea is a white solid consisting of two amino ($-\text{NH}_2$) groups joined by a carbonyl group. Apart of its industrial use urea is also an important biological product; the human body produces 20–30g of urea per day [106]. In industry, urea is produced out of CO_2 and ammonia (which are again produced according to the Haber-Bosch process out of air, water, and natural gas). More than 90% of the synthetically made urea is used as fertilizer. From the residual 10%, the largest applications are the production of UF resins and melamine. The worldwide production of urea exceeds 150×10^6 t/a (2010) [106].

4.1.2. Melamine [108-78-1]

Melamine is a white solid. The aromatic ring of three carbon and three nitrogen atoms carries three amino groups. One molecule of melamine is produced out of six molecules of urea (producing six molecules of ammonia and three molecules of CO_2 as side products). Nearly all melamine is used for producing resins. The global consumption of melamine is 1.3×10^6 t/a (2014), 75–80% thereof by the wood working industry [107].

4.1.3. Ethyleneurea [120-93-4]

Ethyleneurea (2-Imidazolidinone) is a cyclic, substituted urea. The white solid can be produced by reacting urea with ethylene diamine [108]. With formaldehyde ethyleneurea reacts to dimethylol ethyleneurea (DMEU), which is applied in the production of cellulose-based “wrinkle-free” textiles. Because of their high price and their limited ability to form condensates, substituted urea is not used in large amounts for any other purposes [8].

4.2. Phenolic plant compounds

Plants are rich in a wide range of phenolic compounds that are of interest as possible replacements for petrochemical-based phenolics [109].

4.2.1. Lignin [9005-53-2]

Lignin - present in all vascular terrestrial plants - is a complex, three-dimensional, amorphous polymer which holds plant fibers together.

Lignin is the second major compound in wood following cellulose and represents 30% of all non-fossil organic carbon on Earth. It is considered to be the largest aromatic renewable resource [110]. The main monomer units of constituting lignin molecules are 2-methoxy-4-propylphenyl (guaiacyl) in soft wood and a mixture of guaiacyl and 1,5-dimethoxy-4-propylphenyl (syringyl) in hardwood [111], and a mixture of guaiacyl, syringyl, and p-hydroxyphenyl in grass plants [112,113]. These monomers are connected by a multitude of different types of bonds. The lignin availability in nature exceeds 300×10^9 tons, increasing annually by around 20×10^9 t/a [114].

The isolation of lignin from plants, mainly wood, leads to “technical lignins”. The overall composition varies considerably as a function of plant type and of the isolation process, which always involves a depolymerization mechanism [115]. This heterogeneity as well as the unclearly defined chemical structure of lignin limit its utilization [110]. Technical lignins are produced in large quantities as a by-product from chemical wood pulping with $50\text{--}75 \times 10^6$ t/a worldwide [13,110,111,116,117]. However, it is estimated that more than 95% of these lignins are burned to generate energy for the process as well as to recover inorganic pulping chemicals [118].

4.2.1.1. Kraft lignin [8068-05-1]. The dominating technology in pulping is the kraft process with about 89% of the total production capacity [119]. Under caustic conditions using sodium hydroxide, wood is treated at high temperature with sodium sulfide (Na_2S) and lignin bonds are broken [110]. In the last stage new carbon-carbon bonds are formed between lignin units, which leads to new oligomeric structures [119]. Kraft lignin is soluble in caustic or in organic solvents. As kraft lignin is not very water soluble, it is possible to purify it by fractionating out water soluble components, resulting in a low ash content of below 3% [120]. The number-average molecular weight is generally between 1000 and 3000 g/mol. The residual sulfur content is low, typically less than 2%, and the structures bear a high level of phenolic hydroxyl groups [110]. With modern technology, 20–25% of kraft-lignin can be separated from black liquor without compromising the recovery boiler operation [121]. Therefore, there is an increased interest of mills in providing kraft lignin on industrial scale to the market [122]. Worldwide, six industrial producers are evident with an estimated kraft lignin capacity of 160×10^3 t/a (2015), while producing only 75×10^3 t/a [123]. However, most of the lignin is not recovered and used for its fuel value. For many industrial applications as dispersants and emulsifiers, kraft lignin is first sulfonated.

4.2.1.2. Lignosulfonate. The share of the sulfite process in pulping was 3.7% in 2000 [119]. Under acidic conditions and at ca. 125–150 °C, wood is reacted with sulfite. Lignosulfonates contain up to 8% of sulfur [120], most of it as sulfonate groups on the aliphatic side chains. They are water soluble, the number average molecular weight is 15.000–50.000 g/mol, and the structures bear only few phenolic hydroxyl groups [110]. Lignosulfonates are the salts of lignin sulfonic acid [8062-15-5] and bear the additional following CAS-numbers: calcium salt: [8061-52-7], sodium salt: [8061-51-6], ammonium salt: [8061-53-8]. The ash content can be up to 25% [124]. Lignosulfonates have a wide variety of applications, from which the largest one is the usage as concrete water. Combined, the largest producers produce 1.1×10^6 t/a by having a capacity over 1.4×10^6 t/a (2015) of various lignosulfonates [123].

4.2.2. Tannin

Tannins are polyphenolic plant compounds which can be classified into two major categories: condensed (or polyflavonoid) tannins and hydrolysable tannins. The condensed tannins are oligomeric, whereas the hydrolysable tannins are non-polymeric [125]. Condensed tannins consist of many polymeric flavonoids and oligomers, but all based on combinations of gallic acid or its derivate and simple sugars such as

glucose or rhamnose. These tannins comprise a group of polyhydroxy-flavan-3-ol oligomers and polymers linked by carbon-carbon bonds between flavanol subunits [126].

Historically, the main application of tannins has been the hide tanning for manufacturing leather. Nowadays, the field of adhesives, in particular for wood, is another major application and consumes estimated 140×10^3 t/a of tannins (2015) [127]. Beside its ability to be used as binder, tannin resin is characterized by its fungi-resistance as well as its good moisture resistance [128]. These adhesives are, however, not formaldehyde free. Condensed tannins show high reactivity towards formaldehyde [125], whereas hydrolysable tannins have a poor reaction to formaldehyde and other crosslinking agents, and have therefore limited potential for the production of adhesives [7].

The high viscosity of tannin extract solutions has also been correlated to the proportion of very high molecular weight tannins present in the extract [125]. The modification of tannin extracts has primarily the function of lowering their viscosity and results in an improved processability, a longer pot life and improved network formation [4]. The modification can be carried out in various ways, for example by sodium hydroxide [129], which causes degradation of polymeric carbohydrates, urea, which breaks down hydrogen bonds [130], or by sulfitation [4].

The main commercial species of condensed tannins are obtained from the bark of mimosa and quebracho wood [125] and further comprise (radiata) pine bark, pecan nut, and Douglas fir bark. The world production of commercial tannins is estimated to be 1.1×10^6 t/a (2015) [127].

4.2.3. Cashew nut shell liquid [8007-24-7]

Cashew nut shell liquid (CNSL) is a reddish brown dark natural resin present in the cashew nut shell. It is a mixture of phenolic molecules bearing one C15 hydrocarbon side-chain in the meta-position to the hydroxyl group(s). The chains differ in degree of unsaturation varying from none to three double bonds. Anacardic acid, that also bears a carboxylic group in the ortho position, is the major component of natural CNSL. Other components comprise cardanol (phenol with side chain) and cardol (resorcinol with side chain). As anacardic acid decarboxylates and converts into cardanol upon hot extraction, cardanol at 60–70% [37330-39-5] is the dominant component of technical CNSL. An important application of CNSL is as partial phenol replacement in formaldehyde-based resins for various applications. In 2013, 4.4×10^6 t/a of cashew nuts (including shells) were harvested worldwide. As the nut with shell contains approx. 25% of CNSL, it is estimated that 1×10^6 t/a of CNSL were produced [131].

4.3. Proteins

Proteins are large biomolecules consisting of one or more polypeptides, chains of amino acid monomers linked by peptide (amide) bonds. Each protein chain has a complex 3-dimensional multiple folded structures that usually aggregate with other protein chains. They represent a large, versatile group of substances. Different proteins have different sizes, different structures and different amino acid compositions [132]. They are essential parts of living organisms, for example by providing structural or mechanical functions (e.g. muscles), catalyzing bio reactions (enzymes), or cellular adhesion [133]. Proteins comprise an essential feedstock for humans. Proteins have also been used as adhesives for centuries but were replaced by petroleum-based polymers due to cost and durability [134] reasons. The suitability for the application as additives can be enhanced. Pretreatments can denature the protein structure, such as physical methods with high pressure [135], chemical methods with acids [136], bases [137], urea [138], sodium dodecyl sulfate (SDS) [139], and by enzymatic methods [140], resulting in a greater number of active sites [141]. As example, these sites comprise –SH (cysteine), primary (serine) and secondary (threonine) alcohols, carboxylic acid (aspartic acid, glutamic acid), primary amine

(lysine), and phenol (tyrosine) groups. However, a severe disadvantage of protein binders is their poor water resistance. Proteins may be easily washed out because of the absence of a covalent chemical network. Therefore, protein adhesives were historically improved by crosslinking with formaldehyde or copper salts [142]. The utilization of proteins for the production of adhesives becomes interesting, when a considerable amount is produced that is preferably not used for human food consumption. The annual world production of food protein is estimated to be 322×10^6 t/a in the period 1988–1990. Therefrom, 78% is of plant origin and 22% of animal origin [143].

4.3.1. Plant protein

Plant protein sources are considered to be incomplete, as they lack one or more of the essential amino acids, but an important source of lysine. Plant proteins are usually obtained in combination with other plant substances. Thus, the isolation from the plant results in impure proteins, which can be concentrated and purified in additional technical steps.

4.3.1.1. Soy protein. Soybeans are legumes, the seeds of a low-growing field vine. An important reason for growing soy is to obtain soy oil. “Soy protein” exists in several qualities: Soybean flour, a yellowish powder, is obtained by a heat treatment of beans with subsequent shelling and grinding. Defatted flour is produced by the extractive removal of the soy oil from steam-treated shelled and grinded beans with a solvent, e.g. hexane, with subsequent heating (toasting) and grinding. Protein concentrate by the additional extractive removal of substances soluble in water and/or ethanol and/or acid, and soy protein isolate [9010-10-0] by caustic extraction with subsequent precipitation of the protein [143]. During the process, the protein content, as well as the price, increases (see Table 4). For adhesive application it is assumed that the soy proteins contribute most to bond strength, whereas the carbohydrate portion serves as an inert diluent [144]. The carbohydrate portion comprises starch, sucrose, stachyose, and raffinose [143].

In 1997, the world production of soy beans exceeded 107×10^6 t/a, with an estimated total production of soybean protein concentrate and isolate of 130×10^3 t/a and 80×10^3 t/a, respectively [143]. For 2015, a world production of soy beans over 317×10^6 t/a was reported [146]. A very large quantity of low-cost soy flour is not used for human food production and is available for wood adhesive needs [1]. Over recent years, the interest in soy based adhesives has increased rapidly as reviewed by Vnućec et al. [147].

4.3.1.2. Other oilseed proteins. Oilseeds represent important sources of protein. Besides the main oilseed soy and many others, oilseed plants comprise cottonseed, canola, mustard, marmara, and jatropha curcas. The production of cottonseeds, containing 28% of protein, exceeded 30×10^6 t/a (1989) and the production of canola seeds, containing 20% of protein, exceeded 22×10^6 t/a (1989). Mustard seeds have a protein content of 23% [143]. African marmara beans have a high protein content of 29–38%, but these proteins are not available on the market [148]. Jatropha curcas is a tropical oilseed plant that can be used to reclaim land. The protein content of the toxic seeds is up to 32% [149]. For 2010, production of 200×10^3 t/a of jatropha oil in India was estimated [150], which would imply that a similar amount of protein can be obtained.

4.3.1.3. Wheat gluten [8002-80-0]. Cereals are a source of both protein and starch. Wheat flour contains 8–15% proteins, of which 85–90% are gluten proteins [151]. The Latin word “gluten” means “glue”, though this refers to the cohesion of dough [152]. Wheat gluten is defined as water-insoluble proteins that remain after flour dough is kneaded. Starch is washed out of the wheat dough in two steps (Martin process); the resulting wet vital gluten contains about 11.5 wt% protein, 2 wt% starch, and 0.9 wt% fat, next to water [143]. In additional steps, gluten

can be purified and concentrated as a white powder. Usually, an industrial product named “wheat gluten” is recommended to contain 80% of protein [153]. Wheat gluten is a protein complex of hundreds of proteins which can be divided into two main groups, namely the monomeric gliadins [9007-90-3] and polymeric glutenins [9061-41-0], based on their solubility in 70% aqueous ethanol. Glutenin molecules have linear configurations and the potential to form disulfide and other crosslinks [154]. The water solubility is high under alkaline or acidic conditions, and lowest between pH 6.5 and 9.0. The solubility in the isoelectric range can however be increased by enzymatic hydrolysis [143]. The most important applications of gluten are in the food industry. The worldwide production of wheat protein amounts to 400×10^3 t/a [155].

4.3.2. Animal protein

Generally, for animal proteins it is easier to obtain comparably pure protein fractions than it is the case for plant proteins, but they are quite different in their properties. However, the structural proteins are different from the globular proteins as are those in oilseeds, casein, and blood proteins in that they are helical colloids.

4.3.2.1. Glutin [9000-70-8]. Animal glues are obtained through hydrolysis (realized by cooking under acidic or alkaline conditions) of collagen proteins [9007-34-5] from bone, hide, and other tissues [100]. Collagens are structural proteins and belongs to the class of proteins that is with approximately 30% the most abundant in mammals [156]. The degradation product is called glutin, or “technical gelatin”, i.e. less purified gelatin for non-food purpose. It is an aqueous colloidal solutions which is concentrated to a solid content up to 55% [100]. The usage of glutin as adhesive is known since ancient times [157,158]. In fact, the word collagen originates from the old Greek word for “glue”. Bond formation is a result of solidification of the protein due to cooling (sol-gel transition) with reformation of the helical structure and loss of water of the colloid applied to the adherent. As the sol-gel transition is reversible [158], collagen hydrolysate may be regarded as a thermoplastic adhesive. The global demand of gelatin, mainly for food, was 387×10^3 t/a (2014) and expected to reach 486×10^3 t/a by 2020 [156].

4.3.2.2. Casein [9000-71-9]. Casein is, beside water, the major component of milk. These proteins precipitate under acidic conditions. When these proteins are redissolved in caustic, they are called “caseinates”. Casein proteins have an open, random coil structure. Because of this structure and numerous hydrogen bonds both casein and caseinates can form transparent films from aqueous solutions [134]. Casein-based adhesives, formulated from casein, water, calcium hydroxide, and sodium hydroxide have been popular in woodworking [128]. Like most proteins, caseinates have good heat resistance; therefore, they are used for example in fire door bonding [159]. The world production of casein and caseinates were estimated in 2016 to a value of $430\text{--}460 \times 10^3$ t/a [160].

4.3.2.3. Blood. Blood consists predominantly of proteins and water [143]. Because of its excellent foaming ability, dried blood can be used as additive in plywood production [161]. Theoretically, 780×10^3 t/a of blood protein could be collected from meat animals worldwide, however this is not practiced for several reasons [143].

4.4. Carbohydrates

Carbohydrates are non-aromatic biomolecules consisting of carbon, oxygen, and hydrogen, originally in the ratio 1:1:2. Because of their polar and hydrogen bonding functional groups, they have been in use for adhesive applications for many decades in the form of polysaccharides, gums, oligomers and monomeric sugars [162]. Sugars and their derivatives can also be considered as crosslinking agents and are

therefore described in the corresponding paragraph ($\rightarrow$ 2.4). Carbohydrates represent with $\sim 135 \times 10^9$ t/a about 75% of the annually renewable biomass [73].

4.4.1. Starch [9005-25-8]

The carbohydrate starch is produced by many plants as a source of stored energy. It comprises two types of glucose polymers, the predominantly linear but helical amylose with a degree of polymerization up to 1000 glucose units and the branched amylopectin with a degree of polymerization of several thousands. Starch from every plant type is different in appearance, properties, and starch granulate size distribution. Most starches contain ca. 75% amylopectin.

Starch has enormous importance as food source, but is also used in nonfood technical applications, such as the production of paper, paperboard, and as textile sizing agent [163]. Furthermore, it is used as an adhesive in a wide range of products [164]. However, in wood-based materials it is mostly applied as an extender for UF resins for reducing resin consumption and avoiding over-penetration [128]. The global industrial starch production is ca. 60×10^6 t/a (2006), with 73% being corn, 14% tapioca, 8% wheat, and 4% potato starch [163].

4.4.2. Chitosan [9012-76-4]

Chitosan is a polycarbohydrate soluble in acidic aqueous media, which is produced commercially by the (partial) deacetylation of insoluble chitin, occurring in nature as the structural component of the exoskeleton of arthropods and the cell walls of fungi and yeast [165]. Chitosan is the polymer of D-glucosamine with a molecular weight of $1\text{--}5 \times 10^5$ g/mol [166] and bears primary amine, primary alcohol, and secondary alcohol groups. Chitosan is used in many applications [165–167], such as agriculture, water treatment, medicine, cosmetics, and fibers [168] also because of its ability to form strong adhesive interactions [169]. Because of its biocompatibility, they are important as biomedical adhesives, but can also be applied to bond other materials [170,171]. It is estimated that nature synthesizes 10×10^9 t/a of the raw material chitin [170], the part of sea crustaceans alone amounts to 1.6×10^9 tons [167]. The commercial production of chitosan out of shrimp shells is, however, an elaborate process and mainly located in India, Japan, Poland, Norway, and Australia [166]. The global chitosan market was estimated at 13.7×10^3 t/a (2010) with 21.3×10^3 t/a expected in 2015 [172].

4.5. Plant oil

Plant oils are liquid esters of glycerol with three fatty acids, called triglycerides. Depending on the plant species and the extraction conditions, natural oils contain also small quantities of di- and monoglycerides, free fatty acids and other substances such as pigments [171]. Fatty acids with double bonds are called unsaturated. The most important application of plant oils is in food. Historically, multiple unsaturated oils called “drying oils” were also used as coatings. In reality, the oils do not dry but polymerize in a slow process by free radicals via the double bond. Improvement has been made by synthesizing more reactive alkyd resins out of drying oils [83]. Furthermore, the double bonds can be converted into other reactive groups such as epoxides or alcohols [173] to open new reaction possibilities and pathways towards polymers and composites [146].

4.5.1. Soybean oil [8001-22-7]

Soy oil contains $\sim 8\%$ triunsaturated, $\sim 54\%$ diunsaturated, $\sim 23\%$ monounsaturated and $\sim 15\%$ saturated fatty acids. Soybeans account for approx. 60% of the global oilseed production with a production exceeding 317×10^6 t/a (2015) [146]. With an oil content of 17–22% [171], this corresponds to an oil production of $\sim 60 \times 10^6$ t/a.

4.5.2. Palm oil [8002-75-3]

Palm oil is obtained from the fruit pulp of the oil palm and contains

~10% diunsaturated, ~39% monounsaturated, and ~49% saturated fatty acids. Palm oil can be separated into a solid and a liquid fraction. The production volume is 28×10^6 t/a (2004/05) [146].

4.5.3. Castor oil [8001-79-4]

Castor oil is obtained from the seeds of the evergreen castor tree. The fatty acids consist of ~90% ricinoleic acid, which is the only large scale available natural fatty acid that contains, beside one unsaturated bond, a (secondary) alcohol group. The production is 440×10^3 t/a (2004/05) [146].

4.5.4. Rice bran oil [68553-81-1]

Rice bran oil contains 30–40% diunsaturated, ~44% monounsaturated and ~20% saturated fatty acids and is an important by-product of rice processing. Around 820×10^3 t/a (2013) of rice bran oil are produced in India [171], other main producers are China and Japan.

4.6. Various other adhesive systems

Several compositions have proven to be effective adhesives for different applications, however are currently not applied in the wood based panel industry.

4.6.1. Poly(vinyl acetate) adhesive [9003-20-7]

Poly(vinyl acetate) (PVAc) adhesive, also known as white glue, is a viscous dispersion of the thermoplastic polymer poly(vinyl acetate), and may further comprise plasticizers, coalescent, tackifiers, cross-linking agents, fillers, and pigments. Formaldehyde was commonly added as preservative, but because of its toxicity nowadays other preservatives are often used [174]. PVAc is well established as paint and as binder in paper and for solid wood applications including furniture construction. The usage is simple as the adhesive does not need heat to set. After application, the water migrates away and the dispersed particles coalesce to form a film [71]. Therefore, the adhesive is at a disadvantage when the water cannot be removed [174]. PVAc is obtained by radical polymerization of the synthetic monomer vinyl acetate. The world capacity for the monomer is 5.3×10^6 t/a (2005), and 48% thereof is globally used to produce poly(vinyl acetate) homo- and copolymers [72].

4.6.2. Acrylic resins

Acrylic resins are a versatile group of synthetic thermosetting or thermoplastic resins based on acrylic acid, methacrylic acid, and their esters. Main applications are in paints, coatings, adhesives, and sealants. The worldwide production capacity of the monomers acrylic acid and its esters is 6.4×10^6 t/a (2002) [175]. The acrylic resin market is believed to grow to 10.5×10^6 t/a by 2022 [176].

4.7. Thermoplastic processable polymers

Thermoplastics are available in huge amounts and applied in various products of our modern society. These polymers are typically available as solid materials and processed without the usage of solvents in various thermoforming processes of melting followed by solidifying through cooling, such as casting, extrusion, and injection molding [177]. In the wood working industry, thermoplastics, such as ethylene-vinyl acetate (EVA) and polyamides, are in use as adhesives called “hot melts” [178]. One of their main disadvantage is their low thermal stability including their tendency to creep under mechanical stress and elevated temperature [4]. Furthermore, thermoplastics, such as poly(vinyl chloride) (PVC), polypropylene (PP), polyethylene (PE), and polylactic acid (PLA) are processed using thermoforming technologies in combination with wood flour or fibers of natural materials to form wood polymer composites (WPC) [179].

4.7.1. Polyethylene [9002-88-4]

Ethylene, $\text{H}_2\text{C}=\text{CH}_2$, is usually produced from crude oil but can also be made out of (bio)ethanol. Ethylene can be polymerized to PE by free radical polymerization, resulting in highly branched low density polyethylene (LDPE) or by organometallic catalysis, resulting in linear high density polyethylene (HDPE) [83]. PE has many applications comprising plastic bags, packaging material, cable insulation, and pipes. The melting temperature of LDPE is 105–110 °C, the one for HDPE is 130–135 °C [180]. The global production capacity of all forms of PE is on the order of 100×10^6 t/a (2010) [181].

4.7.2. Polystyrene [9003-53-6]

Polystyrene (PS) is produced industrially mainly by free radical polymerization of styrene, an ethylene monomer connected to a phenyl ring produced from crude oil. Expandable polystyrene (EPS) is a lightweight PS material produced from PS by the addition of a low-boiling hydrocarbon foaming agent. PS is used for example to produce technical and household items, as EPS it is used as packaging or insulation material. The melting temperature of PS is 230–270 °C [180]. The worldwide consumption of PS is around 11.4×10^6 t/a (2004) [182].

4.7.3. Polyethylene terephthalate [25038-59-9]

Polyethylene terephthalate (PET) is the polyester from the esterification of terephthalic acid (phenolic ring with two carboxylic groups in para-position) and ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$). Both monomers are derived from crude oil. The largest applications are textile fibers and plastic bottles. The melting temperature of PET is approx. 255 °C [180]. The world production capacity for PET is about 12.4×10^6 t/a (2004) [72].

4.7.4. Polylactic acid [26100-51-6]

Polylactic acid is a renewable and biodegradable polyester. The monomer, lactic acid, is obtained by the fermentation of glucose. As the molecule bears both an alcohol and a carboxyl group, it can be polycondensed although it is first converted into the lactide in industrial production. Applications comprise bottles, cups, packages, and films. The melting temperature of PLA is ~180 °C [183]. The expected combined production capacity of the two leading producers is estimated to reach 300×10^3 t/a by 2018 [184].

5. Parameters for a technical appraisal of adhesives systems

Studies used as references for the present technological description have to fulfill the following criteria to be incorporated in the dataset: (1) the adhesive has to be tested in particleboards or in related veneer based bonding systems as described in the end of the introduction (e.g. when using the so called automated bonding evaluation system (ABES) [52] where the testing principle became standardized [51] in the meanwhile); (2) the pressing parameters pressing time and temperature have to be indicated in the work; (3) the strength properties have to be indicated: internal bond strength for particle based boards or tensile-shear strength for veneer based systems have to be available, and (4) the described adhesives have to be free of added formaldehyde or are incapable of releasing formaldehyde as defined at the end of the introduction (Table 2). The current collection of data should allow for comparing various adhesive systems based on selected technological parameters which are bond strength, as well as pressing temperature and time needed for curing. The selected properties are relevant for wood-particle processing and should enable a first evaluation of the adhesive systems, even though additional parameters such as swelling properties of the boards produced, their water uptake, or the strength in humid conditions would be of interest too, but are not displayed here for simplification and as these results were not available in most of the studies. With these boundary conditions almost 200 references were included in the following data set. As an important parameter for the

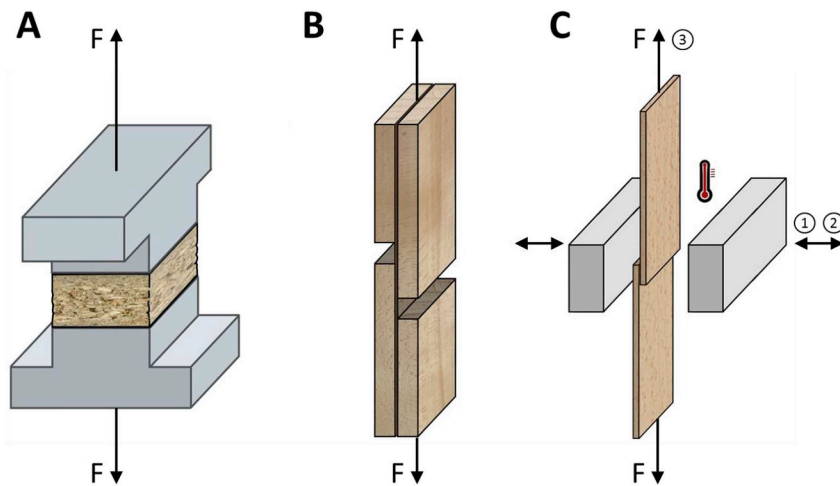


Fig. 2. Test set-ups for mechanical property assessment. A) internal bond (IB) strength showing a particleboard specimen between a pair of brace, B) lap-joint test set up typically used to test structural adhesives in tensile shear mode (TSS), C) method for measuring the effect of press time and temperature on the development of adhesives bond strength (known as ABES test). Numbers indicate the sequence of ① closing and ② opening of the (hot) pressing device and ③ testing tensile shear strength (TSS).

evaluation the so called internal bond strength i.e. the tensile strength perpendicular to the plane of the board, is indicated. The internal bond strength test is a frequently used method to assess the quality of adhesion in particulate based boards, and is additionally one of the required quality parameters in European [185,186] and US [187] standards to classify board types. A simplified test set-up is illustrated in Fig. 2A. Due to a typically lower density of core layers in particleboards, the parameter is usually indicating the strength of the core region of such boards. As the internal bond strength is beside other factors directly influenced by the density in the core layer, the particle properties and their geometry, the adhesive quantity and distribution, the measured strength values are comparable with limitations only. The main group of laboratory particleboards offer a density in the range of 600–750 kg/m³. Values significantly deviating from this level are reported in the subsequent discussion section, in order to allow the reader for considering this limitation.

Shear strength is a frequently used reference parameter for the evaluation of adhesive bond strength of solid wood joints, because it is the most common interfacial stress under service conditions [188]. Using lap-joint tests (Fig. 2B), tensile shear strength is a frequently accessed parameter for classifying adhesives for structural [e.g. 189,190] as well as non-structural [e.g. 191] timber joints, or for plywood [192,193].

The main limitation of the lap-joint test method is the fact that upon reaching a certain bond quality, the tensile shear strength of the bond is equal to, or exceeds corresponding wood strength [194], thus evaluation of bond strength differences may be limited, especially in dry ambient conditions. For the present study, tensile-shear strength was displayed for adhesives which were evaluated using thin veneers (in contrast to solid wood lamellas as used in the standards mentioned above). Such tests (Fig. 2C) are frequently performed to assess the hot-pressing time dependent strength development of adhesives used for particulate-based boards. Here the so called ABES method (Automated bonding evaluation system [52]) or the corresponding standard test methodology [51] is frequently used in wood panel industry. As already described in the introduction the required pressing time is significantly contributing to the total product cost. Thus, this parameter is of great importance for any evaluation of an adhesive and is indicated as pressing factor, i.e. the time needed to cure one mm of particleboard thickness. The required pressing time typically depends also on the selected hot-pressing temperature to a certain degree, whereby higher pressing temperature usually leads to faster heating through and adhesive curing speed when conventional adhesives [4] are used. In contrast to the strength parameters which describe a measured maximum stress value for boards of a certain density, for most cases it is not indicated if the hot pressing parameters used in the various studies represent the optimization limits of the reported adhesives or where

simply chosen for different rationale. Thus, the parameter hot pressing time or press factor is relatively weak compared to strength properties.

The pressing factor of laboratory produced wood based boards may be relatively easy transferred to the conditions available during a wood-based board production. However, pressing factors reached in industrial scale are typically somewhat lower than the ones achieved in laboratory scale. For standard UF adhesives, where pressing factors of 5–12 s/mm are typically used in laboratory production, on industrial scale the pressing factor for the identical adhesive may be as low as 3–7 s/mm using typical hot-pressing temperatures in the range of 180–240 °C.

In contrast, hot-pressing times used for measuring the effect of temperature on the cohesive strength development of adhesives (so called ABES tests, or generalized tests according to Ref. [51]), tests are much more difficult to compare to parameters relevant for board processing industry. The parameters chosen for these tests are less uniform and results are additionally biased by factors influencing the time needed to reach the curing temperature in the bond line. In the references evaluated for the present study, pressing temperatures for the production of lap-joint specimens range from 20 to 200 °C. For the case of thin veneers, bond lines temperatures close to press temperature may be easily reached, which is in great contrast to the case of particleboards where core temperatures above 120 °C are hardly reached also when hot pressing temperatures of > 220 °C are applied (compare discussion in →6.12). Additionally, the thermal conductivity of the wood species (density, moisture content, porosity...), the thickness of the veneer layers and the amount of resin applied may influence the results gained. For the case of solid wood bonding Dunky and Niemz [4] report a specific heating trough time of approx. 1 min/mm solid wood at 100 °C. In order to allow the reader to account for differences derived from veneer thickness, the corresponding value is mentioned when significantly different to 1 mm.

A further aspect is the application of adhesives to the surface of the veneers, which is typically made manually, whereas for the production of particleboards an even distribution of adhesives on particles is required. Thus, testing of adhesives on veneers doesn't necessarily imply a direct applicability of the corresponding adhesive for particleboards as e.g. spreading by spraying or similar technologies for particleboard application requires certain viscosity and other processing limits. This is also the reason why adhesives investigated at the example of veneer lap joints are listed but not discussed in detail as the proof of applicability is not given.

Another important factor worth to be reported as overview would be the cost situation of the evaluated adhesive systems. This factor is very difficult to assess and may vary extremely on a daily basis due to changed market situations. Some of the products reported here are not commercially available in sufficient quantities yet. Additionally the

overall cost situation may be different around the globe, as some products (e.g. various proteins, tannin...) are locally available in relevant amounts, as corresponding industry is on-site, whereby this may not be the case for other regions. Thus, there is no general assessment of the cost situation possible within the frame of this review.

6. Discussion of technological performance

The adhesive classification to one of the following groups (e.g., amino-, or lignin-based) was made according to the main component of the adhesive mixture in terms of relative quantity of adhesive components based on mass. For example an adhesive composed of 70% lignin, 25% of pMDI and some other components would be part of lignin-based adhesives. For this classification no suggestion was made to identify the main adhesion promoting component, which might be pMDI for the case described.

As the focus is on wood based particleboards, results from studies directly related to particleboards are reported and discussed first for each adhesive system with internal bond (IB) strength as main indicator for a strength value (Fig. 3) which is opposed to the press factor in s/mm board thickness. This factor represents one of the most important process related parameters, determining a major part of the final product costs. Additionally, the processing temperature was categorized to be higher or lower than 180 °C. As discussed in the introduction, typical hot pressing temperatures applied for current particleboard production processes range from approx. 180 to 240 °C, mainly influencing the heating up rate, while core temperature remains still limited to approx. 110–120 °C due to physical principles (presence of water vapor). More detailed information on temperature is indicated in the subsequent discussion if significantly different to these standard conditions.

Apart from proper mechanical properties and an economical manufacturing process, further requirements exist on particleboard

adhesives such as moisture resistance or low emissions. A prerequisite of particleboard processing is a sufficient strength development within short press times. The focus on data evaluation is therefore given to dry strength development at this stage. Additional information on durability, moisture resistance is indicated below when available. This factor itself is certainly important for a range of applications, but probably not limiting, as can be seen at the example of UF as one of the hydrolysis unstable resins, being still considered as the most effective binder for wood panel industry. In Fig. 3 only particleboards processed with a press factor < 70 s/mm are reported, representing the largest part of studies.

As a reference to formaldehyde-free alternative systems, commercial urea formaldehyde (UF) based resins (E1, F****, and AsWood® (Dynea AS, Norway) as one example of an ULEF resin) are depicted as ellipses of IB strength and press factors. It is important to compare boards produced under similar laboratory scale conditions, as press factors are clearly lower on continuous industrial presses. As a matter of fact, boards produced with lower emission values require higher press factors to reach sufficient IB strength also when using standard UF systems. Adhesives with the need of high press factors, e.g. when overnight curing was applied, are not included in the graph, but are reported in the text section discussing the individual adhesive systems. The studies using thin veneer based lap-joints report tensile shear strength (TSS) as main property using only values reported from specimens with one veneer direction for Fig. 4. These tests have more limited significance for direct application for particleboards as discussed above. For this test frequently thin veneers typically in the range of 0.6 mm but also up to 3 mm and in some special cases up to 5 mm lamella thickness were used. As the necessary time to transfer heat for adhesive curing from the hot press plates to the bond line also depends on the veneer thickness the necessary curing time is not directly comparable for different adherent thicknesses. To enable some kind of

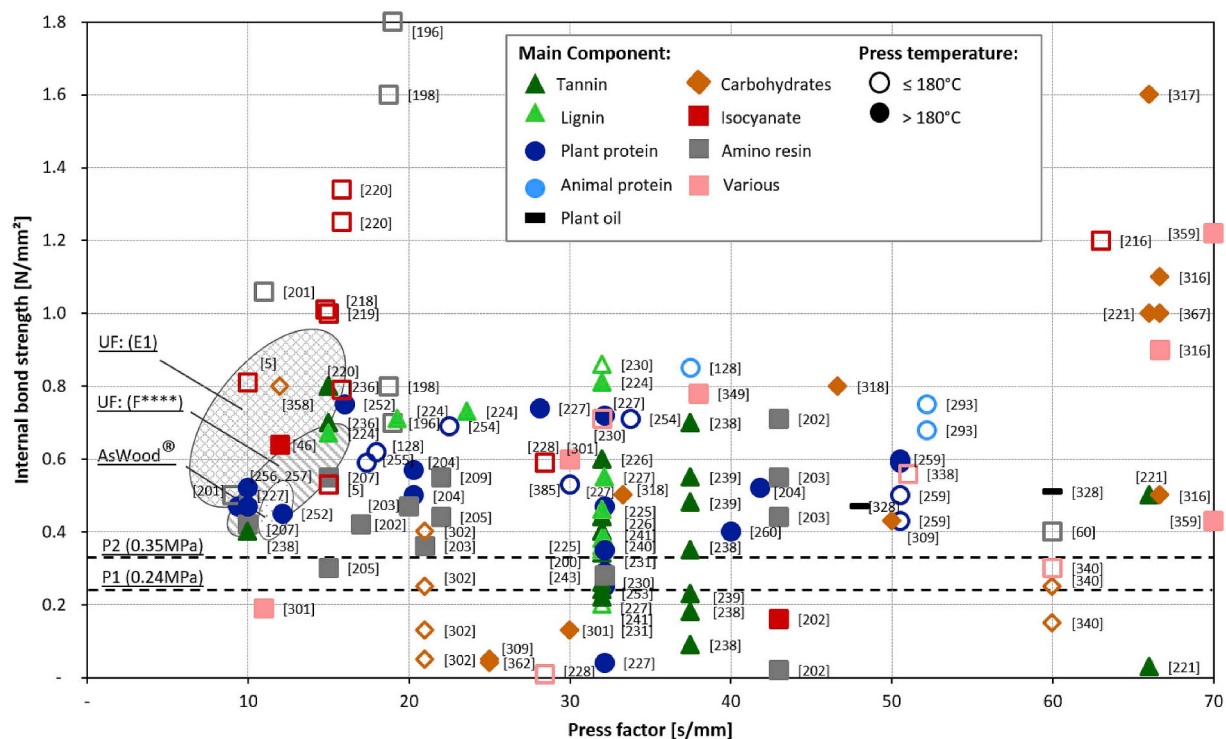


Fig. 3. Overview of the internal bond strengths as a function of pressing factor for adhesives used for particleboard manufacture. The color labelling distinguishes between the main components and the filling of the symbols provides information on the press temperature used. Reference values for P1 and P2 type boards according to EN 312 for 13–20 mm board thickness are indicated as dashed lines. Ellipses are indicating the performance region for current commercially available laboratory particleboards using UF-based adhesives. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

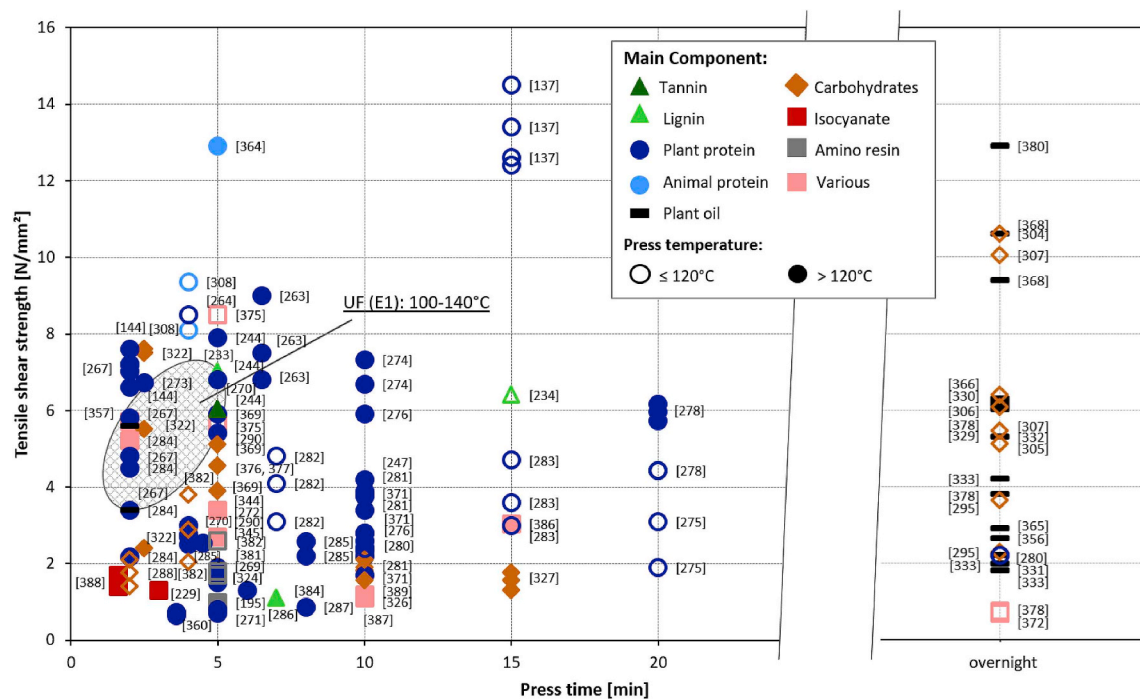


Fig. 4. Tensile shear strength depending on hot pressing time of adhesively bonded veneer lap-joints. The color labelling distinguishes between the main components and the filling of the symbols provides information on the press temperature used. Ellipse is indicating the performance region for current UF-based adhesives as used for industrial particleboard production. References not further discussed in this article are [356, 357, 360, 364–366, 368, 369, 371, 372, 375–378, 380–382, 384, 386–390]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

approximation, the hot pressing time could be reduced by the reader for thicker adherents by approx. 1 min/mm thickness difference. However, a proper correction might not be easy as the heat conductivity depends on several factors such as wood density, moisture content, temperature difference and others. Due to the crosswise alignment of veneers in plywood, with corresponding failure taking place typically in the veneer loaded perpendicular to the fiber direction, results from plywood tests are typically significantly lower than TSS from lap joints using one veneer direction only. Thus, strength values of adhesives tested on plywood samples are not reported here as they may not be directly comparable to the other TSS values.

When discussing the potential of different adhesive groups, only systems with direct particleboard application were considered. As applicability of adhesives for particleboard production is not proven by studies using veneer based model systems, these studies are listed as potential ideas but were not discussed in detail.

6.1. Amino-based adhesives

Background information about history, chemistry and properties of amino based resins and its constituents may be found in various books and reviews [e.g. 4, 8, 159]. Information more related to the application as adhesives for panels may also be found [e.g. 5].

As some kind of exchange of aldehyde using classical amino resin chemistry Deng et al. [195] showed application of urea (→ 4.1.1) glyoxal (→ 2.2.1) already for plywood production. Based on this adhesive recently Younesi-Kordkheili and Pizzi [196–198] used urea glyoxal adhesive with an ionic liquid (N-methyl-2-pyrrolidone hydrogen sulfate) as catalyst also for particleboards. Using a press factor of 19 s/mm at 180 °C hot pressing temperature, the addition of the ionic liquid not only accelerated curing but showed a very positive effect on the mechanical properties resulting in an internal bond (IB) value of 1.85 MPa which was 130% better than using classical ammonium chloride as hardener. Additionally, water absorption and thickness swelling (10%) were significantly improved when using the ionic

liquid. The particleboard showed a comparably high density of 800 kg/m³, by using a spread rate of 10% [199]. Again based on the before mentioned urea glyoxal resin [195], Younesi-Kordkheili and Pizzi [198] obtained an IB strength of 0.8 N/mm² again in boards of 800 kg/m³, which increased to 1.6 N/mm² when using additionally 8% pMDI based on resin solids.

Melamine (→ 4.1.2) glyoxal resin combined with 1% chrome nitrate hardener lead to an IB value of 0.28 N/mm² [200] compared to 0.19 N/mm² when using 3% of conventional ammonium sulfate hardener at a press factor of 32 s/mm. A short pressing time (11 s/mm) was reported in the patent of Detlefsen et al. [201] using ethyleneurea (→ 4.1.3) crosslinked with glutaraldehyde (→ 2.2.4) and post added urea (15%) reaching IB strength of 1.06 N/mm². Reducing the press factor to 9 s/mm resulted in a significantly decreased IB to 0.5 N/mm². Sulzberg and Ma [60] were also using ethyleneurea crosslinked at this time with glyoxal, but they could reach IB strength of only 0.4 N/mm² using long hot pressing times of 60 s/mm. Both patents report moderate press temperatures of 160 °C and approx. 150 °C, respectively.

Despres et al. [202] evaluated commercially available urea dimethoxyethanal (DME) (→ 2.2.2) resin with 5% ammonium sulfate as hardener. Urea-DME resin alone did not perform (IB strength: 0.02 N/mm²) but in combination with further 2% of pMDI (→ 2.3.2) IB values of 0.7 N/mm² were measured, nevertheless using a high press factor of 43 s/mm. Reducing the press factor to 17 s/mm still resulted in IB value of 0.42 N/mm². A similar concept was described by Properzi et al. [203]. They compared both melamine (→ 4.1.2) DME and urea DME with glyoxalic acid (→ 2.2.3) as crosslinking agent, which was further combined with latex, and/or pMDI. The highest IB strength of 0.55 N/mm² was reached using 43 s/mm as press factor. By improving the press factor to 20 s/mm still IB strength 0.47 N/mm² could be reached using urea DME combined with pMDI.

Respectable IB and press factors of 0.50–0.57 N/mm² at 20 s/mm together with 17–20% thickness swelling were achieved by Vidal et al. [204] using lupin flour or soy flour (→ 4.3.1.1) with urea and poly-amidoamine-epichlorohydrin (PAE) (→ 2.6.1) at a ratio of 7/14/1.

In the patent of Dix and Borner [205] melamine was combined with a solution of glycolaldehyde ($\rightarrow$ 2.2.5) and glyceraldehyde. By using 22 s/mm press factor IB strength 0.44 N/mm^2 was reached. When reduced to 15 s/mm, IB dropped to 0.3 N/mm^2 . In order to increase the economic competitiveness Bunzel and Jesse [206] tried to minimize melamine demand and increased the amount of urea instead. Therefore melamine reacted with glyoxylic acid, followed by a reaction with glyoxal and a subsequent addition of urea. The adhesive worked well for MDF boards but wasn't successful for particleboards (IB value $< 0.02 \text{ N/mm}^2$). A two-component adhesive involving one melamine-based component mixed with the before described melamine-urea based resin resulted in a final IB strength of 0.25 N/mm^2 , using 12% adhesive solids. They [207] reported reduced strength properties when urea content was increased together with higher thickness swelling. When using a one component adhesive again composed of melamine (70%), urea (30%), glyoxylic acid (70%), and glyoxal (30%), they recently could reduce the press factor to 10 s/mm while still reaching IB value of 0.42 N/mm^2 . However, thickness swelling (24 h) in the order of 60–70% was mentioned.

Recently 5-hydroxymethylfurfural (HMF) ($\rightarrow$ 2.4.5) was presented by Frei and Kläusli [208] as a non-toxic bio-based formaldehyde substitute which is able to react with urea but also phenol. The particleboards produced with the corresponding HMF-based amino adhesives showed IB strength in the range of $0.3\text{--}0.55 \text{ N/mm}^2$ using less than 10% adhesive spread rate and a press factor subjected to ongoing optimization in the range of currently 18–26 s/mm [209].

A general advantage of amino-based adhesives with rather well known chemistry has to be mentioned which requires basically some adaptations of existing systems. Another advantage is the high availability of the base chemicals urea and melamine, with clear economic advantages especially for the case of urea. Based on the available data reported within the group of amino-based adhesives, the expired patent reported by Detlefsen et al. [201] shows one of the best combination of strength properties combined with a short press time, well in range with studies reported for current ultra-low emitting formaldehyde (ULEF) adhesives. As rather moderate press temperature was reported in the patent, a further reduction in press time is assumed to be possible too. Currently, ethyleneurea and also glutaraldehyde may be regarded as rather expensive when comparing to current solely urea and formaldehyde based resins. On the other side, ethyleneurea is based on comparably economic and available base materials, which might lead to higher economic competitiveness if large scale production might be applied. Combining urea, ethyleneurea and glutaraldehyde crosslinking may be expected resulting in thermosetting adhesive behavior, further resulting in product properties comparable to current available ones.

The melamine-urea system presented by Bunzel and Jesse [207] is reaching relevant strength properties when using short hot pressing times, the latter again in comparable range with ULEF adhesives. The high portion of melamine necessary to reach proper strength properties may represent some economic challenge.

The system of Younesi-Kordkheili and Pizzi [196,197] using urea and glyoxal with an ionic liquid catalyst might be regarded as rather slow based on the press factor values indicated, but in light of the high mechanical properties achieved a further significant reduction in pressing time while still achieving suitable mechanical performance. Glyoxal as simplest substituent of formaldehyde is commercially available in considerable amounts. The positive contribution of the ionic liquid seems to be clearly evident by decreasing the energy of activation of the curing reaction, making crosslinking possible. Currently ionic liquids might be regarded as expensive and the availability might depend on direct request, but only small amounts of only 1 to 3 wt% based on resin solids seem to be sufficient. Very promising results are also evident from their latest approach [198] where small amounts of pMDI (compare also Fig. 5) further improved the already well performing urea-glyoxal base system to a similar extend as the approach with ionic liquids described before.

As the further system with reasonable IB strength and press temperature contains a significant amount of 2% pMDI [202], for further discussion on this adhesive typology the reader is referred to section ($\rightarrow$ 6.2).

HMF-based amino resins [208] are considered to be an interesting idea, as HMF is known as a high reactive compound and might consequently have the potential to result in reactive adhesives. Nevertheless, the current availability of HMF is limited to one pilot plant only. In case technological properties may be sufficient, it may be considered as a medium to long term alternative.

Using veneer lap joints as adherents urea and glutaraldehyde solution [210] were combined with nano- Al_2O_3 . Pressing 5 mm thick lamellas at room temperature for rather long 30 min resulted in tensile shear strength (TSS) of considerable 5.9 N/mm^2 .

6.2. Isocyanate-based adhesives

Isocyanate based wood adhesives are well described in literature. Early reviews are available from the 1970s by Deppe and Ernst [211,212], a general overview of chemistry may be found by Frazier [213] or more recently by Pizzi [5]. As pMDI adhesives ($\rightarrow$ 2.3.2) are frequently used to produce OSB, with about 75% [214] of the annual production in Europe, a couple of specific studies are related to this panel type: [e.g. 215] investigating the effect of isomer ratio and OSB properties just to mention one as example.

Due to concerns about formaldehyde emissions, Gallagher [216] reported in 1982 about possibilities of using isocyanate-based adhesives for particleboards. Among reviewing others he reported about polyurethane-based adhesive: producing particleboards using nearly stoichiometric quantities of MDI and various polyols, an IB value of 1.2 N/mm^2 was reached by using a binder amount of less than 3%. In his study the press was heated at the top side to 125°C and 150°C on the bottom side, using rather long hot pressing cycles ranging from 63 s/mm to 100 s/mm and extremely high density ranging from 1050 to 1350 kg/m^3 , a value almost too high to allow for comparing the results with other particleboards reported here.

Today pMDI adhesives are already well established and mainly applied without additional polyol for panel manufacturing. In the panel-based industry also hybrid systems may be applied where pMDI is used in the core layer e.g. for OSB boards and another formaldehyde-based system is used for bonding the face layers, as sticking of the press to pMDI bonded wood has been a serious issue. PMDI is also a good adhesive for bonding to metals or other substrates. Due to the development of effective release agents this problem does not exist anymore [5], and fully pMDI bonded strand or particle based boards (approx. 1% of the annual production in Europe [214]) are also industrially available. Therefore, the necessity of these releasing agents also represents an additional cost factor. Additionally to the high bonding affinity to metals, pMDI does not offer cold tack. Consequently, wood particle mats sprayed with pMDI do not have an integrity as required for certain production processes [213]. PMDI is also offered in hybrid adhesives combining traditional adhesives such as UF or PF with pMDI applied during blending as one or two-component systems. Beside other factors this is done for biasing the performance and also for improving emission behavior of traditional and usually cheaper adhesives [5].

For industrial use of pure pMDI based particleboards press factors of 5 s/mm or shorter are reported [5]. These low values may be rated as fast compared to almost all other alternative adhesives, but are still higher compared to those reported for fast UF-based systems which may be as low as 3 s/mm. However, when comparing to other ultra-low formaldehyde emitting (ULEF) systems the value may be considered as relatively close to formaldehyde-based ones.

Also on laboratory scale rather short hot pressing times compared to possible other alternative adhesives are evident: Klímek et al. [217] report 9 s/mm, Pizzi [5] 10 s/mm for adhesive loads in the range of 4–6%. All of these panels show additionally high performance in terms

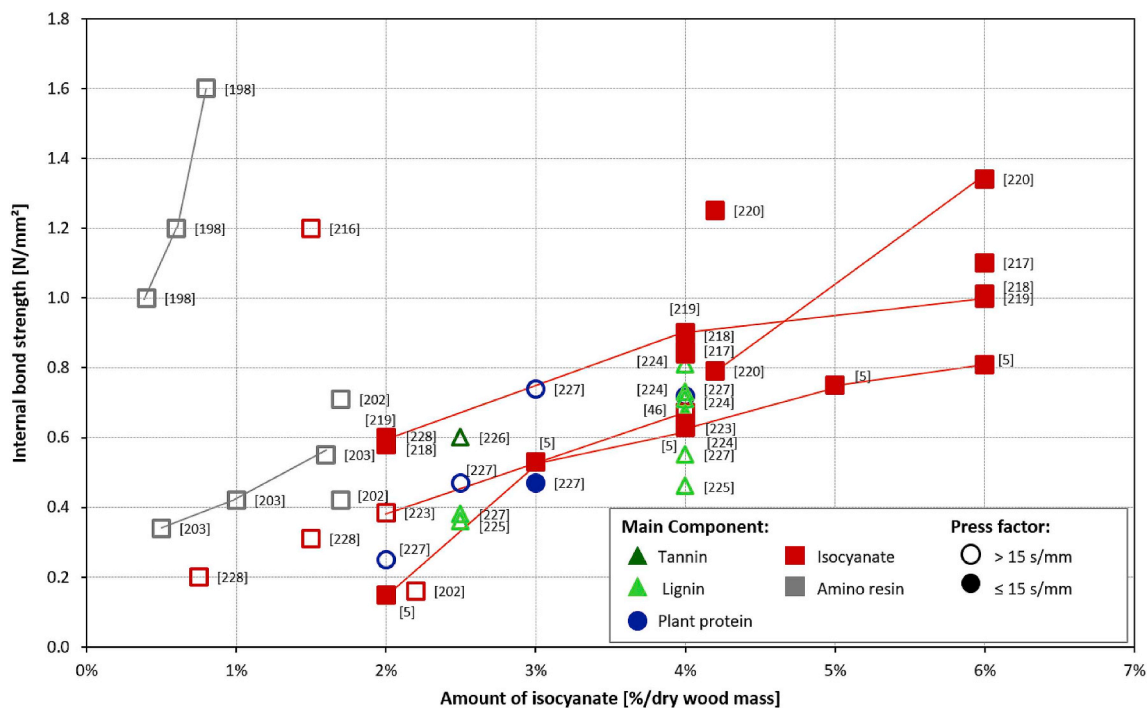


Fig. 5. Dependence of internal bond strength on isocyanate (pMDI only) content used for particleboards. Connected data points indicate values from same studies using similar parameters.

of IB values in the range of 0.85–1.1 N/mm² [217] and showed also good thickness swelling properties [218]. Slightly higher press factors of 12 s/mm [46], 14.4 s/mm [218,219] and up to 16 s/mm pressing time were indicated by others, also using pMDI [220]. High resin loads of 8%, at a high density of 800 kg/m³ combined with an again high press factor of 66 s/mm resulted in exceptional IB strength of 2.2 N/mm², as shown on some kind of reference board while studying other adhesive systems [221]. Additionally, it could be shown that pMDI may also be suitable to adhesively bond alternative agricultural based raw materials instead of wood for particleboard manufacture [222], where traditional UF adhesives showed rather poor performance especially for IB value or thickness swelling. Using miscanthus particles at 600 kg/m³ panel density and 9 s/mm hot pressing time, 4 and 6% pMDI resin load resulted in remarkable IB strength of 0.32–0.34 N/mm².

Considering the comparably (to UF) high price of pMDI the resin loading of panels is particularly crucial for wide-spreading industrial implementation of isocyanate based adhesives. Fig. 5 is giving an overview of measured IB values depending on the amount of pMDI used. Also for adhesives mixed with other compounds, only the pMDI content is indicated here. The total adhesive content in the board may be significantly higher than the pMDI amount for adhesive mixtures.

By using pure isocyanate-based adhesives, Pizzi [5] indicates in his review a set of properties depending directly on adhesive spread rate and hot pressing time. Basically 3% of adhesive loading seems to be some kind of lower value combined with a hot pressing factor of 15 s/mm to achieve panel qualities as required for interior application, while 5% would be necessary to achieve also humidity resistance.

Dix and Marutzky [220] combined emulsified and non-emulsified pMDI with various extenders, such as tannins (→ 4.2.2), starch (→ 4.4.1), and gluten (→ 4.3.2.1). Using pure 6% non-emulsified pMDI resulted in particleboards with high IB strength of 1.3 N/mm² in dry conditions and fulfilled requirements also for particleboards intended for humid environments. Substituting up to 20% of the pMDI (total of 4.2% pMDI) with the mentioned extenders resulted still in high IB values when maize starch was used, whereas the use of gluten resulted in a more pronounced decreasing in IB value and higher thickness swelling.

Klimek et al. [217], investigated only adhesive load levels of 4 and

6%, whereby both levels exceeded by far the required standard levels when using wood particles.

Papadopoulos et al. [219] compared pMDI and EMDI for their suitability to produce particleboards and found out that (using 14.4 s/mm, 650 kg/m³, 180 °C) also a low level of 2% resin load was sufficient to reach requirements for interior application. At these low spread rates some advantages of EMDI over pMDI could be identified. Additionally, better dimensional stability compared to UF could be found [218].

In order to enable less reactive adhesive compounds provide acceptable bond performance various mixtures of those with pMDI are available. From Fig. 5 it seems that the addition of a dominating quantity (more than just a typical quantity for extenders) of other compounds such as lignin, tannin, or protein do not result in a systematic improvement of panel performance. Basically, the values reported for the various combinations of components with pMDI are performing very close or within the indicated range [5,218] of pure pMDI without the addition of other components. Thus, it is questionable, if the addition of such compounds is really contributing to the performance of such adhesives mixtures and if these combinations have the potential to minimize significantly the pMDI consumption. Otherwise they have to be regarded as sole cost factor without an obvious added value, as the total adhesive spread rate (including the other compounds) is for most cases significantly above the indicated one for the pMDI component.

Various studies are available to crosslink natural components like lignin or tannin with pMDI. El Mansouri et al. [223] showed beside other mixtures glyoxalated (→ 2.2.1) lignin (→ 4.2.1) with pMDI at a mixing ratio of 60:40 and a spread rate of 10% adhesive related to the total solid of the particleboard. Thus, the adhesive mixture results in 4% pMDI content in the particleboard. Panels produced thereof resulted in IB values of up to 0.78 N/mm², which is very close to their own reference (IB strength: 0.67 N/mm²) using an adhesive load of (2% and) 4% pure pMDI [224]. Also IB value after boiling was only marginally different for cases where glyoxalated lignin was involved. Again glyoxalated lignin combined with pMDI was investigated [225]. Also here 10% resin load (corresponding to a total of 4% pMDI) was used, resulting in IB values depending on density in the range of 0.46–0.53 N/mm².

Combinations of 55% glyoxalated lignin with 25% pMDI (total of 2.5% pMDI content related to panel mass) and 20% of mimosa tannin resulted in IB strength of 0.36–0.38 N/mm². A similar concept is also shown by Ballerini et al. [226] who used tannin, pMDI and glyoxal (70%:21%:9%) with a total of 12% adhesive content in the panel, corresponding to approx. 2.5% pMDI content in the panel, which resulted in IB strength of 0.6 N/mm². Amaral-Labat et al. [227] used various combinations of glyoxalated soy flour (→ 4.3.1.1) combined with/without tannin and pMDI. Basically their result are close to the expected ones considering the corresponding pure pMDI references, whereby the mixture of glyoxalated soy flour combined with tannin and 3% pMDI showed a significantly higher performance related to the direct reference.

In the range of pMDI contents below 2% only single studies are available. Urea (→ 4.1.1) glyoxal resins with an IB strength of already 0.8 N/mm² (density 800 kg/m³) could be further improved from 1.0 N/mm² up to 1.6 N/mm² by adding only small amount of 0.4–0.8% pMDI based on wood, as shown by Ref. [198]. Properzi et al. [203] combined urea (→ 4.1.1) or melamine with dimethoxyethanal (DME) (→ 2.2.2) (U/M:DME 1:2) as amino-resin precursor using various combinations with pMDI. For 8% total resin load (80% U-DME, 20% pMDI corresponding to a total of 1.6% pMDI related to wood dry mass) their boards showed strength values of 0.38–0.52 N/mm². The results showed influence on press factor used, which was varied from 20 to 32 s/mm, but also influence of temperature and moisture content was observed. Using additionally latex with M-DME and various amounts of pMDI at a total of 10% resin load IB strength ranged from 0.34 to 0.55 N/mm². Also for this study IB values increased with increasing pMDI from 0.5% to 1.65% related to the dry mass of wood when hot pressing for 43 s/mm. Using the adhesive proposed here but without addition of pMDI still similar and partly also better IB values (up to 0.44 N/mm²) compared to those with 0.5% pMDI could be reached, when manufacturing parameters were optimized. It may thus be concluded that at these very low pMDI levels, the pMDI component shows a less dominant behavior for the total bonding performance of this adhesive system, as the adhesive is capable of working also without the addition of pMDI.

Also in the range of low isocyanate contents Johns [228] described in his patent blends of polyisocyanate and furan resins based on furfuryl alcohol (→ 2.4.4). With adhesive spread rate of 3% solids related to wood dry mass various degrees of mixture were reported. Basically again a direct relationship of isocyanate content and performance is evident here, with IB values ranging from 0.5 N/mm² for 100% isocyanate to only 0.05 N/mm² for 100% furan adhesive. As the furan seems to improve bonding performance for a single case only, this strategy does not seem to extend the range towards lower pMDI spread rates significantly.

pMDI is one of the single formaldehyde free adhesive systems which are already available and applied in industrial scale for the production of particleboards. Typical performance of pure pMDI adhesives as function of resin amount might be in the range between the upper [217–220] and the lower performance values [5] shown in Fig. 5. Based on reported experimental data lowest resin amounts used were in the range of 2% pMDI. As some studies could pass and others failed P3 [185] threshold values at this adhesive content it seem to be some kind of minimum adhesive spread value. Consequently, as adhesive contents below 2% pure pMDI were not reported in literature it is unclear if resin contents might still be lowered while maintaining P3 particleboard classifications [185]. Combined adhesive systems using small amounts of pMDI (0.2–0.8% pMDI, total of 10% adhesive solids) showed very good performance in terms of IB strength for the case of a urea-glyoxal-based adhesive system [198]. Amounts in the range of 1 to almost 2% pMDI result in acceptable IB values still above 0.4 N/mm² when at total adhesive solid amount of 8–10% is used together with other components e.g. melamine-dimethoxyethanal [203] or urea-dimethoxyethanal [202]. Unfortunately information about the contribution of pMDI to this adhesive performance is not indicated, only that the result

that urea dimethoxyethanal did not perform at all as sole adhesive system, whereas melamine dimethoxyethanal provided considerable strength without pMDI, but was somewhat improved when pMDI was used in addition.

Regarding the group of various polyphenols- or plant protein-based adhesives used in combination with pMDI, the contribution of these natural compounds is more questionable from the point of pMDI view. Within the studies of course some improvement compared to the pure pMDI reference was measured, and the adhesives showed also some kind of performance without pMDI. Opposing these studies, the use of pure pMDI seems to perform in a similar or slightly improved range to most of the mixed adhesive systems. Especially in light of total adhesive consumption, where spread rates around 10–12% adhesive solids have been applied results in 6–8% higher adhesive solids compared to pure pMDI adhesives. It is thus questionable if it is worth using 2.5 to 5 times more adhesive compounds to slightly improve board performance. Additionally, these compounds might be more sensitive to press factor reduction or suffer more if some kind of humidity treatment is involved [224]. Having a closer look this is of course an oversimplification as some approaches might perform above the average [224,226,227].

For industrial application MDI spread rates ranging from 2 to 4% for core layer and 6–8% when used in surface layer have been reported [12]. Other aspects which have to be mentioned are related to cost and availability. As reported earlier (→ 2.3.1) world MDI production volume is in the range of 3.4×10^6 t/a, a number indicating a good availability for industrial use. On the other hand, a comparably high price volatility of pMDI is observable when tracking the price situation of previous years, which might depend on the small number of producing companies. Again related to cost apart of the adhesive, the cost of the needed releasing agents and the reduced press factor should be considered. The latter is further discussed below (→ 7). Emissions from the panel product are not evident, but some issues resulting from toxicity of the adhesive itself and operational safety during panel production should be considered.

Little literature using lap-joint specimens is available as veneers typically fail to bond when pMDI adhesive is used. One systematic evaluation of the effects of process variables on lap-shear strength of pMDI bonded aspen veneers was made available by Smith [229]. He investigated the influence of press temperature, bond time, moisture content, open assembly time and resin level on TSS using an ABES apparatus. Despite the overall findings related to their aim of the study that TSS increases with press temperature, bond time, open assembly time and moisture content, and decrease with resin level, it was surprising that the overall TSS level surpassed 2 N/mm² only for single cases. Thus the TSS measured with the use of such experimental set ups is substantially below the levels of traditional adhesives (compare Fig. 4), whereas the performance of the board products is known to be fully comparable.

6.3. Lignin-based adhesive systems

Studies investigating particulate-based boards with adhesives possessing a dominating amount of kraft lignin (→ 4.2.1.1) or liginosulfonate (→ 4.2.1.2) in the adhesive mixture were reported in the following studies. A recent review summarizing, beside others, the development of lignin-based adhesives is available in Hemmilä et al. [21].

Philippou et al. [230] achieved highest IB strength of 0.86 N/mm² using a press factor of 32 s/mm together with very good moisture resistance. As wood particle feed material they used hydrogen peroxide activated wood particles, a treatment identified to be crucial for achieving mechanical properties of the produced panels. These particles were crosslinked using a spread rate of only 7% adhesive solid, containing a mixture made of 60% ammonium liginosulfonate and 40% furfuryl alcohol (→ 2.4.4) for their best combination. Using 70% liginosulfonate and 30% furfuryl alcohol IB value increased from 0.48 N/mm² for 3% adhesive solids up to 0.96 N/mm² when 11% adhesive

solids were used. Ferric chloride and maleic acid ($\rightarrow$ 2.8.2) were investigated as catalysts but did not show a positive effect. Without using furfuryl alcohol, IB strength dropped to 0.32 N/mm^2 . Johns et al. [231] used a similar concept with nitric acid as wood pretreatment but IB values of only $0.25\text{--}0.36 \text{ N/mm}^2$ could be reached when producing flake boards.

Up to high IB strength of 0.81 N/mm^2 , again using 32 s/mm as press factor, was reached within the studies of El Mansouri et al. [223,224] using glyoxalated ($\rightarrow$ 2.2.1) low molecular mass calcium lignosulfonate crosslinked with pMDI ($\rightarrow$ 2.3.2) and a spread rate of 10% adhesive related to wood solids in the particleboards produced. A reduction of the press factor down to 15 s/mm still resulted in 0.67 N/mm^2 IB using a ratio of 60% glyoxalated lignin and 40% pMDI, corresponding to a total of 4% pMDI related to dry mass of wood. See the discussion for isocyanate based adhesives ($\rightarrow$ 6.2). This adhesive mixture achieved additionally a considerable IB strength of approx. 0.2 N/mm^2 after 2 h of panel water-boil using the higher one of the mentioned press factors. This value dropped to 0.12 N/mm^2 for 15 s/mm press factor. The influence of spread rate was also investigated: down to 8% adhesive load related to the dry mass of wood in the panel still exterior grade levels could be passed. An adhesive load of 6% (corresponding to a total of 2.4% pMDI related to dry mass of wood) resulted in low IB values after boiling, but still considerable dry IB strength of 0.49 N/mm^2 . As further optimization potential an increase in hot pressing temperature was proposed which was only 195°C for the experiments reported. For the boards produced, a low perforator value of 0.6 mg/100g formaldehyde content was additionally reported.

Using calcium lignosulfonate (60%/40% pMDI, corresponding to 4% pMDI related to wood dry mass) and 32 s/mm press factor Lei et al. [225] achieved IB strength of 0.46 N/mm^2 . By using a mixture of glyoxalated calcium lignosulfonate in addition to mimosa tannin ($\rightarrow$ 4.2.2), and pMDI (55%/20%/25%), an IB value of 0.36 N/mm^2 was reported. A slightly higher IB value of 0.55 N/mm^2 was mentioned by Amaral-Labat et al. [227] when using glyoxalated kraft lignin, cross linked with pMDI (4% related to the wood dry mass) and again using a press factor of 32 s/mm . As adhesive mixture glyoxalated kraft lignin, glyoxalated soy flour ($\rightarrow$ 4.3.1.1), and pMDI (50%/25%/25%; corresponding to 2.5% pMDI related to dry mass of wood) was applied, while achieving IB strength of 0.38 N/mm^2 .

The general advantage of lignin-based adhesives is the lignin availability as a renewable resource lignin from various big scale pulping processes. From the studies available it might also be concluded that lignin-based adhesives work for particleboard manufacture only, when combined with an additional crosslinker, which might be pMDI or furfuryl alcohol. Without the use of such crosslinking agents dramatic reduction in panel performance has been observed. For lignin adhesives using furfuryl alcohol [230] as the crosslinker an oxidative pre-treatment of the wood particles was mentioned to be crucial. This represents a new and thus additional process step obviously causing additional costs. The reported performance of the panel was rated as very good in dry conditions, as well as, after water treatments. Additionally, the low spread rates (3–11% of total adhesive solids, composed of e.g. 70% lignosulfonates, 30% furfuryl alcohol) resulted at least in reasonable dry strength. Only the press factor reported may be qualified as relatively high, but within the studies no effort was made to reduce it. In view of the high mechanical properties it seems reasonable that hot pressing time may be significantly reduced, possibly when combining with some acids as accelerators. The current production volume of furfuryl alcohol is one to two orders of magnitude below the one of pMDI. Same as pMDI, furfuryl alcohol may be classified as toxic component which is also suspected of causing cancer as a pure component. Nothing about possible emissions from cured adhesive systems was reported.

As second pathway, pMDI was used to crosslink various lignin resources [223–225,227]. Kraft lignin and lignosulfonates was pre-treated by glyoxalation in most cases. Comparing with the references

bonded with a total of 4% pMDI reported within the same series of studies, adhesive systems using 10% adhesive content (thereof a total of 4% pMDI) performed up to 20% better in terms of IB strength for some cases. When comparing with other studies using pMDI ($\rightarrow$ 6.2) as main or sole component, the additional use of lignin does not seem to significantly improve performance to justify the dramatic increase in adhesive load when using lignin. It is thus questionable or basically a matter of economic (and possibly ecological) evaluation if a significant reduction in pMDI resin load may be achieved by the utilization of a comparably high quantity of lignin.

Bond performance using thin veneer lap-joints report relatively high shear strength values of approx. 7 N/mm^2 at a hot pressing time of only 5 min [232,233]. Therefore, Liu and Li [233] used demethylated kraft lignin and polyethylenimine (PEI) ($\rightarrow$ 2.6.2) as crosslinking agent (best performance at 1:1 wt ratio). They reached additionally to high dry TSS also a considerable strength after boiling the joints. A moderate hot pressing temperature of 120°C was used in their study. Li and Geng [232] used kraft lignin together with polyaminoamide-epichlorohydrin (PAE) ($\rightarrow$ 2.6.1) as crosslinking agent (best ratio indicated to be 3:1) hot pressed at $140\text{--}160^\circ\text{C}$. Again comparably high water resistance was reported. Also a shorter hot pressing time as low as 1 min was investigated, which resulted in TSS of still more than 3 N/mm^2 for a lignin to PAE ratio of 5:1. Both studies had to apply relatively high amounts of liquid adhesives ($420\text{--}600 \text{ g/m}^2$) due to the low solid content of only 16–20% of adhesive systems, which might be seen as some critical point for this adhesive system, when particleboard production is intended.

Adhesives using sorghum lignin and extruded sorghum lignin blended with soy protein (isolated or modified) are shown by Xiao et al. [234]. Again relatively high TSS of $6.2\text{--}6.6 \text{ N/mm}^2$ could be achieved, but using a comparably long hot pressing time of 15–20 min at 104°C hot pressing temperature and by using 3 mm thick veneers.

6.4. Tannin-based adhesive systems

Pizzi [13,125,235] and his group are probably the driving force for studies related to and developments with tannin ($\rightarrow$ 4.2.2) based adhesives. Out of a series of studies they [236] achieved best performance in terms of IB strength and press factor by using quebracho tannin hardened with tris(hydroxymethyl)nitromethane (TN [126–11–4]) and/or the use of additional silica. For a variety of these adhesive mixtures IB strength in the range of $0.5\text{--}0.8 \text{ N/mm}^2$ and 8–15% thickness swelling were achieved at comparably short hot pressing times of 14–15 s/mm. Best IB values for tannin systems are obtained when TN was used as a formaldehyde source which enables crosslinking. As a microbiocide TN is produced by reacting nitromethane with formaldehyde [237] and acts by releasing trace amounts of formaldehyde. According to the definition given in the introduction it is therefore not considered to be a formaldehyde-free adhesive. However, it is still worth of being mentioned as the authors' claim that TN does not lead to aldehyde emissions. According to their explanation, TN decomposes partly during board pressing but when the boards cool down after the adhesive curing, the equilibrium shifts back towards the formation of TN. Any small amounts of free formaldehyde are trapped in TN and shouldn't contribute to emission any longer.

In an earlier work auto-condensation of various tannin sources (40% aqueous solution) using a press factor of 37.5 s/mm was investigated [238]. Pecan nut pith (IB strength: 0.7 N/mm^2) and pine bark (IB strength: 0.35 N/mm^2) tannin catalyzed by a lignocellulosic substrate performed significantly better than mimosa (IB strength: 0.18 N/mm^2) and quebracho tannin (IB strength: 0.09 N/mm^2). The latter ones needed additionally a weak Lewis acid as alkali dissolved silica to induce auto-condensation, whereas pecan nut pith tannin resulted still in considerable IB strength of 0.4 N/mm^2 when the press factor was reduced to as fast as 10 s/mm .

Pine tannin extract with glyoxal ($\rightarrow$ 2.2.1) alone, or glyoxal and

triacetin [226] at different ratios reached IB 0.44 N/mm^2 at a press factor of 32 s/mm . IB could be increased to 0.6 N/mm^2 by using glyoxal together with pMDI ($\rightarrow 2.3.2$) (2.5% based on dry wood mass).

In a patent [239], again the use of pecan nut and mimosa tannin is described using additionally SiO_2 , AlCl_3 , H_3BO_3 . Here IB values of $0.55/0.48 \text{ N/mm}^2$ using a press factor of 37.5 s/mm at 185°C have been indicated. Various other studies with lower IB values in the range of $0.16\text{--}0.4 \text{ N/mm}^2$ using comparable high press factors of $32\text{--}37.5 \text{ s/mm}$ were achieved by using pine and mimosa tannin with furfuryl alcohol ($\rightarrow 2.4.4$) as crosslinker [240]; or maritime pine tannin [241,242].

Thebault et al. [243] used ozonolysis and reduction of sunflower oil ($\rightarrow 4.5$) (10%) to produce aldehydes, which were used to form resins with radiata pine tannin (90%). Using again comparably high pressing factors of 32 s/mm IB strength of rather low 0.22 N/mm^2 were reached.

Compared to lignin the two main differences from the view of particleboard application are noticeable. One is a difference in availability with world tannin production volume being about one order of magnitude below that of lignin, whereby for the case of lignin still huge amounts aren't made available yet. The second is related to the performance of produced products, which is significantly depending on the tannin source (plant species and type) used. In contrast to lignin based adhesives, most tannin-based adhesives reported here react and perform to some degree without the use of pMDI, which becomes evident when looking at the studies reporting on autocondensation of tannin. This pathway might be an interesting one in the light of the achievable low pressing factor of only 10 s/mm , while still fulfilling standard requirements for interior applications [238]. When using tannin for autocondensation the limited resistance to moisture shall be mentioned. As second one the tannin resource has to be discussed. Only pecan nut pith tannin reacted fast enough and performed in an appreciable range, whereas other tannin sources performed significantly inferior. Pecan nut pith tannin might be considered as tannin source only locally occurring in Southeast US with limited availability.

The strategy of curing quebracho or mimosa tannins with TN [236] might be interesting from performance view, but it is still questionable if the compounds used may be considered as formaldehyde free, as already discussed before. Curing tannin with glyoxal [226] resulted in acceptable performance, but it is questionable if the rather long hot pressing time could be reduced to an acceptable level. Similar as for other adhesive systems (e.g. $\rightarrow 6.3$) the additional use of a considerable amount of pMDI was able to bias the performance. When using pMDI at such amounts (e.g. 2.5% based on wood dry mass as used in the cited study) the contribution of the tannin compound might become inferior (compare also discussion in $\rightarrow 6.2$) and the application of tannin might become questionable from economical point of view (compare also $\rightarrow 6.3$).

One study [244] on Douglas fir tannin together with polyethylenimine (PEI) ($\rightarrow 2.6.2$) as crosslinker (2:1) was available using veneers as adherent hot pressed for 5 min at 140°C . High TSS of 6 N/mm^3 could be reached by using low 12% solid content in the adhesive mixture which resulted in high necessary spread rates of 400 g/m^2 . Similar to other low solid content adhesives the high amount of water represents an issue when particleboards production is intended.

6.5. Plant protein-based adhesive systems

The development of a commercial soy-based adhesive was started by Kaichang Li of the Oregon State University, who claimed to be inspired by mussel protein. Marine adhesive proteins are strong and water-resistant, but also expensive and not readily available. As these proteins contain high amounts of 3,4-dihydroxyphenylalanine (DOPA) [245] these amino acids were grafted onto inexpensive and abundant soy protein, whereby the adhesive properties of soy protein were enhanced [246]. Next to grafting of DOPA, also other phenolic hydroxyl functional groups can be added to the soy protein ($\rightarrow 4.3.1.1$) structure [247]. However, when grafting DOPA onto soy one is building up plain

DOPA chains on the outside of the chain and the “curing” of mussel protein in nature is accompanied by a chain of enzyme reactions. Instead of modifying the soy protein, a synthetic crosslinking agents has been introduced. The commercial adhesive contains polyamidoamine-epichlorohydrin (PAE) ($\rightarrow 2.6.1$) Kymene as a curing agent. The soy-based adhesive consisting of “about 87% of soy protein and 13% polyamide resin” has been introduced by Columbia Forest Products to replace UF resins in the production of US American interior grade plywood [248]. The plywood produced thereof, named PureBond®, represents the largest usage of renewable formaldehyde-free binders in the wood working industry, although the critical ingredient of the adhesive is still derived from fossil fuels. By the end of 2007, all seven plywood hardwood plants of Columbia Forest Products already converted to the soy based adhesive “SoyAd™”, produced by Ashland [249]. However, due to their high viscosity, these adhesives are not suitable for the production of particleboards. Several studies are based on this concept and suitability for particleboard production is stated by Vnucec et al. [214]. In the review of Gui et al. [250] the system OZERO® is indicated to be used to produce particleboards, and the adhesive SOYBABY® [251] is reported to be used for industrial MDF production in China. However, technical data about the process and resulting products of these soy-based adhesives for particleboard panels were not available.

Plant protein based adhesives directly used to produce particleboards reported in literature show enormous differences especially regarding press time. Coated wood particles with soy flour (20% slurry) and water, which were dried for 1 h to reach 2% moisture content, following by a blending of these particles with polyethylenimine (PEI)-maleic anhydride-NaOH solution ($\rightarrow 2.6.2$, $\rightarrow 2.8.2$) have been studied by Gu and Li [252]. A chosen press factor of 16 s/mm showed IB strength of approx. 0.75 N/mm^2 at 170°C hot pressing temperature. Reducing the press factor to 12 s/mm resulted in a decrease in IB strength to approx. 0.45 N/mm^2 . Depending on the density used best IB value reached almost 0.8 N/mm^2 for 800 kg/m^3 or 0.6 N/mm^2 with 700 kg/m^3 as board density.

Various variations of glyoxalated ($\rightarrow 2.2.1$) soy flour ($\rightarrow 4.3.1.1$) crosslinked with pMDI ($\rightarrow 2.3.2$) (4% related to dry wood mass) were prepared [227] and resulted in high IB strength of $0.72\text{--}0.74 \text{ N/mm}^2$ when using 32 s/mm for hot pressing. Comparably high adhesive viscosity of $1200\text{--}1760 \text{ mPa}\cdot\text{s}$ was mentioned for soy-glyoxal solutions possessing 30% resin solids. No further precise information was provided on the measure taken for the high water content after resins application. Through addition of tannin ($\rightarrow 4.2.2$) the pMDI amount could be reduced to 3% without a loss in IB strength. Fast press factors of 9.4 s/mm still resulted in IB strength of 0.47 N/mm^2 using again a total of 3% pMDI. Defatted soy flour and urea ($\rightarrow 4.1.1$) [253] reached an IB strength of 0.28 N/mm^2 at a press factor of 32 s/mm . Upon the addition of chest nut tannin ($\rightarrow 4.2.2$) and glyoxal, the IB value increased to 0.35 N/mm^2 .

Krug and Tobisch [128] extensively reviewed beside others suitability of various protein-based adhesives for wood-based products and compiled experimental data from studies which are hardly accessible: thereof data from Kehr [254] using 67% soy protein together with 33% casein ($\rightarrow 4.3.2.2$) as one adhesive and another one based on wheat gluten Detailed results for various process conditions (adhesive solids, pressing time or particle humidity) are additionally indicated.

The combination of soy protein and casein an expected dependency of resin load and IB strength could be shown, with highest changes between 9% resin load (IB strength: 0.45 N/mm^2) to 15% resin load (0.68 N/mm^2). Interestingly the wheat protein based adhesive showed only little dependency of IB strength ($0.69\text{--}0.73 \text{ N/mm}^2$) on pressing time within the range ($22\text{--}56 \text{ s/mm}^2$) observed, but was significantly biased by the moisture content of the particles prior to pressing (9–25% moisture content resulted in IB strength $0.25\text{--}0.52 \text{ N/mm}^2$ and thickness swelling of 18%–9%) [385]. For both adhesive systems, wheat and soy based ones, higher moisture content of the particles resulted in

better panel performance. The typical step of pre-drying of particles has not been reported within these studies, therefore a need for longer pressing times compared to conventional adhesive systems was indicated.

In the patent of Thames et al. [255] a mixture of isolated soy protein 61%, and several additives such as nitric acid 9%, kraft lignin 4% ($\rightarrow$ 4.2.1.1), calcium oxide 3.7%, sodium benzoate 3.7%, zinc sulfate heptahydrate 0.6% were used. They claimed to achieve IB values of 0.59 N/mm² when using a press factor of 17 s/mm. Density of the board was not indicated; but for their own references mentioned within the same study typically 720–785 kg/m³ were reported. Also this system contained 70% of water in the adhesive mixture, requiring particle drying after adhesive application. Including all additives an extremely high adhesive solid content of 18% for the case of face layer particles and 23% for core layer particles were used.

In their studies Khosravi et al. [256,257] produced particleboards using 10% binder amount based on dry mass consisting of either soy protein isolate or wheat gluten ($\rightarrow$ 4.3.1.3) with the aim of investigating various process conditions and short press factors of 10 s/mm. The results reveal that using the dispersion as an adhesive is preferable to using the dry protein and also the preparation parameters of the dispersion influenced results. As the adhesives had rather low solid contents (10–22%) drying of the coated particles was again necessary for some cases. For the best case IB strength of 0.52 N/mm² was achieved but combined with high water absorption and thickness swelling (> 50%). In contrast to the studies reported by Prasittisopin and Li [258] relatively high IB strength of 0.63 N/mm² could be achieved when using extremely long press times of 90 s/mm only. At the example of a flake board soy flour and PAE as curing agent was used. Despite of the high press factor pre-drying of particles seemed to be necessary. Slightly shorter but still long pressing times (50 s/mm, IB strength: 0.4–0.6 N/mm²) were needed for wheat protein combined with PEG as reported by Metzger [259].

Again similar performance was reached by Vidal et al. [204] using isolated soy protein (SPI) with NaOH as the only additive. They reached an IB value of 0.52 N/mm² when using 42 s/mm as press factor. Extremely high thickness swelling (99% thickness increase) after 24 h water immersion was observed.

Zhang et al. [260] described in their patent a combination of soy flour with a copolymer styrene and maleic anhydride together with triethanolamine. Their produced particleboards reached an IB strength of 0.4 N/mm² at a press temperature of 210 °C and a press factor of 40 s/mm.

The commercial availability of the vegetable protein based adhesives including PAE as crosslinker for an industrial product, namely plywood, may be regarded as a general advantage as it could be shown that the adhesive is already available in corresponding quantities and is fulfilling the needs of a large scale industry.

As concept with the shortest pressing time [227] within this group for discussion the reader is again referred to the section of pMDI based adhesives ($\rightarrow$ 6.2). Comparably short hot pressing time was reached by Khosravi et al. [256,257], who achieved additionally reasonable IB strength. However, as a clear disadvantage of this concept it has to be mentioned that their adhesive system does not include any crosslinker and showed therefore rather poor humidity resistance.

In another approach [252], using a standard reagent typically used in paper industry - PEI as crosslinker seems to be another possible route out of this adhesive group. The high resin load needed for their adhesive [255], necessary because of a low solid content, may be regarded as a clear disadvantage as such a high load would result in long drying times. In the review of Gui et al. [250] the high viscosity of resins, and/or the low solid content of only 28–40% was identified as main issue for this adhesive group when particleboards have to be produced. For most studies related to particleboards, as mentioned here, some pre-drying of sprayed particles as additional process step was necessary to lower the induced moisture after adhesive application. A special focus on

dispersibility, solid content and viscosity can be found elsewhere [261]. The use of dispersions is thus preferable [256,257] and sodium hydroxide solution as dispersing and denaturing agent was also recommended [262].

As mentioned before, plenty of literature is available especially for using soy-based adhesives applied on veneer based specimens. These systems are well investigated and resulted in commercial availability and also wide use in plywood and flooring industry [214].

Using maple veneer, a spread rate of 100g/mm² on a dry basis and only 5min hot pressing at 120 °C high TSS values of 9 N/mm² could be achieved with isolated soy protein with MgO (6:1) [263]. Even after water storage or boiling test and subsequent re-drying values in similar range have been reported. In wet stage TSS dropped to 1 N/mm². The adhesive applied here had a low solid content of 27% only, which was increased to 36% by using soy flour again with MgO (6:1) resulting in TSS of 6.8 N/mm². Again good values after water storage and boiling followed by re-drying were achieved. However, soy flour alone just performed in dry conditions same as an adhesive made of insoluble carbohydrates with MgO which showed lower TSS of 3.5 N/mm² in dry conditions. Further references using soy protein as main resin component are not described in detail due to long press times [361,370].

An extremely fast and humidity resistant adhesive was proposed by Wang et al. [264]. They used canola protein isolate ($\rightarrow$ 4.3.1) modified by grafting poly(glycidyl methacrylate) chains (GMA). At a hot press temperature of 110 °C already after 1min some kind of plateau in TSS could be achieved. 4 min hot pressing time resulted finally in TSS of 8.5 N/mm². Best results were achieved at a GMA grafting degree of 82%.

Several studies refer to the concept of Li [265] described above using polyamidoamine-epichlorohydrin (PAE) as reactant to bond soy protein which usually result in high TSS values in dry state ranging between 5 and 7.5 N/mm². Lorenz et al. [144] were investigating various soy resources co-reacted without and with PAE in a quantity of 5% based on dry adhesive solids. Best TSS was achieved using a commercial soy isolate together with PAE. Additionally a wet strength of 5 N/mm² was recorded after only 2min of hot pressing time at 120 °C. Similar results with higher pressing times (5min) were achieved by Li et al. [266] using a soy protein isolate combined with 12.5% of PAE still resulting in TSS of 6 N/mm² after boiling and re-drying, and 2 N/mm² when performed in wet conditions. Brady et al. [267] reported in their patent various protein sources i.e. animal and vegetable based ones. Soy was mentioned to be particularly useful. Additionally to PAE they used a non-urea diluent for achieving lower viscosities of the formulation, which would be particularly favorable for particleboard or MDF production. The viscosity reduction should be achieved by adding a compound possessing multiple alcohol functionalities such as glycerol. Several other studies again reported relatively short press times using soy bean based adhesives [268,269]. In their study Hunt et al. [268] observed a negative influence of the dispersion aids on wet strength of soy flour based adhesives, while this was not observed for soy concentrates. Additionally, promising high temperature performance could be observed using block shear tests at 230 °C [269].

In another study PEI in combination with isolated soy protein and additionally 10% maleic anhydride ($\rightarrow$ 2.8.2) was used [270]. Similar systems were reported [271,272] using palm kernel, but both investigating plywood which wasn't in focus of the present study.

Still high TSS values were achieved using modified defatted soy flour combined with a range of synthetic adhesives (UF based, polyvinyl acetate adhesive (PVAc $\rightarrow$ 4.6.1),...) using short hot (120 °C) pressing times of only 2.5min (3 mm veneer thickness) [273]. Wang et al. [274] were successfully modifying isolated soy protein with sodium dodecyl sulfate (SDS) and achieved high TSS using 10min pressing time (180 °C). Investigating the influence of pH conditions on modification procedure they found significantly higher wet strength values when modification was performed between pH 4.6 (3.6–5.6), close to proteins isoelectrical point. Cottonseed protein [275] was again

modified with SDS but pressed for 20 min at 80 °C reached only TSS 3.1 N/mm². Still considerable dry and wet strength values were reached when de-fatted soy flour was modified by 5% of 2-octen-1-ylsuccinic anhydride as unfolding reagent [276] using 5 mm thick lamellas which were hot pressed for 10 min at 150 °C. Various versions of cottonseed based proteins (meal, also water washed, and cottonseed protein isolate) were investigated by He et al. [277–279]. Rather long pressing times of 20 min resulted still in high TSS while water resistance could be improved by using tung oil (→ 4.5) (wet TSS 3.5 N/mm²). Cottonseed meal was already used in very early studies [280] comparing its properties with those of peanut meal and casein (→ 4.3.2.2).

Modification of de-fatted soy flour [281] or isolated soy protein [282,283] with urea has been reported too, resulting in moderate TSS values. Wescott and Birkland [284] claimed improved dry and wet strength for urea-denaturated soy flour in their patent. Slightly better values (TSS 4.7 N/mm²) were achieved by using guanidine hydrochloride instead of urea (→ 4.1.1) [282] together with wet shear strength values of less than TSS 2 N/mm². A similar comparison using urea, guanidine, alkali, SDS or a heat treatment is presented by others [275,283].

Furthermore a variety of modification procedure for proteins can be found in literature: various soy proteins reported contain modification by or addition of S-acetyl cysteamine or dopamine [247], nano-scale montmorillonite (MMT) or polyisocyanate [285], epichlorohydrine (→ 2.5) and ammoniumhydroxide [286] and epoxy resins [287]. Glutaraldehyde (→ 2.2.4) was used to modify grain protein [288] or mustard seed protein under alkaline conditions [289]. Calcium hydroxide was added to soy protein isolate [290] which showed significant improvement of both, dry- and wet shear strength at the example of plywood. Further information is available in a recent review [214].

A study rather related to solid wood bonding using 5 mm thick wood lamellas was reporting high TSS of 12.4–14.5 N/mm² [137] using isolated soy proteins or wheat gluten bonded with different citric acid and NaOH hardeners (15 min press time at 110 °C).

As alternative to soy protein, marama protein derived from a South African indigenous oil seed legume was also proposed [291].

6.6. Animal protein-based adhesive systems

In the review from Krug and Tobisch [128], unpublished results from Kehr and Sirch [292] were reported using casein (→ 4.3.2.2) as a reference concept. This casein bonded particleboard resulted in comparably high IB value ranging from 0.64 to 0.85 N/mm² for press times of 22–38 s/mm together with very low thickness swelling of only 8–11%.

Pure caseinate and also caseinate crosslinked with small amounts of enzyme (transglutaminase) at different temperatures were investigated by van Herwijnen et al. [293]. Using high press factors of 52 s/mm at 110 °C resulted in IB value of 0.68 N/mm² without enzyme and 0.75 N/mm² when enzymes were used. By using approx. 10% adhesive content thickness swelling was either improved by high temperature curing (pure casein) or when enzyme crosslinking was involved. Enzyme ideally crosslink the protein at temperatures of 50 °C, the 110 °C were chosen to dry the boards to their final moisture content. Also veneer based TTS values are available for this study showing considerable 5.7 N/mm², however, using a hot press cycle with a total of 21 min pressing time. Additional casein-based resins [383] and aqueous polymer-isocyanate wood adhesives comprising whey protein isolate [363] needed long press time.

Using the thermoplastic properties (setting at cold temperature) of bone glue (glutin → 4.3.1.3) at 10 and 20% adhesive amount prepared particleboards achieved IB strength of 0.56 N/mm² [294]. A long overnight pressing time was used which was chosen due to the necessity of cooling down the panel. By using hot-pressing combined with a technical cooling the total cycle could possibly be reduced to processing times comparable with those described for thermoplastic processable

polymers (→ 6.12).

Opposing the moderate pressing time with the considerable IB values [292] some further improvements in hot pressing time might still be possible. On the other hand a high price of pure casein was mentioned [128] generating the need of substituting major parts of the animal protein with more economic compounds such as plant based ones (e.g. → 4.3.1.1).

Both further particleboard concepts, the one based on crosslinked casein [293] as well as the one for bone glue [294] seem to be relatively far away from industrially relevant hot pressing times. For the prior one some optimization potential by genetic modification of the enzymes may be expected.

Spent hen protein applied on veneer lap joints [295] modified by urea or sodium dodecyl sulfate SDS showed high dry TSS of up to 8 and 9 N/mm², and still considerable wet strength of approx. 3 N/mm² using short 3 min press time at 110 °C.

Dry blood powder (→ 4.3.2.3) containing 80% protein content was used with an antifoaming agent and NaOH at long 60 min press time at 70 °C [296]. For this adhesives TSS of 4 N/mm² could be achieved. Using fresh cow blood and beside other chemicals additionally ethylenediaminetetraacetic acid (EDTA) [297] an application for plywood using a hot pressing time of 5 min at 120 °C was presented which achieved results comparable to a PF reference. In this patent a possible application for particleboard was described [298] also.

6.7. Starch-based adhesive systems

Using extracted native and carboxymethyl modified starch (→ 4.4.1) of oil palm trunk as a powder Selamat et al. [299] achieved high IB strength of 1.0 and 1.3 N/mm², but they used an extremely high press factor of 240 s/mm. Thickness swelling after 2 h was reported to be in the range of high 70%.

Amini et al. [300] used glutaraldehyde (→ 2.2.4) modified corn starch slurry again with a high press factor of 240 s/mm. IB values achieved 0.6–0.9 N/mm² depending on density of PB produced and again relatively high thickness swelling values of 30–35% after 2 h have been reported. In the patent of Eriksson et al. [301] adhesives were proposed using corn starch (10–20 wt %) and a solution of polyvinyl amine (→ 2.6.3) (0.8 wt% based on solid wood). A press factor of 30 s/mm with a hot press temperature of 185 °C resulted in IB strength of 0.6 N/mm². The same authors proposed also corn starch (10% based on solid wood) but this time combined with a polyethylene imine (PEI) (→ 2.6.2) solution (2.3 wt% based on solid wood) and a short press time of 11 s/mm but achieved only an IB strength of 0.2 N/mm².

Using again shorter pressing times of 21 s/mm Tondi et al. [302] investigated combinations of corn starch, sucrose (→ 2.4.2) and tannin (→ 4.2.2). As best IB value 0.4 N/mm² was reported using 53% starch, 13% sugar and 33% tannin at a density of 750 kg/m³. High reactive furan derivatives such as 5-hydroxymethyl furfural (HMF) (→ 2.4.5), hydroxyl-acetyl-furan (HAF) and mono and dihydroxy-dimethyl-furanone (DDF) were hypothesized to be involved in hardening and crosslinking reactions.

Starch can be regarded as relatively low cost, widely available product. Upon heating in contact with water, starch gelatinizes, i.e. the crystalline structure of amylose and amylopectin is broken down to form a viscous suspension. When cooled, the starch molecules, mainly amylose, rearrange themselves in a process called retrogradation to form a gel. Some kind of crosslinking reaction might be necessary when a certain humidity resistance is desired. Such reactions were not analyzed explicitly in the available studies. The two concepts of Eriksson et al. [301] and the one of Tondi et al. [302] report data with the best ration of IB strength and press factor within this group of adhesives. In the first concept, the need of an additional polymer was shown, which was applied as solution as starch alone wasn't able to perform satisfactorily [301]. Adding polyvinyl amine to the main component starch, resulted in appropriate IB value, when a comparable high press

factor of 30 s/mm was used, but no information about shorter pressing time was indicated. Possibly the high IB value of 0.6 N/mm^2 would allow some reduction in press time. On the other hand the contribution of these small amounts of polymer, i.e., polyvinyl amine alone would be very interesting, as without its use IB strength was reduced dramatically by 80%, while changes in starch content in the particleboard did not alter the performance. For the other concept, using again small amounts of polyethylene imine solution, relevant press factors are shown. But for this example performance in terms of IB strength was comparably poor.

In the other concept described by Tondi et al. [302], again starch alone performed very poorly, also when adding sugar up to 30%. Only the addition of NaOH improved properties, even more when tannin was also added. The level of entire performance might be considered as too low in general, as a further reduction in hot pressing time might be needed and the reported density is somewhat over the average tending to increase IB values. Without scientific verification the contribution of some high reactive furan derivatives was hypothesized. In case they are involved in the concept, they are assumed to occur at temperatures above 200°C [221] as discussed later ($\rightarrow 6.8$). Such conditions would be only available when producing very thin boards in combination with long hot pressing times as required for thermoplastic processable polymers ($\rightarrow 6.12$).

The press time of the other concepts [299,300] may be regarded as too long to be considered as relevant for any particleboard production, whereby no effort was shown if a (dramatic) reduction might be possible though.

Veneer lap-joints bonded with starch-g-polyvinyl acetate ($\rightarrow 4.6.1$) latex [303] and an epoxy resin-modified ($\rightarrow 2.7$) corn starch adhesive resulted in high TSS values ranging from 4.5 N/mm^2 to almost 6 N/mm^2 . This was achieved at the optimum hot pressing time of long 25 min at $80\text{--}90^\circ\text{C}$. In wet conditions TSS was still 2.5 N/mm^2 . Best mechanical performance in the range of $5\text{--}10 \text{ N/mm}^2$ were achieved by various other authors [304–308] again using corn starch by using a pressing time of 24 h at room temperature. Similar adhesives and again 24 h pressing time resulting in only 2.3 N/mm^2 [308].

6.8. Sugar-based adhesive systems

The combination of corn syrup, isocyanate, polyols and water, described in a patent by Capps et al. [358], resulted in a resin, which achieved high strength values (IB: 0.8 N/mm) at short press time (12 s/mm), despite of a low proportion of isocyanate in the total particleboard of only 0.7%. With the original aim of producing glass and rock mineral wool Jackson et al. [309,310] proposed in their patents adhesives setting at high temperature based on citric acid ($\rightarrow 2.8.1$), glucose ($\rightarrow 2.4.1$) and a nitrogen source. The product ECOSE® [311] (Knauf Insulation GmbH, Fürnitz, Austria) [312] is commercially available for the products mentioned above. In the patents mentioned previously, the use of such adhesives to produce particle-, MDF and OSB boards is described. As examples in the patent particleboards with a low to moderate density ranging from 550 to 640 kg/m^3 , 12–14% resin load (50% resin solids), and hot pressing temperature of 220°C were mentioned resulting in IB values of $0.4\text{--}0.5 \text{ N/mm}^2$ using a high pressing factor of 50 s/mm. Reducing the press duration by 50% resulted in a total loss of IB strength [362]. The adhesives were described of having thermosetting character with Maillard reaction as a characteristic one producing melanoids.

In a similar approach Umemura et al. [313] investigated particleboards and identified 25% citric acid and 75% sucrose ($\rightarrow 2.4.2$), as an aqueous solution of 59 wt%, as the optimum ratio for adhesives used to produce panels. They used an even higher press factor of 66 s/mm together with resin contents ranging from 5 to 40% and a comparably high density of 800 kg/m^3 . For the case of higher (30 and 40%) resin contents sprayed particles had to be dried before further processing. Particleboards with 30% resin solids showed highest IB values of up to 1.6 N/mm^2 , together with a considerably low thickness swelling value

of only 12%. Reducing the adhesive content to 10% resulted in a significant reduction in IB strength to 0.5 N/mm^2 . In a further approach using again citric acid and sucrose Widyorini et al. [314] reached only IB strength in the range of $0.2\text{--}0.4 \text{ N/mm}^2$ when pressing for 85 s/mm. Similar results were achieved when using only citric acid as adhesive [315]. Boards were also made out of sweet sorghum bagasse particles [316] using 20% of adhesives with different ratios of sucrose and citric acid. Pure citric acid reached an IB strength of 0.9 N/mm^2 and pure sucrose 0.5 N/mm^2 . The best mixtures being 10:90 and 15:85 citric acid to sucrose with up to 1.17 N/mm^2 at a press factor 67 s/mm. It has to be noted that after adhesive application the particles had to be dried at 80°C for 12 h. In a similar approach, boards were made out of nipa fronds by Santoso et al. [340] bonded by maltodextrin (oligomer of glucose ($\rightarrow 2.4.1$)) and citric acid.

Based on a patent of Umemura [317], Zhao and Umemura [221] used wattle (mimosa) tannin ($\rightarrow 4.2.2$) with sucrose in 40% solution and resin contents ranging from 10 to 40 wt%. Due to the high water content re-drying of sprayed particles was again necessary. Relatively independent of the adhesive content IB value between 1 and 1.2 N/mm^2 were reached using a high press factor of 66 s/mm, relatively thin boards of only 9 mm thickness and comparably high density of 800 kg/m^3 . Increasing of press temperature further increased IB value to 1.5 N/mm^2 . As optimum proportion of tannin to sucrose a ratio of 25/75 was identified. Omitting the step of pre-drying resulted in a dramatic loss of IB strength. In a follow up study [318] the influence of press temperature and pressing time was analyzed: higher press temperature and curing time improved properties, whereas a reduction of pressing time to 33.3 s/mm resulted in a dramatic reduction of IB strength to a value of 0.5 N/mm^2 when still using 40% resin solids.

From thermal analysis it was found that reactions take place basically above 200°C and it was assumed that the creation of 5-hydroxymethyl furfural (HMF) ($\rightarrow 2.4.5$) out of sucrose under heat [221] and acidity might occur. Further improvement of properties resulted from an addition of citric acid to the above mentioned mixture of tannin and sucrose, which resulted in a distinct lowering of reaction temperature and less thickness swelling [319]. Thus, already at lower hot pressing temperature significant better IB strength and thickness swelling values were reached, with improved values for both parameters of higher citric acid addition or higher pressing temperature.

In order to investigate the contribution of oil palm trunk components compared to the auto-adhesion of binderless particleboards [320] made thereof, Lamaming et al. [321] used glucose, sucrose, or starch ($\rightarrow 4.4.1$) as additives to extracted and non-extracted oil palm trunk particle material. 20% of such additives were hot pressed for extensive 250 s/mm (800 kg/m^3) and resulted in IB value of approx. 1.7 N/mm^2 for glucose, and 1.9 N/mm^2 for the case of sucrose as additive to non-extracted particle material.

Concluding from the above described articles the typically used compounds for adhesive mixtures are considered harmless, but the reaction compounds formed during hot pressing are hard to classify. Possibly a discoloration has to be expected in view of the production parameters used. From the point of view of a process it seemed to be noticeable that drying of adhesive sprayed particles was identified to be necessary for most cases, representing an additional production step related to current state of the art. Mechanical performance may be considered as potentially high, depending beside of pH on process temperature and processing time. High ($160\text{--}200^\circ\text{C}$) particleboard core temperature was identified for reacting of compounds, representing values clearly above currently achieved core temperatures. Typically this temperature is limited by particleboard humidity combined with steam pressure by approx. 120°C . As discussed later ($\rightarrow 6.12$) in the example of thermoplastic processable polymers as particleboard binders, achieving such high core temperature require either very thin panel thickness or very long pressing times. The hot pressing time for such adhesives does not seem to be limited by a reaction time but rather by the thermal conductivity of the particles.

Veneer lap joints were bonded with beech wood xylan dispersion [322] that were crosslinked beside other compounds with either trimethylolpropane triacetoacetate (AATMP) and dissolved polyvinylamine ($\rightarrow$ 2.6.3) or diluted polyvinylamine as dispersing agents. By using moderate hot pressing conditions of 120 °C and very short hot pressing times of only 2.5 min TSS of 5.5–7.6 N/mm² could be achieved. In wet conditions high TSS values of up to 4.5 N/mm² could be measured. Same authors [323] used various gums (locust bean gum, guar gum, xanthan gum and tamarind gum) dispersions and same conditions as mentioned before but 10 min hot pressing time. The bonds showed TSS of up to 7.5 N/mm². Due to the high viscosity of the adhesive only 6 wt% solid content could be used. However, adhesives fulfilled some benchmark values according to EN 204 for indoor application of non-load carrying solid wood bonding.

6.9. Animal polysaccharide based adhesive systems (Chitosan)

To our knowledge no direct application of animal polysaccharide as particleboard adhesives are available in literature. Using veneer based lap-joints the following approaches can be found. A chitosan phenolic-laccase system ($\rightarrow$ 4.4.2) [324] was applied as wood adhesive to bond veneer lap-joints. Hot pressing for 5 min at 105 °C resulted in TSS of relatively low 1.8 N/mm². By using double lap-joints bonded with 6% of high molecular weight chitosan, 1% of glycerol, and 5 mmol/L of trisodium citrate dehydrate ($\rightarrow$ 2.8.1) as adhesive TSS of 6 N/mm² in dry and 1.6 N/mm² in wet conditions were reached [325]. Moreover, pressing was performed overnight at 40 °C.

Also examples of plywood bonded with chitosan-based adhesive can be found in literature [326]. Chitosan powder ($\rightarrow$ 4.4.2) dissolved in 1% acetic acid solution or chitosan with addition of glucose ($\rightarrow$ 2.4.1) [327] was applied in three-layer plywood. The bonding properties of the Maillard-reacted chitosan showed a bond strength increased gradually with increasing glucose, which however strongly depends on the chitosan type.

6.10. Plant-oil based adhesives

Acrylated epoxidized soy oil ($\rightarrow$ 4.5.1) with acrylic acid [328] was mixed with hydroquinone, and 1,4-diazobicyclo[2.2.2]octane, acting as free-radical inhibitor and catalyst, respectively. Relatively long pressing time of 48–62 s/mm at 200 °C resulted in IB strength depending on pressing time between 0.47 and 0.55 N/mm² using wheat straw particles. The adhesive may be described as comparably complex, but it outperformed standard urea-formaldehyde resins regarding IB value and thickness swelling, which was attributed to the high compatibility of the adhesive to the wheat straw particles used. It may thus be regarded as some alternative when special (non-wood) particles have to be used.

Starting with a patent of Brady et al. [267], who propose soy oil together with polyamidoamine-epichlorohydrin (PAE) ($\rightarrow$ 2.6.1) and glycerol as adhesive which was applied on lap joints. Applying a short hot pressing time of only 2 min at 120 °C resulted in moderate TSS of 3.4–5.6 N/mm².

Basically all of the subsequent studies testing oil based adhesives needed an overnight curing duration (up to 24 h) at room temperature to create some kind of polyurethane adhesive. Therefore, castor oil ($\rightarrow$ 4.5.3) and castor oil based polyols [329,330] together with toluene 2,4-diisocyanate (TDI) ($\rightarrow$ 2.3.3) and some combinations using additional glycosylated potato starch ($\rightarrow$ 4.4.1) or glycerol and sebacic acid were investigated using veneer lap-joints, which resulted in TSS of 6–6.3 N/mm². Castor oil was also used in another study [331] were lower TSS of 2 N/mm² was determined. Another investigation examined the use of deoxidized palm oil ($\rightarrow$ 4.5.2) (by phthalic acid) based polyester polyol together with polymeric methylene diphenyl diisocyanate (pMDI) ($\rightarrow$ 2.3.2), which resulted in TSS of 5.3 N/mm² [332]. Various oils (castor oil, soy oil or rice-bran oil ($\rightarrow$ 4.5.4)) together with toluene sulfonic

acid (catalyst sulfuric acid) and ethylene glycol were used [333], whereby best values were reported for castor oil (up to TSS 4.2 N/mm²). Again palm oil-based polyester polyol reacting with pMDI and TDI were used to produce PU adhesives for wood bonding (TSS 5.1 N/mm²) [334]. Additional oil plant based polyurethane resins were investigated by Maminski et al. [373,374].

6.11. Various other adhesive systems

Pizzi [335] reported results from company literature from Miller and Shonfeld (2002), who used ozonolysis-reduced cashew nut shell liquid (CNSL) ($\rightarrow$ 4.2.3) to manufacture particleboards and lap-joints, whereby particleboards were reported to reach IB strength of 1.05 N/mm². Unfortunately no press time was reported here. However, comparable short pressing time was applied for the lap-joints, which were bonded at 120–180 °C for 3 min and resulted in TSS of 6.8 N/mm². The ozonolysis was performed in order to produce cardanolaldehyde and hydroperoxide, the latter was further reduced to another aldehyde. The two aldehyde groups and the reactive sites on the aromatic ring of the cardanol containing liquid, react readily to form a crosslinked network during hardening. Altogether the approach is difficult to evaluate, as hot pressing times for particleboard applications are not available. Pizzi [335] discussed in his article that industrial press times should be achievable.

Philippou et al. [230] proposed hydrogen peroxide pre-activated wood particles and bonded these with furfuryl alcohol ($\rightarrow$ 2.4.4) using 7% adhesive solids. Using only furfuryl alcohol as adhesive IB value resulted in 0.71 N/mm² and thickness swelling in cold water of 26% (24 h). The latter was significantly reduced to approx. 10% when furfuryl alcohol was combined with some amounts of lignosulfonate ($\rightarrow$ 4.2.1.2), which was described and discussed in a prior section ($\rightarrow$ 6.3). Beside other systems Johns [228] proposed also furfuryl alcohol based adhesives which performed only when combined with an isocyanate based one.

Cellulose nanofibrils (CNF) were used to produce particleboards in a wet process by Amini et al. [336]. An IB of 0.45 N/mm² was reached using 85% wood particles and 15% of CNF at a press factor of 84 s/mm. When using 3% PAE ($\rightarrow$ 2.6.1) as crosslinking agent in addition, mechanical properties increased significantly.

A poly(vinyl acetate) (PVAc) ($\rightarrow$ 4.6.1) adhesive was used to produce particleboards by Kowaluk and Fuczek [337]. The adhesive had to be diluted in water to reduce its extremely high viscosity, resulting in a final resin solid content of approx. 26% only. As IB value 0.27 N/mm² was indicated, but no detailed information regarding process conditions were available, instead they were mentioned to be close to industrial ones. Compared to standard particleboard adhesives PVAc may be regarded as rather expensive. The high viscosity of the resin may cause procedural issues as indicated by the significant amount of water needed for diluting the adhesive. On the other side no chemical curing is taking place but the adhesive is setting by drying. Also the end product might offer complete different properties due to the thermoplastic character of the adhesive. Furthermore, Peshkova and Li [379] investigated poly(4-vinyl phenol) as wood adhesive, however the press time needed was 50 min.

Particleboards produced with a commercial acrylic resin ($\rightarrow$ 4.6.2) (multifunctional methacrylic monomer, ethoxylated bisphenol A dimethacrylate) was shown by Amazio et al. [338]. By using a high press factor of approx. 40–50 s/mm at 180 °C IB of 0.47–0.56 N/mm² were reached, representing higher values than the urea-formaldehyde reference adhesive. Applying 10 wt% resin solids based on wood dry mass thickness swelling in the range of 20% was measured, again lower values compared to the urea-formaldehyde reference. No optimization of hot pressing time was reported. Thus the authors claim that the adhesive is able to undergo a fast curing process in presence of peroxides, which was supported by thermal analysis data.

Citric acid ($\rightarrow$ 2.8.1) as binder was used to produce boards with

sweet sorghum bagasse particles [316, 367] using 20% of citric acid reached an IB value of 0.9 N/mm^2 at a press factor of 67 s/mm. In a further studies, bamboo-based particleboards [315,339] were produced at a press factor of 85 s/mm using 15% and 30% resin content. IB strength ranged from 0.35 to almost 0.6 N/mm^2 , together with very low thickness swelling (2–9%) depending on particle type and resin content. The authors explained the result that carboxyl groups from citric acid were ester linked with hydroxyl groups from bamboo. Using starch as an additive to citric acid IB value up to 1.3 N/mm^2 could be reached [339]. Citric acid as a pure binder for nipa fronds particleboards reached 0.35 N/mm^2 at 60 s/mm [340]. In all studies particles had to be re-dried before hot pressing to reduce moisture content.

Particleboard produced without the use of an additional adhesive may also be a pathway to produce boards. Premodification of particles may be needed, as example Suhasman et al. [341,342] oxidized lignocellulosic particles with hydrogen peroxide and iron (II) sulfate. They reached IB values up to 0.49 N/mm^2 at high press factors of more than 100 s/mm. Moreover, particle materials inherently containing certain chemical compounds required for self-bonding adhesion may be an alternative for premodification of particles. As example Hashim et al. [320] used oil palm biomass as feed material reaching sufficient IB values, however at press factors of more than 800 s/mm. Furthermore flax, jute, kenaf, coconut husk, bagasse or other materials were also used as reviewed elsewhere [343].

Polyketone as main component [344,345] was used as wood adhesive together with proteins (*Jatropha curcas* L. ($\rightarrow$ 4.3.1.2) and soy ($\rightarrow$ 4.3.1.1)) acting as reactive component. Veneers of 4 mm thickness were coated with aqueous emulsions consisting of proteins and chemically modified thermosetting aliphatic polyketone. Hot pressed for 5 min at 200°C resulted in rather low TSS of $2.7\text{--}3.4 \text{ N/mm}^2$ depending on the protein used.

6.12. Thermoplastic processable polymers

arlborn et al. [359] investigated the influence of processing conditions of thermoplastically processable polymers. They obtained IB strength of more than 2.0 N/mm^2 for extruded maleated polyethylene based particleboards, whereas 1.2 N/mm^2 could be reached for non-extruded boards. A high amount of polymer related to wood (2:8) was needed together with a high press factor of 70s/mm.

Li et al. [346] mixed creeping wild rye particles with 20% high-density polyethylene (HDPE) ($\rightarrow$ 4.7.1) and 2.8% polymeric methylene diphenyl diisocyanate (pMDI) ($\rightarrow$ 2.3.2) to produce particleboards. In order to provide sufficient time to melt HDPE high 92 s/mm were used as press factor, which resulted in high IB strength of 0.89 N/mm^2 . Recycled low-density polyethylene (LDPE) was used by Idris et al. [347] to bond particleboards of water melon peels. In their experimental design up to 70 wt% of LDPE was used. Best IB values of 0.58 N/mm^2 were reached at 60% LDPE content. At 30% LDPE the panel showed

moderate IB strength 0.35 N/mm^2 . A wood plastic composite using a flat-press process was reported by Hung and Wu [348], which is the same process type as used for particleboard production. Hereby esterified bamboo particles were combined with HDPE using a press cycle consisting of heating for 40 s/mm (200°C) and subsequent cooling for 60 s/mm to reach 25°C panel temperature. The use of 20% HDPE resulted in IB strength of 0.3 N/mm^2 which was increased to IB strength of 2 N/mm^2 for 40% HDPE, having a comparably high density of $800\text{--}890 \text{ kg/m}^3$. A significant increase in IB strength was shown when acetylated wood was used, which improved interfacial adhesion of wood to HDPE.

Polystyrene ($\rightarrow$ 4.7.2) (35% solids) again combined with pMDI (3%) as reactive component was used by Xu et al. [349]. These systems are a combination of two binders, as it is very unlikely that HDPE or polystyrene react with pMDI. They reached IB strength of 0.78 N/mm^2 using again high 38 s/mm as press factor at 190°C . Some kind of particulate-based boards using polyethylene terephthalate (PET) ($\rightarrow$ 4.7.3), expanded polystyrene (EPS), or polyethylene (PE) were produce as well [350]. Best results were achieved by using 50% EPS and 50% wood, dissolved in gasoline before.

Hu and Guo [351] produced wood fiber composite boards using polylactic acid (PLA) ($\rightarrow$ 4.7.4) fibers. They also added ammonium lignosulfonate ($\rightarrow$ 4.2.1.2). The high press factor of 84 s/mm at 170°C resulted for the best cases in IB value of up to 1.7 N/mm^2 when 70% wood fiber, 30% PLA and addition of further 10% ammonium lignosulfonate was used.

Composites using again a flat-press process were produced by Wu et al. [352] using bamboo particles and ground PLA pellets in 1:1 wt ratio. They investigated beside others influence of hot pressing temperature and cooling rate and found increased crystallinity of PLA particles within the board together with higher IB values (up to 2 N/mm^2) for higher press temperatures. Cooling rate did not influence mechanical properties (press cycle 60 s/mm heating, cooling 21 s/mm, target density 780 kg/m^3).

Regarding competitiveness of particleboards produced with thermoplastic polymers IB values reached seem to be sufficient. Nevertheless, the total product performance is assumed to be significantly different to current standard particleboards, especially when creep is becoming important, e.g. in climatic areas where higher average temperature and humidity might occur. Also in view of the high quantities of polymer addition, which was mentioned to be in the range of 20–70%, the resulting products might rather be comparable to some wood plastic composites, than to particleboards. Obviously this high polymer amounts would contribute significantly to the product price. Considering the pressing factors reported before, the performance and material composition of these products still seem to play a minor role. In contrast to reactive polymers, the pressing factors using the thermoplastic behavior of polymers (i.e. polyolefins as well as PLA) are limited by the time needed to reach the corresponding softening or melting temperature in the core of the panels and the necessary subsequent cooling time for setting the polymers.

In Fig. 6 the temperature development of a hot pressed industrial fraction of core layer particles without the presence of any additional polymer, using a target density of 650 kg/m^3 and initial wood particle humidity of 6% is presented for two different panel thicknesses (10 and 19 mm). A more detailed description on hot pressing condition in wood based composite is reviewed by Wei et al. [353]. For the present example the temperature development was observed on a $50 \times 50 \text{ cm}^2$ laboratory hot press operating at 220°C . Due to the small dimensions of the laboratory hot press compared to an industrial one, developing steam might leak from the board edges and allow therefore some kind of particle drying during hot pressing. According to these measurements a 19 mm laboratory particleboard would reach a feasible melting region of various thermoplastic polymers in the core layer after 500s (120°C), 700s (150°C), or after 850s (170°C), resulting in press factors only for the heating-up period ranging from 26 to 44 s/mm. This press

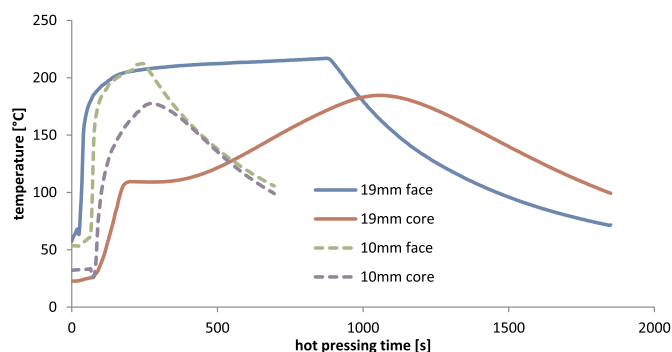


Fig. 6. Development of core and face temperature of compressed core layer wood particles in a laboratory hot press operating at 220°C (measurements by Konstantin Rudolf).

factor does not consider a time for wetting the wood particles, nor a possibly necessary subsequent time needed for solidifying the polymers.

Some reduction in heating time might be achieved by further decreasing the moisture content of the core layer particles to minimize the plateau phase reached after approx. 200s, visible at the 19 mm core particles at a temperature slightly above 105 °C. Possibly for industrial hot press dimensions only extremely dry wood particles have to be used, as the steam from evaporated moisture out of the wood particles may hardly be able to leak from the panel. For the case of the laboratory board, this time was presumably necessary to evaporate the remaining humidity of the wood particles and the period lasted for approx. 200s. Consequently the press factor necessary for heating up the core layer of a 19 mm board might be reduced by 10 s/mm resulting still in 34 s/mm to reach 170 °C in the core. Clearly disadvantageous for the panel would be the long impact of temperatures above 200 °C reached at the face of the boards already after 140s. This long exposure to high temperature might result in discoloration and degradation of the face layer.

At the example of the particleboard with only 10 mm thickness the resulting pressing factors for heating would be considerably lower with corresponding values ranging from 12 s/mm (120 °C) to 23 s/mm (170 °C). Subsequent to the heating period cooling is assumed to be necessary to re-solidify the thermoplastic polymer also here, which represents a technology currently not applied in typical continuous particleboard manufacturing plants. The cooling time shown in Fig. 6 was observed by cooling down the closed laboratory press plates with fresh water. In an industrial continuous press equipped with a powerful and thus expensive cooling section, it is assumed that this time might be significantly lower than shown above.

From the above mentioned limitations, someone could conclude, that thermoplastic polymers might be applicable for very thin particleboards or face layers only. The introduction of thermoplastic polymers might alter product properties and might raise the necessity of introducing a cooling section subsequent to the hot press.

7. Other considerations

In his review Pizzi [13] identified four broad classes of challenges for introducing bio-based adhesives systems. Presumably these challenges exist for all new adhesives types, irrespective whether they are based on synthetic or bio-based primary material. These challenges are.

- related to their performance and application in relation to current adhesives,
- challenges related to their cost in relation to the cost of current benchmark adhesives,
- challenges related to the supply of raw materials, and last but not least
- challenges related to resistance to their introduction.

For adhesive systems providing a certain performance, which is basically expected when products produced thereof are able to fulfill standard requirements, the possibly dominating challenge is the one regarding the cost. For a cost driven industry, such as the wood based panel industry, this is especially essential. Here not only the cost of the adhesive itself is crucial, but the total cost involved for producing the final product, which is a particleboard in the case considered. At the example of an assumed cost structure of an average European particleboard plant, with an total annual production capacity of 540.000 m³ [354], which is assumed to be based on fulfilling E1-emission particleboards, an average produced panel density of assumed 630 kg/m³, and producing for simplification only one panel thickness (i.e. 16 mm), cost scenarios for three currently industrially used, and one industrially available ultra-low emission systems (amino-based) and their intended emission classes were estimated and are shown in Fig. 7.

Industrially relevant input data for such cost estimations is difficult to obtain, however, based on some existing references [10–12] and own assumptions, input data was estimated. Someone might doubt the magnitude of the individual values selected for the E1 reference board, which is acting as basis for the cost calculation of the other boards. The figure should basically only allow for visualizing the dramatic effect small changes in adhesive cost, their relative quantity needed and pressing time would have on total product cost. Some of the parameters such as wood cost or energy cost might be assumed to have a rather fixed contribution to the total cost of the board and only marginally respond to changes in the adhesive systems. Therefore these values were generously estimated. Others, like resin cost directly change with changed resin raw material cost and necessary resin load, this is why corresponding input values are based on concrete inquiries made to adhesive producers and their recommendation for adhesive loading of panels. Costs such as total depreciation or personal cost become relatively high when the total annual plant productivity changes, which is the case when the press-factor has to be changed as a result of adhesive

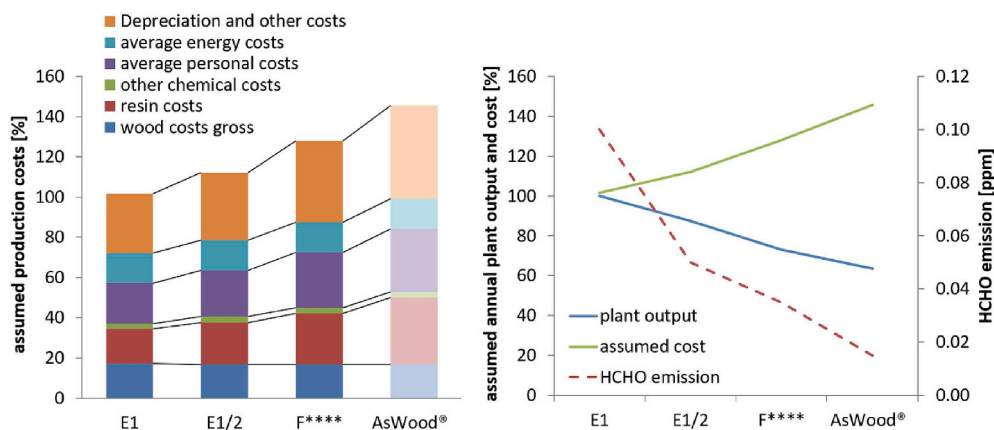


Fig. 7. Left: Estimated production cost of a 16 mm thick particleboard bonded with adhesive systems of different emission class. Right: estimated relative cost, annual plant productivity and expected formaldehyde (HCHO) emission of particleboards produced with the different adhesive systems.

technology applied. The cost calculation was performed using a cost calculation program which was generously provided by Stefan Weilharter from Metadynea Austria GmbH (Krems, Austria).

From the graph in Fig. 7 it is evident, that lower intended emissions classes (values as provided from adhesive manufacturers), generally increase the total cost of the particleboard significantly. Here relative differences of approx. 35% of adhesive cost, when comparing a standard E1 to the ultra-low emitting system, were assumed, together with a slightly changed adhesive content for the individual adhesive systems. The contribution of the adhesive related to the total product cost reported here is well in line with values reported in literature [12]. Another main cost effecting parameter is the one deriving from the plant productivity. By changing the assumed press factor of 3.5 s/mm for a standard E1 particleboard to assumed 5.4 s/mm for a ultra-low emitting adhesive system the total plant productivity would change by approx. 35% based on the original 540.000 m³ (Fig. 7 right). This at first view, a small change in processing speed increases relative depreciation and personal cost significantly. It is thus evident, that also small changes in productivity significantly affect the cost structure and thus the final product price. Speculating about legislatively forced changes in adhesive system for major parts of the industry sector would consequently result in a dramatic loss and probably shortage in production capacity of the affected region, e.g. a continent, as to date none of the ULEF nor formaldehyde-free alternative adhesive systems are able to compete with pressing times reached by standard urea-formaldehyde adhesives.

Challenges regarding the supply of the adhesive raw material as indicated above require consideration of the scale of particleboard industry. The world production volume of particleboards in 2015 was estimated to approx. 84 mio. m³ [355]. Of this volume, Europe contributes with a share of approx. 30 mio m³ and China as single largest producing country with approx. 20 mio m³. Based on an assumed average density of 650 kg/m³ approx. 55 mio metric tons of particleboard are produced worldwide. Adhesive spread rates ranging from 10 to 14% based on wood dry matter are assumed to require some 5–7 mio to standard adhesives. Obviously alternative adhesives have to be able to cope with corresponding quantities. For the special case of pMDI which require a significantly lower adhesive load still some 2–3.5 mio to of adhesive would be required when assuming an average spread rate of about 3–6%, which corresponds to the worldwide production volume of MDI in 2004.

8. Conclusion and future perspective

Based on the considerations presented above the technological performance of a few formaldehyde-free adhesive systems is relatively close to the currently dominating amino-based adhesives. In order to allow for a fair comparison a current ULEF system which is characterized by formaldehyde emission at- or below the level of natural wood shall serve as current benchmark for the evaluation of novel formaldehyde free alternatives.

- pMDI may be regarded as the most obvious formaldehyde free adhesive candidate. This conclusion is supported by the fact that this system is already in industrial use not only for OSB production but also in particleboard industry, albeit in comparably small amounts. In Europe 1% of total production volume are estimated to be pMDI based. Regarding cost structure a direct comparison to the standard adhesive systems defined above is not possible, as some hardware modification in the production process would be necessary compared to standard amino-based adhesives. This is necessary due to the extremely low adhesive spread rate of pMDI and the required use of releasing agent. In any event, pMDI adhesive is approx. 5–10 times more expensive based on solids compared to an E1 UF adhesive. As only few suppliers are able to provide pMDI adhesives, within the last few years, a considerable price volatility of pMDI was observed, making it difficult to guarantee stable particleboard

Table 1
Overview of regulations for formaldehyde emission and content (perforator) for particleboards. Values in bold are indicated in the corresponding standards, others are derived values.

emission class	product standard	year	chamber methods	EN 717-1	perforator method	desiccator method
E3	ETB Guideline	1980	ASTM E 1333	2.3 ppm [22]	EN 120	JIS A 1460
E2	ETB Guideline, EN 312, EN 13986	1980/2004		1 ppm [22]	90 mg/100g	
E1	ETB Guideline, EN 312, EN 13986	1980/1985/2004	0.14 ppm [23,24]	0.1 ppm (0.124 mg/m ³)	30 mg/100g 8 mg/100g	0.75 mg/l [25]
E1 plus	EN 13986	2004		0.065 ppm	4 mg/100g	0.35–0.04 mg/l [25]
E ½ resp. E0.5	IKFA IOS-MAT-0003, EPF-S European panel federation	2008/2009		0.05 ppm	2.7 mg/100g	0.2–0.25 mg/l [25]
E 1/3	German Association of Producers of Prefabricated Houses, IKFA IOS-MAT-0003	2003		0.03 ppm	7.5 mg/m ³ [23] 3.5–3.9 mg/m ³ [23]	
CARB 1	CARB ATCM 93120	2009	0.18 ppm	0.13 ppm [23]	(8 mg/100g) equivalent to E1 [24]	1.5 mg/l
CARB 2	CARB ATCM 93120	2011	0.09 ppm	0.065 ppm [23]		0.5 mg/l 0.3 mg/l
ULEF	CARB ATCM 93120	2007	0.05 ppm	(0.1 ppm) equivalent to E1 [24]	0.22–0.60 mg/100g [26] 0.15–0.28 mg/100g [26]	0.03–0.09 mg/l [24]
F**	JIS A 5908					0.02–0.11 mg/l [24] 0.2–0.35 mg/l [24]
F***	JIS A 5908	2003	0.07 ppm [24] 0.04 ppm [24]	0.07 ppm [25] 0.03–0.04 ppm [25] 0.002–0.009 ppm [26] 0.003–0.007 ppm [26,28] < 0.016 ppm (99% of wood species) [27]		
F****	JIS A 5908		< 0.023 ppm (99% of wood species) [27]			
green wood						
wood dried @ 20°C-30 °C						
wood dried @ 60 °C						
wood dried @ 140 °C						

Table 2

Adhesives defined as “formaldehyde free” included in the present study may only contain components depicted in the fields showing white background.

	Components made out of formaldehyde	
	Yes	No
Components capable of releasing formaldehyde	Yes no	e.g. paraformaldehyde, hexamine, HMMM, methylolated urea e.g. pMDI e.g. Sugar, plant compounds (i.e. lignin...) Numerous compounds

prices. A continuous supply of pMDI seems to be an additional uncertainty. pMDI might be able to deal with comparably low spread rates of only 2–4% for the core layer, and 6–8% for face layers [12], whereas UF requires significantly higher spread rates. The achievable press factor may be in the range of more than 5 s/mm in industrial scale, influencing both the relative product cost as well as the production capacity as discussed above. In addition it has to be mentioned that occupational health and safety requirements during panel production for pMDI processing plants would have to be regarded as a further issue which seems to be less critical when amino-based adhesives are processed. Depending on daily pMDI price situation such adhesives could lead to similar but also significantly higher particleboard costs at comparable emissions during use as could be reached by ultra-low emitting (ULEF) amino-based systems.

Regarding other alternative adhesive candidates compared to pMDI, clear conclusions are more difficult, as the available information is mainly based on single scientific publications or several publications by the same group of scientists. Also, important questions with regard to up-scaling towards industrial feasibility are still open in many cases.

- As amino-based adhesives are the group currently mainly applied, a lot of aspects are in favor of this system. The industrial availability of one part of the base chemicals namely urea or melamine is given and their pricing is well known.

As reactant a range of alternatives have been proposed, but industrial implementation is still missing.

Ethyleneurea crosslinked with glutaraldehyde showed competitive laboratory press factors together with satisfying IB values [201]. Significantly higher raw material prices for both base components compared to urea and formaldehyde are obviously expected. Same applies to the melamine, urea, glyoxylic acid and glyoxal [207] adhesive which also allows comparably short pressing times and by reaching relevant mechanical properties. Combining urea-glyoxal with small amounts of pMDI [198] resulted in exceptional IB values indicating the potential to further improve the press factor applied. Urea and HMF [208] as interesting option was presented. HMF is expected to be a high reactive compound implying the theoretical potential to result in short press times. However, an industrial availability of the compound HMF is currently not given, but in the pilot scale only.

- For the lignin based adhesives a majority of the faster reacting and well performing adhesives contained additionally to lignin pMDI. Here comparable pMDI quantities to those of using pMDI as the sole adhesive were applied, plus the additional lignin. It is thus highly questionable if the lignin is really significantly contributing to the adhesion, or if the lignin is just an additional cost factor increasing further the total price of the adhesive.

- Within the group of tannins, the study on quebracho tannin together with tris(hydroxymethyl)nitromethane with additional silica [236] resulted also in relevant performance and relatively short laboratory press factors of 14–15 s/mm. Availability of selected tannin might be sufficient for a limited region only (South America). Additionally some discussion may arise regarding a potential formaldehyde emission, although it is claimed to be not a formaldehyde-emitting source by the proposing authors.
- Soy flour together with a crosslinker such as the polyamidoamine-epichlorohydrin (PAE) Kymene® system provided by Hercules (now Solenis™) or the one with PEI-maleic anhydride and NaOH are considered as the faster protein-based adhesive systems [252]. For both systems the high amount of moisture introduced during adhesive application is considered as a serious issue. An additional drying step after soy flour application as slurry represents an additional process step compared to current industrial practice as long as no other solution for dealing with the high viscosity of the slurry and the consequently high amount of induced humidity is proposed. Availability of soy flour may be regarded as depending on geographical location. US, Brazil and Argentina are listed as the world dominating producers.
- From the group of animal proteins casein [128] performed relatively good. Still significant progress in pressing time would be required and the adhesive cost were identified to be an issue. The amount of casein is in short supply for large applications.
- Starch-based adhesives basically performed either low or were applied using high press factors.
- For plant based polysaccharides industrial adhesive systems from other industry sectors are available and performance of produced panels seems to be sufficient. The currently needed high reaction temperatures require pressing times orders of magnitude higher than established ones.
- Thermoplastic polymers with melting points significantly above 115 °C are possibly also no option due to the comparably long heating time.

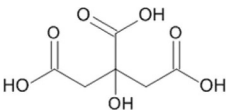
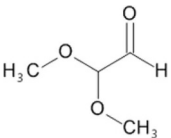
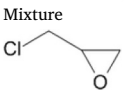
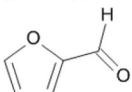
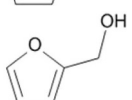
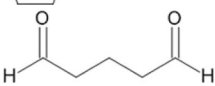
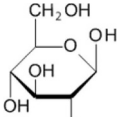
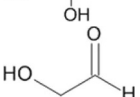
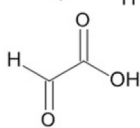
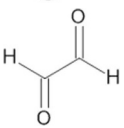
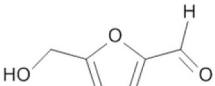
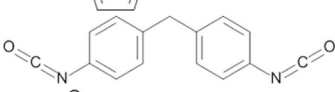
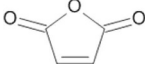
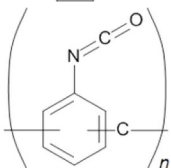
Acknowledgement

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Table 3
Overview of crosslinking agents.

Crosslinking agent	Chapter	Structural formula	Hazards		
					H350 (may cause cancer) H351 (suspected of cancer causing)
			GHS06	GHS08	
Citric acid	2.8.1.		No	No	No
Dimethoxyethanal	2.2.2.		No	No	No
EPI	2.3.4.	Mixture	No	Yes	Yes (H351)
Epichlorohydrin	2.5.		Yes	Yes	Yes (H350)
Formaldehyde	2.1.		Yes	Yes	Yes (H350)
Furfural	2.4.3.		Yes	Yes	Yes (H351)
Furfuryl alcohol	2.4.4.		Yes	Yes	Yes (H351)
Glutaraldehyde	2.2.4.		Yes	Yes	No
Glucose	2.4.1.		No	No	No
Glycolaldehyde	2.2.5.		No	No	No
Glyoxalic acid	2.2.3.		No	No	No
Glyoxal	2.2.1.		No	Yes	No
HMF	2.4.5.		No	No	No
MDI	2.3.1.		No	Yes	Yes (H351)
Maleic anhydride	2.8.2.		No	Yes	No
pMDI	2.2.2.		No	Yes	Yes (H351)

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Table 3 (continued)

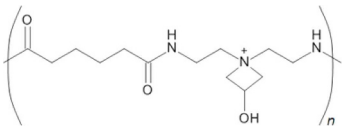
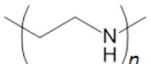
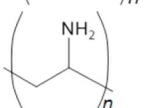
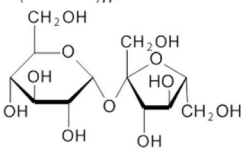
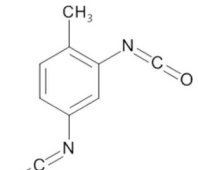
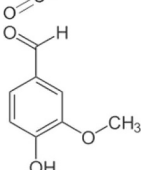
PAE	2.6.1.		No	Yes	Yes (H350)
PEI	2.6.2.		No	No	No
Polyvinylamine	2.6.3.		No	No	No
Sucrose	2.4.2.		No	No	No
TDI	2.3.3.		Yes	Yes	Yes (H351)
Vanillin	2.2.6.		No	No	No

Table 4
Composition of different soy protein qualities and their prices [144,145].

Soy protein form	Protein (%)	Fat (%)	Carbohydrate (%)	Price (2014)
Flour and grits				~ 23–25 c/lb
Full fat	41.0	20.5	38.5	
High fat	46.0	14.5	39.5	
Low fat	52.5	4.0	43.5	~ 25 c/lb
Concentrate	66.2	0.3	33.5	1\$/lb
Isolate	92.8	< 0.1	8.0	1.9\$/lb

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