Manufacturing Medium-density Fiberboards and Wood Fiber Insulation Boards Using a Blood Albumin Adhesive on a Pilot Scale

Kolja Ostendorf, Patrick Reuter, and Markus Euring *

An albumin adhesive derived from animal blood was used for the first time for the production of two kinds of fiberboard in a dry process: medium-density fiberboard (MDF) and wood fiber insulation board (WFI). Additionally, the curing for WFI was completed using an innovative hot-air/hot-steam (HA/HS) process. There is a general importance to develop alternatives to substitute common binding agents, such as urea-formaldehyde (UF) or polymeric methylene diphenylene diisocyanate (pMDI) resins, and to develop value-added opportunities for such waste material from slaughterhouses. An adhesive analysis was performed to understand the curing reaction of these protein adhesives, which showed good properties in regards to viscosity or gel time. The physical-mechanical results showed on the one hand that the albumin adhesive could compete with UF-bonded MDF regarding tensile strength and modulus of rupture in conformity to the European Standard, but it failed to meet requirements for thickness swelling. The albumin adhesive also can compete with pMDI bonded WFI regarding tensile and compression strength, but it showed non-viable results for short-term water absorption.

Keywords: Blood powder meal; Blood albumin; MDF; Hot-press; Hot-air/hot-steam process; Wood fiber; Insulation board

*Contact information: Georg-August-University of Goettingen, Faculty of Forest Science and Forest Ecology, Buesgen-Institute, Department of Forest Botany and Tree Physiology, Buesgenweg 2, Goettingen 37077, Germany; *Corresponding author: meuring@gwdg.de*

INTRODUCTION

Blood albumin is an animal protein with a long historical use as adhesive for wood-based products. There are several patents from early to the mid- 20th century that indicate the popularity of animal protein-based glues, *e.g.*, Henning (1920), Lindauer (1923), Cone (1934), and Gossett *et al*. (1959). At that time, plywood, airplane constructions, and furniture were glued with albumin-based adhesives (Detlefsen 1989). With the invention of synthetic resins, such as phenol-formaldehyde resin (PF) and urea-formaldehyde resin (UF), these kinds of protein adhesives almost vanished due to their limited availability, higher price, and shorter shelf-life (Sellers 1985; Detlefsen 1988).

In regards to actual developments in the wood-based panel industry, there is an increasing demand for natural adhesives due to several aspects (Adhikari *et al*. 2017). On one hand, the common UF adhesives are based on crude oil, which is non-renewable and dependent on unsteady oil prices (Wilson 2010). On the other hand, and more importantly, UF and related resins emit formaldehyde, which is carcinogenic for humans (IARC 2006; Pizzi and Mittal 2011; European Chemical Agency 2014). Based on these facts, there have been several studies with the goal of (partially) substituting synthetic resins with natural or green alternatives, enzymes such as laccase (Euring *et al*. 2015; Kirsch *et al*. 2016, 2018), plant proteins such as wheat gluten (Lei *et al*. 2010) or soy (Fan *et al*. 2016), and blood albumin (Lin and Gunasekaran 2010).

The strong performance of synthetic resins has led to high standards for adhesives applied in the wood industry, and these same levels of performance would need to be met by modern natural binders as well. There are several challenges to face, such as the handling of adhesives, which can be troubled by a high viscosity, low solids content, long pressing times, or insufficient moisture and resistances to water and mold. These challenges are due to the complex chemical structure of proteins and the fact that protein sources usually contain different types of proteins. The motivation to overcome these obstacles is to create a health- and environmental-friendly product which is completely based on natural resources (Frihart and Lorenz 2017). Blood or products derived from it are used in several areas, such as agriculture (animal food, fertilizer), the food industry (colorant, foaming and gelling agent, emulsifier, dietary supplements, *etc*.), medicine, pharmacy, and microbiology (Bah *et al.* 2013; Ofori and Hsieh 2014).

The history of fiberboards is derived from the pulp and paper industry and can be traced back to 1898. Due to inhomogeneous wood pulping processes at that time, waste fibrous material that was oversized or too bundled for paper production were utilized to produce an early type of insulation board. All boards were fabricated in a wet process, which offered several disadvantages, especially the limited maximum possible thickness of 12 mm. The first efforts of producing fiberboards in a dry process were in 1945. Fifteen years later, the first plant for producing MDF was set up in the USA (Deppe and Ernst 1996; Irle *et al*. 2012). This was a breakthrough for MDF production and the dry process itself, but it simultaneously meant a creeping decline for the wet process due to its disadvantages, *i.e.*, wastewater, limited board thickness, and screen print surface. Today, MDF belongs to the most important type of wood-based panel (Deppe and Ernst 1996).

The industry for wood fiber insulation board (WFI) is steadily growing due to an increased demand for healthy living (Dorsch *et al*. 2017) and upcoming national regulations for thermal insulation of buildings (Asdrubali *et al*. 2015). Natural building and insulating materials are capable of both generating an improved indoor climate as well as strong thermal and sound insulating properties (Reyer *et al*. 2002; Dorsch *et al*. 2017). Today, most of WFI is produced within a dry process in a similar manner to MDF. The difference is in the curing method: while MDF is cured by pressing it between two hot plates under high pressure, WFI is cured *via* a steam-air-mixture that flows through the fiber mat, supplying a maximum temperature of 100 °C. Therefore, the used binders are limited to those hardening at such temperature levels, which are namely polyurethane resins (PUR) such as polymeric methylene diphenylene diisocyanate (pMDI). However, this kind of synthetic resin is both high-cost and hazardous for humans due to the formation of aerosols when sprayed onto fibers (Euring and Kharazipour 2013).

In 2013, Euring and Kharazipour patented a new curing technology for WFI, utilizing a combination of hot air (HA) and hot steam (HS). First, the fiber mat is heated up by hot air to variable temperatures (80 °C to 160 °C). Then, hot steam is injected for 10 to 30 s, which leads to a prompt increase in temperature by taking advantage of the condensation effect. Thereby, the application of the binders used is no longer limited to those PUR resins. Thus, the application of natural binders for the fabrication of WFI becomes a lucrative research approach; such research has already been completed for the enzymatic treatment of fibers or UF resin (Euring *et al*. 2015; Kirsch *et al*. 2018).

Except for the previously mentioned plywood adhesive applications, there have been no considerable approaches using blood protein binders for board manufacturing or in appropriate research. Yang *et al.* (2006) used different protein hydrolysates, *inter alia* blood meal, in combination with PF-resins in different solid-to-solid ratios. The medium-density fiberboard (MDF) produced with blood-PF-resin were stated to fulfill the requirements for exterior use according to the American National Standard ANSI A208.2 (2016). The only reported experiments on developing a blood meal-based adhesive have been stated by Li *et al.* (2018). They modified a blood-meal-water-solution (28%) with different additives to improve their properties.

Therefore, this study focuses on the application of an innovative animal protein-based adhesive for the production of two types of fiberboards for the first time: MDF and WFI. And more specifically: completely natural-based and no formaldehyde emitting fiberboards. The fiberboards were manufactured in a dry process and their physical-mechanical properties were tested and compared to boards bonded with UF (MDF) and pMDI (WFI).

Additionally, an adhesive analysis was performed with regards to gel time, viscosity, and pH value for a better understanding of the curing reaction of albumin adhesive. This research constitutes a pioneering study, in view of the fact that there have been no comparable studies that utilize an albumin adhesive sprayed onto wood fibers within a dry process for the production of these kinds of fiberboards.

EXPERIMENTAL

Materials

Wood fibers

Coniferous wood (80% spruce wood and 20% fir wood) was defibrated into fibers with application of a thermo-mechanical-pulping (TMP) process and supplied by GUTEX Holzfaserplattenwerk H. Henselmann GmbH & Co. KG (Waldshut-Tiengen, Germany). 15 kg wood fibers were used with a moisture content of 10% per batch.

Blood albumin

Whole blood powder (Vollblutpulver) from pork was provided by Fritz Häcker GmbH & Co. KG (Vaihingen an der Enz, Germany). The amount of albumin adhesive was 15% based on absolute dry mass of the wood fibers.

Urea-formaldehyde resin

Commercial UF-resin Kaurit 340 with a solid content of 68%, a pH value of 7.5, and a molar ratio F/U of 1:1 was obtained from BASF SE (Ludwigshafen, Germany) and used for reference MDF. The amount of UF was 10% referred to absolutely dry wood fibers.

Hydrophobic agents

HydroWax of the type 138 for MDF and Syntec Blue for wood fiber insulation boards with solid contents of 60% and 55%, respectively, were purchased from SASOL Wax GmbH (Hamburg, Germany) and used in this study. The MDF and WFI were treated with 1% Hydrowax 138 and 2% Syntec Blue respective based on absolute dry mass of wood fibers.

Polymeric methylene diphenylene diisocyanate

Commercial pMDI I-Bond WFI 4370 from Huntsman Corporation (Rotterdam, Netherlands), with a minimum methylene diphenyl diisocyanate (MDI) of 60% and a minimum standard of 13% polyol, was used for reference WFI. The amount of pMDI used was 4% based on the absolutely dry mass of the wood fibers.

Methods

Analysis of the used adhesives

Before gluing, the adhesives (UF, pMDI, and albumin adhesive) were analyzed to draw potential conclusions on their gluing properties. Therefore, the adhesives were analyzed for their pH value according to EN 1245 (2011), their viscosity conforming to EN 12092 (2002), their gel time in accordance to EN 9396 (2001), and their solid contents according to EN 827 (2006). The gel time was measured at a temperature of 105 °C to simulate the thermal conditions inside the boards while pressing. Regarding the viscosity, the analysis was conducted with a rheometer, which measured the viscosity at different shear rates (s^{-1}). For the later results, the viscosity was shown for 511 s^{-1} and 1000 s^{-1}. All measurements were performed at an adhesive temperature of 20 ± 2 °C and were repeated four times. As an exception, the pMDI resin was only examined on its solids contents, and the pH was measured using a pH indicator instead of a pH meter. The other test was not conducted due to sensitive laboratory equipment.

Production and Testing of MDF and WFI

Both MDF and WFI were produced at the Biotechnikums (Göttingen, Germany) own pilot plant in a dry process. Before gluing, the fibers were dried in the integrated flash tube at 130 °C to a moisture content of approximately 6% to 7%.

The albumin adhesive was prepared several hours before application by mixing 27% blood powder with 46% water and 27% sugar alcohol as bonding agent. Before application, the adhesive was sieved, and 1% to 2% of hydrophobic agent was added. Regarding UF-resin, 2% of an ammonium sulphate solution was added as hardener. The glue was analyzed as described above and then blended with wood fibers with the help of an air-pressure atomizer spray nozzle. Afterwards, the glued fibers were loosened in the cyclone and transferred to the fiber bunker *via* a conveyer belt. Previously, UF-variants were gently dried to a moisture content of 8% to 9%. Albumin-treated fibers were not dried to avoid protein degradation by drying with high temperatures (≥ 60 °C) to yield a moisture content of 15%. Therefore, the press time factor had to be adjusted later on.

Next, fibers were spread to a homogenous fiber mat and were pre-pressed as a last step before curing. For the MDF, with a board size of 600 mm × 450 mm, a desired density of 800 kg/m³, and a thickness of 10 mm, curing took place in a hot press (G. Siempelkamp GmbH & Co. KG, Krefeld, Germany) at a temperature at 200 °C. For WFI, fibers were cured *via* hot-air/hot-steam (HA/HS) according to methods by Euring *et al*. (2015) and Kirsch *et al*. (2018), with a board size of 650 mm × 650 mm, a final density of 180 kg/m³, and a thickness of 40 mm. First, the fiber mat was heated up to 130 °C; then hot-steam was injected for 10s. The self-engineered hot-air/hot-steam apparatus was equipped with a hot air unit (Leister Technologies GmbH, Hagen, Germany) and hot-steam unit (MG Dampftechnik, Bedburg, Germany), which enabled the production of insulation boards in a batch mode. For WFI bonded with pMDI, two types of references were prepared, one by just applying hot-steam for 60 s to simulate the industrially preferred curing method and the other by combining hot-air/hot-steam likewise to albumin adhesives. A hot-steam induced curing for 60 s was completed for the albumin adhesive as well, but the results were rejected due to lack of measurability of highly unstable boards.

Each treatment was replicated four times. After conditioning at 20 °C and 65% relative humidity (RH) for MDF and 23 °C and 50% RH for WFI, the boards were tested for their physical-technological properties. The MDF samples were tested for internal bond strength (IB) in accordance with EN 319 (1993), modulus of rupture (MOR) according to EN 310 (1993), and thickness swelling (TS) according to EN 317 (1993). Additionally, the formaldehyde emission was measured by a gas analysis method according to EN 12460-3 (2016). The WFI were tested relative to their tensile strength/IB according to EN 1607 (2013), compression strength (CS) in accordance to EN 826 (2013), and short-term water absorption (WA) according to EN 1609 (2013). All tests, except TS or WA, were conducted with a universal testing machine (Zwick/Roell Z010; Zwick Roell Group, Ulm, Germany) with a maximum capacity of 10 kN.

Table 1. Overview of the Manufactured Boards within this Study Separated for Panel Type and each Conducted Variant

Parameter	Panel Type						
	MDF			WFI			
	UF-Ref.	A1 (MDF)	A2	pMDI (HS)	pMDI (HA/HS)	A1 (WFI)	A3
Gluing (%)	10	15	15	4	4	15	15
Curing time (s/mm)	9	21	21	1.5	6	6	6
Hydrophobic agent (%)	1	/	1	/	/	/	2
Curing process	hot press (200°C, 200bar)			hot-steam	hot-air/hot-steam		
Thickness (mm)	10			40			
Density (kg/m³)	800			180			
Repetitions	4			4			

Note: UF-resin, pMDI-resin, albumin adhesive without (A 1) and with addition of 1% (A 2), and 2% of hydrophobic agent (A 3). pMDI cured *via* hot-steam (HS) and albumin adhesive/pMDI *via* hot-air/hot-steam (HA/HS) treatment.

RESULTS AND DISCUSSION

Adhesive Analysis

The results for the analysis are summarized in Table 1. The albumin-based binders showed slight changes in their pH value, whereas the pure albumin adhesive (A 1) showed a pH of 7.46. The pH was slightly increased through addition of 1% (MDF) of hydrophobic agents to 7.47 (A 2) and 2% (WFI) to 7.55 (A 3). Compared to the references, UF showed a pH of 7.64 and the used pMDI had a pH range of 5.1 to 5.5.

Regarding the gel time at 105 °C, there was an accelerated curing or rather coagulation of the albumin adhesives when adding 1% or 2% of hydrophobic agent from 79.8 s (A 1) to 76.5 s (A 2) or 67.5 s (A 3). The UF resin took the longest time for curing with 171.2 s, whereas the gel time of the pure pMDI was not measureable due to the fact that the curing reaction is initialized by the presence of active hydrogen (Dunky 2002).

Table 2. Results for Adhesive Analysis of the Used Adhesive Systems

Adhesive	pH	Gel Time (s)	Solid Content (%)	Viscosity (mPa·s) Shear Rates (s^{-1}) 511	Viscosity (mPa·s) Shear Rates (s^{-1}) 1000
UF-Ref.	7.64 (± 0.02)	171.2 (± 8.18)	62.8 (± 0.92)	480.9 (± 9.47)	418.3 (± 2.49)
A 1	7.46 (± 0.02)	79.8 (± 0.5)	57.8 (± 3.32)	213.4 (± 7.69)	185.7 (± 2.26)
A 2 (MDF)	7.47 (± 0.01)	76.5 (± 9.61)	52.6 (± 0.96)	266.2 (± 6.29)	216.7 (± 3.37)
A 3 (WFI)	7.55 (± 0.01)	67.5 (± 4.36)	49.9 (± 0.42)	274.6 (± 7.62)	213.4 (± 2.75)
pMDI-Ref.	5.1 to 5.5 (pH indicator)	/	99.5 (± 0.20)	325 to 475 (Huntsman 2010)	

Note: UF-resin, pMDI-resin, albumin adhesive without (A 1) and with addition of 1% (A 2), and 2% of hydrophobic agent (A 3). Analysis was completed for pH-value, gel time, solid content, and viscosity for two different shear rates. The standard deviation is shown in parentheses.

The solid contents of the used albumin glues were 57.8% (A 1), 52.6% (A 2), and 49.9% (A 3). The UF-reference had a solid content of 62.8% (UF) and 99.5% of the pMDI-reference.

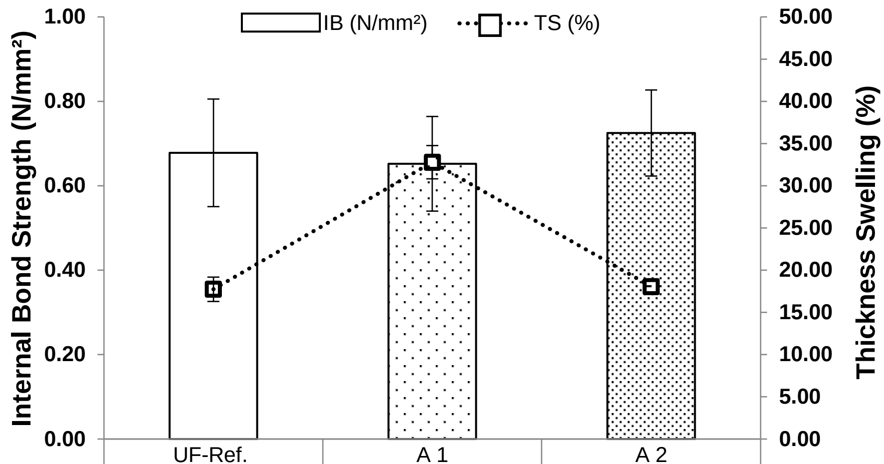
Concerning the viscosity of the protein adhesives, the addition of hydrophobic agents led to a slight increase between 266.2 mPa·s (A 2) and 274.6 mPa·s (A 3) at a shear rate of 511 s^{-1}, and 216.7 mPa·s and 213.5 mPa·s at 1000 s^{-1} towards the pure albumin adhesive (A 1) with 213.4 (511 s^{-1}) or 185.7 mPa·s (1000 s^{-1}). The highest viscosity was measured for the UF and pMDI references. The UF showed a viscosity of 480.9 mPa·s at 511 s^{-1} or 418.3 at 1000 s^{-1}. According to the manufacturer, the viscosity of pMDI resin ranged between 325 mPa·s and 475 mPa·s (Huntsman 2010).

Overall, the adhesive analysis for albumin glues revealed some correlations. One observation was that by adding hydrophobic agents to the albumin adhesive, the pH increased and the solids content was lowered. This was due to the alkaline paraffin dispersions HydroWax 138 (pH 9) and Syntec Blue (pH 9.5), which showed low solid contents and yielded higher water contents of solutions A 2 and especially A 3. This could be considered as being a negative factor for further processing because more water was applied to the fibers, which extended the pressing time. On the other hand, the viscosity was increased, which still allowed an easy handling, especially a good sprayability of the adhesives. The adjustment of the viscosity was a sensitive measure because of the wettability onto wood together with a penetration into wood (Dunky 2002). Cheftel *et al*. (1992) observed an increased viscosity with alkalization due to a partial protein unfolding. The general reduction of viscosity on higher shear rates could be explained by structural changes within the adhesive systems that regulated the smoothness behavior of its polymer chains (Pal 2006).

Another positive impact was the reduction of the gel time, which might have been due to the mentioned alkalization of the glue, leading to a partial protein denaturation and thus an accelerated coagulation. The hardened protein adhesives had a gel-like consistency while the UF samples were hard and brittle. The curing reaction for UF resins starts at temperatures above 80 °C and ends at 100 °C to 110 °C (Siimer *et al*. 2003). Therefore, a fully cured resin at this measuring temperature of 105 °C was assumed.

Physical-technological Properties of MDF

The results for IB and TS are summarized in Fig. 1. The internal bond strength (IB) provides a measure of the tensile strength perpendicular to the panel and is an important parameter for the gluing quality. The thickness swelling describes the swelling behavior within 24 h of a MDF specimen stored in a water bath and is likewise to TS an indicator for gluing quality.



	UF-Ref.	A 1	A 2
IB (N/mm²)	0.68	0.65	0.73
TS (%)	17.74	32.79	18.06

Fig. 1. IB and TS of albumin adhesive-bonded MDF without (A 1) and with (A 2) addition of 1% hydrophobic agent and a 10% UF-reference (IB is illustrated as bars, and the TS is pictured as lined markers); requirements for 10-mm-thick MDF for IB according to EN 622-5 (2010): ≥ 0.6 N/mm² and for TS according to EN 622-5 (2010): ≤ 15%

Using the pure albumin adhesive, boards achieved an IB of 0.65 N/mm² and 0.73 N/mm² when hydrophobic agent was added, whereas UF-reference gained an IB of 0.68 N/mm². The European standard EN 622-5 (2010) for 10-mm MDF requires a minimum value of 0.6 N/mm² for IB, so every variant conformed to this requirement.

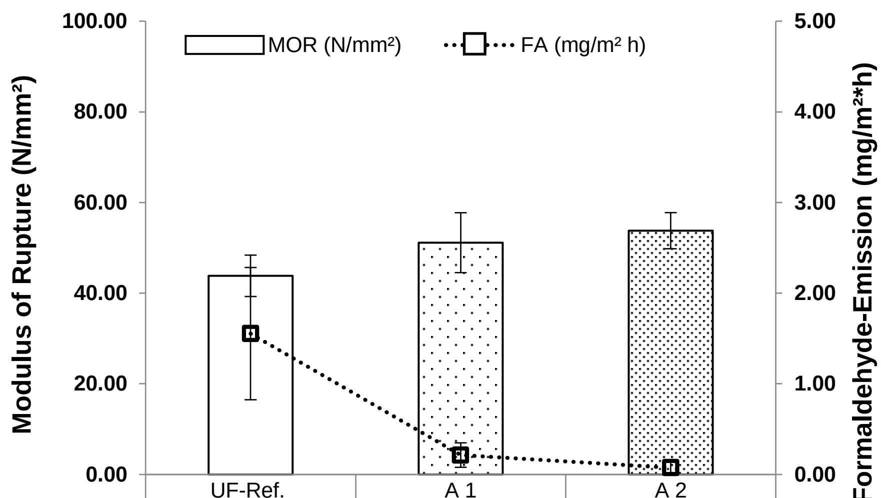
Regarding the results for TS, there was an expected reduction from 32.8% (A 1) to 18.1% (A 2) when adding hydrophobic agent to the albumin adhesive. The UF-reference reached a value of 17.7% for TS. According to EN 622-5 (2010), a maximum TS value of 15% is mandatory. In conclusion, none of the tested variants were able to achieve this value specification.

The results showed that albumin adhesive could compete with the UF resin in regards to IB and TS. Until now, there were no actual studies about the utilization of a pure blood meal-based adhesive for the production of MDF or WFI. Yang *et al.* (2006) tested the performance of blood meal mixed with a PF resin, which gained improved properties compared to UF- or PF-bonded fiberboards. The albumin adhesive is able to interact with hydroxyl groups on the wood fiber surfaces adhesively by forming hydrogen bonds (Li *et al.* 2018). On an intramolecular level, the albumin itself is linked cohesively by disulfide bridges (Lin and Gunasekaran 2010). This caused a sufficient gluing but was not stable against water, which was underlined by the high TS for A 1. In general, the stability of hydrogen bonds between wood and protein adhesive is highly dependent on the presence of water, which is able to weaken or even breaking these kind of intermolecular forces (Nordqvist 2012). Through addition of 1% hydrophobic agent (A 2), there was a clear but insufficient decrease in TS to meet the standard.

In contrast, there was a marginal increase in IB. This might have been due to the alkaline hydrophobic agent (pH 9) causing a slight alkali modification of the protein. Alkaline modification is a proper way to modify proteins (Hettiarachchy *et al.* 1995; Hale 2013). The results were supported by the adhesive analysis of the albumin adhesives, where A 2 showed an improved curing reaction compared to the untreated A 1. Simultaneously, the viscosity slightly increased for A 2, possibly leading to a better adhesive penetration into wood for an enhanced interaction with the components.

The additional insufficient values for TS with UF-bonded MDF could be explained by the fact that the used K 340 belongs to the low formaldehyde-containing UF resins with an F/U molar ratio of 1:1, which are unstable against hydrolysis (Dunky and Niemz 2002). Arising from this recognition, a future solution might be a slight increase of hydrophobic agent (up to 1.5%).

The MOR and results of the formaldehyde emission are summarized in Fig. 2. The MOR describes the force required for a MDF specimen to fail when it is centrally charged. The formaldehyde emission measured *via* gas analysis describes the emitting level of MDF specimen within 4 hours and a temperature of 60°C and air volumetric flow rate of 60 l/h under normal pressure.



	UF-Ref.	A 1	A 2
MOR (N/mm²)	43.83	51.14	53.79
FA (mg/m² h)	1.55	0.21	0.07

Fig. 2. MOR and formaldehyde emission (FA) of albumin adhesive-bonded MDF without (A 1) and with (A 2) addition of 1% hydrophobic agent and a 10% UF-reference (MOR is illustrated as bars, and the FA is pictured as lined markers); requirements for 10-mm-thick MDF for MOR according to EN 622-5 (2010): ≥ 22 N/mm² and for FA according to EN 13986 (2015): ≤ 4.5 mg/m²·h for category E1

For MOR, values of 43.8 N/mm² (UF-Ref.), 51.1 N/mm² (A 1), and 53.8 N/mm² (A 2) were achieved. The European Standard for 10-mm MDF demands a minimum MOR of 22 N/mm², which all of the tested variants were able to conform to by more than two fold.

With respect to the formaldehyde emission measured *via* method of gas analysis, there was an explicit reduction for the adhesive with 0.21 mg/m² h (A 1) and 0.07 (A 2) mg/m² h towards the UF-Reference with 1.55 mg/m² h. According to EN 13986 (2015) for the classification of formaldehyde release from wood based panels measured by gas analysis method, there is a maximum emission of ≤ 4.5 mg/m² h for E1 categorized boards. In this study, all of the produced boards were able to meet this threshold.

The results showed that the albumin adhesive was able to outclass results for MOR of UF-bonded boards while emitting virtually no formaldehyde. The low formaldehyde emission of the albumin adhesive formulations is based on a natural emitting level of wood for formaldehyde as metabolite caused by partial thermal wood degradation (Salem and Böhm 2013). There was a slight increase in MOR when adding 1% of hydrophobic agent, due to a possible alkaline modification. Regarding formaldehyde emission of UF-bonded MDF, the low emitting potential can be explained by the low molar F/U ratio. By reducing formaldehyde content in the UF, the emission level naturally decreased but is also negatively affecting mechanical properties (Dunky 2002).

Overall, a noteworthy critical evaluation of the results of albumin adhesive-bonded MDF was the high moisture content after gluing and resultant higher pressing time. When looking at industrial measures, the pressing time for UF-bonded MDF differs between 9 s/mm and 11 s/mm depending on the plant type (Mantanis *et al*. 2018). In this study, the pressing time for albumin bonded MDF was 21 s/mm. Therefore it was more than doubled in comparison to UF (9 s/mm). From an industrial perspective, this would result in higher production costs and a decreased board output.

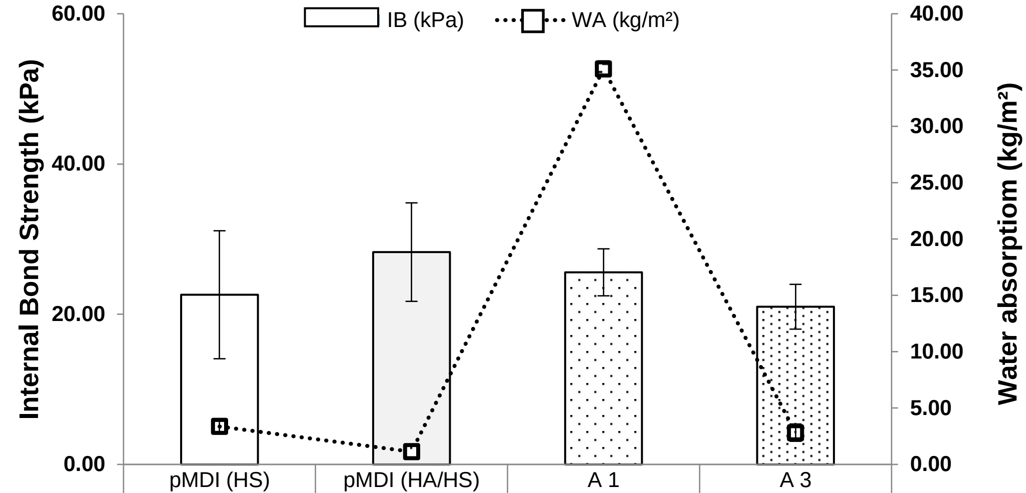
As an optical disadvantage, the dark glue line of the resulting fiberboard was noteworthy, due to the brownish color of the albumin adhesive. In further investigations there should be some pre-drying experiments with different temperature ranges for albumin adhesive-glued fibers to test if protein denaturation occurs and if there is a possible negative impact on board properties.

As preliminary conclusion, this study showed promising first results for albumin adhesive bonded MDF. The boards showed good mechanical properties while almost no emission of carcinogenic formaldehyde. Though, there is a further need of optimization towards commercially produced MDF, especially in regard to reduce thickness swelling.

Physical-technological Properties of WFI

Figure 3 shows the IB and WA for WFI. The IB is measured in the same manner as for MDF. The WA describes the water uptake of WFI specimen within 24 h when it is exposed to constantly 10 mm water up to the lower edge. In regards to the pMDI references, the IB improved using the hot-air/hot-steam (28.3 KPa) instead of merely applying hot-steam (22.6 kPa) for curing. The same applies to the values for WA with values of 3.38 kg/m² (pMDI (HS)) and 1.13 kg/m² (pMDI (HA/HS)). In relation to the albumin adhesive formulations, there was a decrease in IB *via* adding 2% of a hydrophobic agent (21.0 kPa for A 3). In contrast, there was an explicit improvement for WA when adding a hydrophobic agent to the albumin adhesive, gaining a value of 2.82 kg/m² in comparison to A 1 with 35.1 kg/m².

The results for IB and WA for WFI reasonably confirmed the results for MDF that the albumin adhesive-bonded WFI could compete with the pMDI-bonded references. However, there was a decrease in IB strength when adding 2% hydrophobic agent to the albumin glue. In contrast to the adhesives analysis where the addition of a paraffin emulsion showed an improved curing reaction, the addition did not lead to enhanced IB properties. Roffael *et al*. (2005) observed that there is no negative influence on board properties when adding 0.1% to 1% of a paraffin solution to fiberboard. When there is more than 1%, there might be an exceeded coating effect of wax particles on fiber surfaces (Back 1987), preventing the protein from building up a covalent bonding as stated above or a fiber-to-fiber bonding. However, the addition of paraffin is indispensable for a sufficient reduction of the water absorption when using albumin adhesive.



	pMDI (HS)	pMDI (HA/HS)	A 1	A 3
IB (kPa)	22.59	28.27	25.58	20.99
WA (kg/m²)	3.38	1.13	35.11	2.82

Fig. 3. IB and WA of albumin adhesive-bonded WFI *via* hot-air/hot-steam without (A 1) and with (A 3) addition of 2% hydrophobic agent and two different cured 4% pMDI references using 60 s hot-steam (pMDI (HS)) and hot-air/hot-steam (pMDI (HA/HS)); IB is illustrated as bars, and the WA is pictured as lined markers

In relation to a product from the industry, GUTEX Thermowall® which requires a minimum IB of 20 kPa and WA of > 1 kg/m² (GUTEX 2019a), the elevated results for albumin bonded WFI are at least comparable regarding IB. The addition of 2% hydrophobic agent certainly led to a massive decrease in water uptake but is not sufficient enough to meet values less than 1 kg/m².

When comparing the two pMDI-references, there was an increase in IB and a decrease in WA when curing *via* hot-air/hot-steam, which demonstrated that this resin was fully crosslinked at temperatures above 100 °C (Euring and Kharazipour 2013; Euring *et al*. 2015). Due to the higher temperatures, the mobility of the polymers within the resin was enhanced and thus their ability of crosslinking was improved (Zeppenfeld and Grunwald 2005).

Figure 4 shows the results for CS. The CS is measured by applying a defined compressive force perpendicular to the surface of a WFI specimen up to 10% compression. For the pMDI-references, there was an increase of CS from 150.4 kPa (pMDI (HS)) to 200.9 kPa (pMDI (HA/HS)) when curing WFI boards with hot-air/hot-steam instead of merely hot-steam. The albumin adhesive-bonded WFI gained CS values of 228.5 (A 1) and 232.9 (A 3).

The results showed that the albumin variants could compete with those bonded with pMDI. The protein-bonded variants showed an even higher pressure resistance. In relation to these references, pMDI (HA/HS) showed an improved value for CS compared to pMDI (HS), which indicated a fully cured resin with enhanced adhesive strength like discussed for IB. Regarding the albumin adhesive, there was no decrease in CS when adding a hydrophobic agent, which meant that the paraffin might have affected the IB in a negative way, but did not necessarily affect the CS.

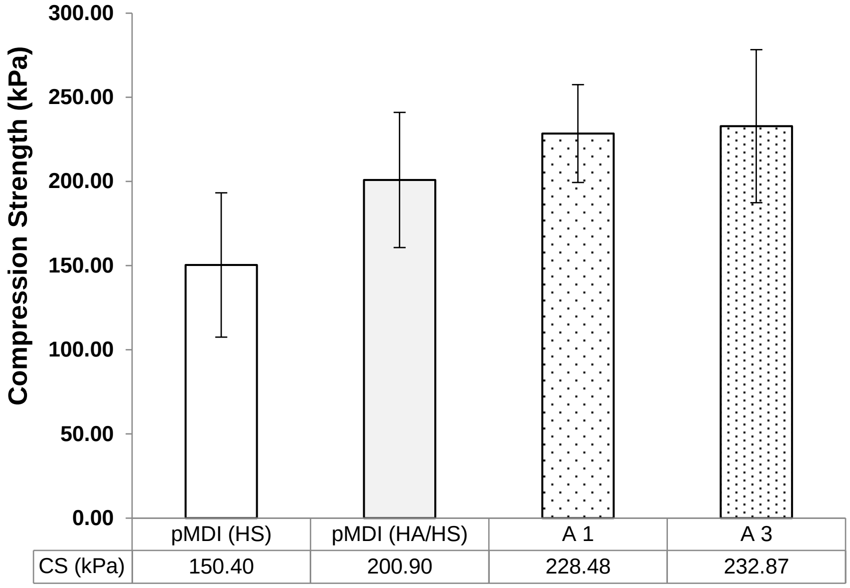


Fig. 4. CS of albumin adhesive-bonded WFI *via* hot-air/hot-steam without (A 1) and with (A 3) addition of 2% hydrophobic agent and two different cured 4% pMDI references using 60 s hot-steam (pMDI (HS)) and hot-air/hot-steam (pMDI (HA/HS))

A comparable industrial, commonly pMDI-bonded WFI showed board properties of 20 kPa (IB), 150 kPa (CS), and WA of < 1 kg/m² (GUTEX 2019a). The obtained results were comparable to such a product, except for WA.

For a better understanding, further repetitions should be completed, such as an up-scaling to industrial scale. Furthermore, tests with blow-line gluing should be implemented where the protein-glue is exposed to heat.

Initially, this study focused on if the protein adhesive was suitable for the production of WFI in general and if the occurred bonding was sufficient enough for gluing fibers in such a low-density range by using the hot-air/hot-steam process. It was shown that with some limitations regarding WA, the adhesive effect of animal-based protein on wood fibers was suitable for the production of pressure-resistant WFI

Nonetheless, in regards to WFI, thermal insulation properties need to be realized in future studies. First investigations regarding thermal conductivity were carried out. The thermal conductivity of the used fiber material (GUTEX Thermofibre®) in packed state is λ_D = 0.038 W/mK (GUTEX 2019b). The thermal conductivity of the comparable GUTEX product (180 kg/m³, 40 mm) is 0.043 W/mK (GUTEX 2019a). After loosening, gluing and re-compacting to 180 kg/m³ and a thickness of 40 mm, a thermal conductivity between 0.043 and 0.044 W/mK was measurable, indicating that thermal conductivity is in particular dependent on the density and moisture content of the board and not on type of binding agent or board thickness (Foglia 2006; Sonderegger and Niemz 2009; Brombacher 2015).

This study constitutes a feasibility study for an albumin adhesive for manufacturing MDF and WFI on a pilot-scale, showing good properties in terms of sprayability and mechanical properties of the boards. However, there are some questions left regarding the pricing and availability of blood meal as a basis for albumin adhesive. Following, there is a theoretical exemplary calculation for hog: According to Warriss and Wotton (1981), hog blood amounts 5.3% on total slaughter weight. For 2019, a worldwide emergence of 114.59

million metric tons in pig slaughter weight is estimated (Statista 2019). This leads therefore to a theoretical amount of pig blood of 6 million metric tons. Under consideration of 80% moisture content in pig blood (Okanovic *et al*. 2010) the (theoretical) yield of blood meal from fresh blood is about 1.2 million metric tons. One ton of the used albumin adhesives contain 27% blood meal, making it possible to produce 4.44 million metric tons of albumin adhesive out of 1.2 million metric tons blood meal. In comparison, the wood based panel industry consumes approximately 18.5 mio. t of amino-resin (such as UF-resin) and 470,000 t of pMDI (EUWID 2018). The provider, Fritz Häcker GmbH, claimed a price range for (ready-to-use) albumin adhesive between 00.33 and 0.85 $/kg, depending on the purity of the basic materials. Looking at translated UF-resin prices at about 0.32 $/kg (EUWID, 2017), the adhesive costs could be more than doubled in worst case. Given these sheer figures, especially in regard to the amino resin, the albumin adhesive would not be able to replace common resins at any scale. However, imaginable could be the use as environmental-friendly and no-emission niche product. Due to its long historical use, especially in the US, there should be a broad acceptance within the population for this kind of fully natural product, together with appropriate marketing campaign.

CONCLUSIONS

1. The analysis of the albumin adhesive resulted in partially improved properties in comparison to urea-formaldehyde (UF) or polymeric methylene diphenylene diisocyanate (pMDI) resin such as lowered gel time and viscosity and showed therefore good process ability for application on wood fibers.
2. The albumin adhesive for gluing wood fibers was found to be a suitable natural-based alternative to UF resins for the production of no-emission, environmental-friendly medium-density fiberboard (MDF).
3. The albumin adhesive for gluing wood fibers was also a suitable natural-based alternative to pMDI for the production of pressure-resistant, environmental-friendly wood fiber insulation board (WFI).
4. The hot-air/hot-steam process was suitable for curing this natural-based albumin adhesive for the production of WFI and also improved the performance of pMDI.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) grant EU 124/3-1 given to Markus Euring.

REFERENCES CITED

Adhikari, B. B., Appadu, P., Chae, M., and Bressler, D. C. (2017). “Protein-based wood adhesives current trends of preparation and application,” in: *Bio-based Wood Adhesives*, Z. He (ed.), CRC Press, Boca Raton, FL, USA, pp. 1-58. DOI: 10.1201/9781315369242-1

ANSI A208.2 (2016). "Medium density fiberboard (mdf) for interior applications," Composite Panel Association, Leesburg, VA, USA.

Asdrubali, F., D'Alessandro, F., and Schiavoni, S. (2015). "A review of unconventional sustainable building insulation materials," *Sustainable Materials and Technologies* 4, 1-17. DOI: 10.1016/j.susmat.2015.05.002

Back, E. L. (1987). "The bonding mechanism in hardboard manufacture," *Holzforschung* 41(4), 247-258. DOI: 10.1515/hfsg.1987.41.4.247

Bah, C. S. F., Bekhit, A. E.-D. A., Carne, A., and McConnell, M. A. (2013). "Slaughterhouse blood: An emerging source of bioactive compounds," *Compr. Rev. Food Sci. F.* 12(3), 314-331. DOI: 10.1111/1541-4337.12013

Brombacher, V. (2015*). Untersuchungen zur Optimierung von Holzfaserdämmstoffen in Abhängigkeit von Rohstoff, Herstellverfahren und Aufschlussbedingungen [Investigations on the Optimization of Wood Fiber Insulating Materials Depending on Raw Material, Production Process and Pulping Conditions]*, Doctoral Dissertation, Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland. DOI: 10.3929/ethz-a-010580551

Cheftel, J.-C., Cuq, J.-L., and Lorient, D. (1992). *Lebensmittelproteine: Biochemie, Funktionelle Eigenschaften, Ernährungsphysiologie, Chemische Modifizierung* [*Food Proteins: Biochemistry, Functional Properties, Nutritional Physiology, Chemical Modification*], Behr's Verlag & Co., Hamburg, Germany.

Cone, C. N. (1934). "Adhesive and process of making the same," U.S. Patent No. 1976436.

Deppe, H.-J., and Ernst, K. (1996). *MDF – Mitteldichte Faserplatten* [*MDF – Medium Density Fiberboard*], DRW-Verlag Weinbrenner GmbH & Co. KG, Leinfelden-Echterdingen, Germany.

Detlefsen, W. D. (1989). "Blood and casein adhesives for bonding wood," in: *Adhesives from Renewable Resources*, R. W. Hemingway, A. H. Connor, and S. J. Branham (eds.), ACS Publications, Washington, D.C., USA, pp. 445-452. DOI: 10.1021/bk-1989-0385.ch031

Dorsch, L., Kaiser, C., Niklasch, W., Schoepgens, H., and Spritzendorfer, J. (2017). "Marktübersicht – Dämmstoffe aus nachwachsenden rohstoffen [Market overview – Insulation materials from renewable raw materials]," Druckerei Weidner GmbH, Rostock, Germany.

Dunky, M. (2002). "Bindemittel und Verleimung [Binding agents and gluing]," in: *Holzwerkstoffe und Leime – Technologie und Einflussfaktoren* [*Wood Materials and Glues – Technology and Influencing Factors*], M. Dunky and P. Niemz (ed.) Springer Verlag, Berlin, Germany, pp. 249-641. DOI: 10.1007/978-3-642-55938-9

EN 310 (1993). "Wood-based panels; Determination of modulus of elasticity in bending and of bending strength," European Committee for Standardization, Brussels, Belgium.

EN 317 (1993). "Particleboards and fibreboards; Determination of swelling in thickness after immersion in water," European Committee for Standardization, Brussels, Belgium.

EN 319 (1993). "Particleboards and fibreboards; Determination of tensile strength perpendicular to the plane of the board," European Committee for Standardization, Brussels, Belgium.

EN 622-5 (2010). "Fibreboards - Specifications - Part 5: Requirements for dry process boards (MDF)," European Committee for Standardization, Brussels, Belgium.

EN 826 (2013). “Thermal insulating products for building applications - Determination of compression behaviour,” European Committee for Standardization, Brussels, Belgium.

EN 827 (2006). “Adhesives - Determination of conventional solids content and constant mass solids content,” European Committee for Standardization, Brussels, Belgium.

EN 1245 (2011). “Adhesives - Determination of pH,” European Committee for Standardization, Brussels, Belgium.

EN 1607 (2013). “Thermal insulating products for building applications - Determination of tensile strength perpendicular to faces,” European Committee for Standardization, Brussels, Belgium.

EN 1609 (2013). “Thermal insulating products for building applications - Determination of short term water absorption by partial immersion,” European Committee for Standardization, Brussels, Belgium.

EN 9396 (2001). “Plastics - Phenolic resins - Determination of the gel time of resols under specific conditions using automatic apparatus,” European Committee for Standardization, Brussels, Belgium.

EN 12092 (2002). “Adhesives - Determination of viscosity,” European Committee for Standardization, Brussels, Belgium.

EN 12460-3 (2016). “Wood-based panels - Determination of formaldehyde release - Part 3: Gas analysis method,” European Committee for Standardization, Brussels, Belgium.

EN 13986 (2015). “Wood-based panels for use in construction - Characteristics, evaluation of conformity and marking,” European Committee for Standardization, Brussels, Belgium.

Euring, M., and Kharazipour, A. (2013). “Method for producing wood materials and/or composite materials,” World Patent No. WO/2013/127947.

Euring, M., Kirsch, A., and Kharazipour, A. (2015). “Hot-air/hot-steam process for the production of laccase-mediator-system bound wood fiber insulation boards,” *BioResources* 10(2), 3541-3552. DOI: 10.15376/biores.10.2.3541-3552

Europäischer Wirtschaftsdienst GmbH (EUWID) (2017). “EUWID Special: Wood-Based Panels,” *Special Issue* 13.10.2017, 17.

Europäischer Wirtschaftsdienst GmbH (EUWID) (2018). “EUWID Special: Wood-Based Panels,” *Special Issue* 05.10.2018, 18-19.

European Chemicals Agency Regulation 605/2014 (2014). “Commission Regulation (EU) No 605/2014 amending, for the purposes of introducing hazard and precautionary statements in the Croatian language and its adaptation to technical and scientific progress, Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures,” European Union, Brussels, Belgium.

Fan, B., Zhang, L., Gao, Z., Zhang, Y., Shi, J., and Li, J. (2016). “Formulation of a novel soybean protein-based wood adhesive with desired water resistance and technological applicability,” *J. Appl. Polym. Sci.* 133(27), DOI: 10.1002/APP.43586

Foglia, A., Sonderegger, W., Niemz, P., Bader, H. and Weber, A. (2006). “Untersuchungen zur Wärmeleitfähigkeit neuartiger Holzwerkstoffen und Werkstoffverbunde [Studies on the thermal conductivity of new types of wood-based panels and composite materials],” *Forschungsbericht Zürich: ETH Inst. Baustoffe Nr. 2004.02*

Frihart, C. R., and Lorenz, L. F. (2017). "Protein adhesives," in: *Handbook of Adhesive Technology – 3rd Edition*, A. Pizzi, and K. L. Mittal (eds.), CRC Press, Boca Raton, FL, USA, pp. 145-175.

Gossett, J. M., Estep, M. H., and Perrine, M. J. (1959). "Production of glue from soluble blood," U.S. Patent No. 2874134.

GUTEX (2019a). *Technisches Merkblatt GUTEX Thermowall®/-NF/-gf/-L* [Technical Data Sheet *GUTEX Thermowall®®/-NF/-gf/-L*], Technical Data Sheet 2019-04, GUTEX Faserplattenwerk, Waldshut-Tiengen, Germany.

GUTEX (2019b): Technisches Merkblatt *GUTEX Thermofibre®* [Technical Data Sheet *GUTEX Thermofibre®*], Technical Data Sheet 2019-05, GUTEX Faserplattenwerk, Waldshut-Tiengen, Germany.

Hale, K. (2013). *The Potential of Canola Protein for Bio-Based Wood Adhesives*, Doctoral Dissertation, Kansas State University, Manhattan, KS, USA.

Henning, S. B. (1920). "Glue and process for manufacturing the same," U.S. Patent No. 1329599.

Hettiarachchy, N. S., Kalapathy, U., and Myers, D. J. (1995). "Alkali-modified soy protein with improved adhesive and hydrophobic properties," *J. Am. Oil Chem. Soc.* 72(12), 1461-1464. DOI: 10.1007/BF02577838

Huntsman (2010). *Sicherheitsdatenblatt I-BOND® WFI 4370*, Technical Safety Data Sheet, Huntsman Holland BV, Rotterdam, Netherlands.

Irle, M. A., Barbu, M. C., Reh, R., Bergland, L., and Rowell, R. M. (2012). "Wood composites," in: *Handbook of Wood Chemistry and Wood Composites* (2nd Edition), R. M. Rowell (ed.), CRC Press, Boca Raton, FL, USA, pp. 321-412.

International Agency for Research on Cancer (2006). "Formaldehyde, 2-butoxyethanol and 1-tert-butoxypropan-2-ol," *IARC Monog. Eval. Carc.* 88, 1-478.

Kirsch, A., Ostendorf, K., Kharazipour, A., and Euring, M. (2016). "Phenolics as mediators to accelerate the enzymatically initialized oxidation of laccase- mediator-systems for the production of medium density fiberboards," *BioResources* 11(3), 7091-7101. DOI: 10.15376/biores.11.3.7091-7101

Kirsch, A., Ostendorf, K., and Euring, M. (2018). "Improvements in the production of wood fiber insulation boards using hot-air/hot-steam process," *Eur. J. Wood Wood Prod.* 76(4), 1233-1240. DOI: 10.1007/s00107-018-1306-z

Lei, H., Pizzi, A., Navarrete, P., Rigolet, S., Redl, A., and Wagner, A. (2010). "Gluten protein adhesives for wood panels," *J. Adhes. Sci. Technol.* 24(8-10), 1583-1596. DOI: 10.1163/016942410X500963

Li, X., Li, J., Luo, J., Li, K., Gao, Q., and Li, J. (2018). "A novel eco-friendly blood meal-based bio-adhesive: Preparation and performance," *J. Polym. Environ.* 26(2), 607-615. DOI: 10.1007/s10924-017-0976-7

Lin, H., and Gunasekaran, S. (2010). "Cow blood adhesive: Characterization of physicochemical and adhesion properties," *Int. J. Adhes. Adhes.* 30(3), 139-144. DOI: 10.1016/j.ijadhadh.2009.10.003

Lindauer, A. C. (1923). "Blood-albumin glue," U.S. Patent No. 145954.

Mantanis, G. I., Athanassiadou, E. T., Barbu, M. C., and Wijnendaele, K. (2018). "Adhesive systems used in the European particleboard, MDF and OSB industries," *Wood Mater. Sci. Eng.* 13(2), 104-116. DOI: 10.1080/17480272.2017.1396622

Nordqvist, P. (2012). *Exploring the Wood Adhesive Performance of Wheat Gluten*, Doctoral Dissertation, KTH Royal Institute of Technology Stockholm, Sweden.

Ofori, J. A., and Hsieh, Y.-H. P. (2014). "Issues related to the use of blood in food and animal feed," *Crit. Rev. Food Sci.* 54(5), 687-697. DOI: 10.1080/10408398.2011.605229

Okanovic, D., Ristic, M, Kormanjos, S., Njezic, Z., Lilic, S. and Grujic, R. (2010). "Chemical and nutritional quality of slaughter pigs by-products," *Quality of Life* 1(1), 55-60. DOI: 10.7251/QOL1001055O

Pal, R. (2006). *Rheology of Particulate Dispersions and Composites*, CRC Press, Boca Raton, FL, USA. DOI: 10.1201/9781420016048

Pizzi, A., and Mittal, K. L. (2011). *Wood Adhesives*, CRC Press, Boca Raton, FL, USA.

Reyer, E., Willems, W., and Müller, A. (2002). *Kompendium der Dämmstoffe* [*Compendium of Insulating Materials*], Fraunhofer IRB-Verlag, Stuttgart, Germany.

Roffael, E., Schneider, T., Dix, B., and Buchholz, T. (2005). "Zur Hydrophobierung von Mitteldichten Faserplatten (MDF) mit Paraffinen. Teil 1: Einfluss der chemischen Zusammensetzung des Paraffins und des Emulgatortyps auf die Hydrophobierung von MDF [On paraffin sizing of medium density fiberboard (MDF). Part 1: Influence of the chemical composition of paraffin and type of emulsifier on the hydrophobic properties of MDF]," *Holz. Roh. Werkst.* 63(3), 192-203. DOI: 10.1007/s00107-004-0556-0

Salem, M. Z. M., and Böhm, M. (2013). "Understanding of formaldehyde emissions from solid wood: An overview," *BioResources* 8(3), 4775-4790. DOI: 10.15376/biores.8.3.4775-4790

Sellers, T. (1985). *Plywood and Adhesive Technology*, CRC Press, Boca Raton, FL, USA.

Siimer, K., Kaljuvee, T., and Christjanson, P. (2003). "Thermal behavior of urea-formaldehyde resins during curing," *J. Therm. Anal. Calorim.* 72(2), 607-617. DOI: 10.1023/A:1024590019244

Sonderegger, W. and Niemz, P. (2009). "Thermal conductivity and water vapour transmission properties of wood-based materials," *Eur. J. Wood Prod.* 67(3), 313-321. DOI: 10.1007/s00107-008-0304-y

Statista (2019): "Hog and pig farming," (https://www.statista.com/study/44286/hog-and-pig-farming-in-the-us/), accessed 4 December 2019

Warriss, P. D. and Wotton, S. B. (1981). "Effect of cardiac arrest on exsanguination in pigs," *Res. Vet. Sci*. 31, 82-86. DOI: 10.1016/S0034-5288(18)32526-8

Wilson, J. B. (2010). "Life-cycle inventory of formaldehyde-based resins used in wood composites in terms of resources, emissions, energy and carbon," *Wood Fiber Sci.* 42, 125-143.

Yang, I., Kuo, M., Myers, D. J., and Pu, A. (2006). "Comparison of protein-based adhesive resins for wood composites," *J. Wood Sci*. 52(6), 503-508. DOI: 10.1007/s10086-006-0804-5

Zeppenfeld, G., and Grunwald, D. (2005). *Klebstoffe in der Holz-und Möbelindustrie* [*Adhesives in the Wood and Furniture Industry*], DRW-Verlag Weinbrenner GmbH & Co. KG, Leinfelden-Echterdingen, Germany.

Article submitted: August 17, 2019; Peer review completed: November 23, 2019; Revised version received: January 7, 2020; Accepted: January 8, 2020; Published: January 14, 2020.
DOI: 10.15376/biores.15.1.1531-1546