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INTERDISCIPLINARY DOCTORAL SCHOOL

Faculty of Furniture Design and Wood Engineering

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RESEARCH ON THE MANUFACTURING OF LIGNOCELLULOSIC COMPOSITES WITH LOW FORMALDEHYDE EMISSION

ABSTRACT

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BRAȘOV, 2021

TO ....

Examination Jury

Named by Rector Order University Transilvania Braşov
No. 828 from 23.11.2021

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Date, time and place of the public defense of the doctoral thesis: 17.01.2022, hour 12.00, room LIII3

Any assessments or observations on the content of the paper will be sent electronically, in due time, to the address 1

At the same time, we invite you to take part in the public meeting to defend my doctoral thesis.

Thank you.

CONTENT

NOTATION LIST

Parameter name	Symbol	Unity of measure
Particle sizes distribution	D_p	%
Mass of the particles collected in the sieve	m_f	g
Total mass of the particles sample	m	g
Pressing temperature	T	°C
Modulus of elasticity	E_m	N/mm^2
The distance between the centers of the supports	l_1	mm
The width of the test sample	b	mm
The length of the test sample	a	mm
The thickness of the test sample	t	mm
Increase the force, in newtons, on the right portion of the deformation load curve	F_2-F_1	N
Increase the deflection to half the length of the test piece (suitable for F_2-F_1)	a_2-a_1	N
Bending strength (Modulus of rupture) (MOR)	f_m	N/mm^2
Maximum force (breaking force)	F_{max}	N
Internal bond (IB)	F_t	N/mm^2
Formaldehyde content of the solution for each sample, per hour	G_i	mg
The values of the formic aldehyde content corresponding to first hour	G_1	mg/m^{2}h
The values of the formic aldehyde content corresponding to second hour	G_2	mg/m^{2}h
The values of the formic aldehyde content corresponding to third hour	G_3	mg/m^{2}h
The values of the formic aldehyde content corresponding to fourth hour	G_4	mg/m^{2}h
Absorption of the solution from the specimens	A_S	ml
Absorption of distilled water	A_B	ml
Slope of the calibration curve for the standard formaldehyde solution	f	mg/ml
Surface of the sample subjected to formaldehyde release test	F	m^2
Volume of the volumetric flask	V	ml
The average value of formic aldehyde content	G_m	mg/m^{2}h
Moisture content	U	%
Density	ρ	kg/m^3

LIST OF ABBREVIATIONS

Detailed name	Abbreviation used in the thesis
Formaldehyde emission class	E1, E2, E3
Japan emission class, equivalent to the European emission class E1	F**
Emission class E0	F***
Emission class Super E0	F****
Magnesium lignosulfonate	Lignex MG
Hydrogen peroxide	H_2O_2
Sodium hydroxide	NaOH
Hydrochloric acid	HCl
Closite Na+	Nanoclay
Iron sulphate	$FeSO_4$
Substance acidity	pH
Magnesium lignosulfonate powder 15%	L15
Magnesium lignosulfonate powder 20 %	L20
Magnesium lignosulfonate powder 50% %	L50
Oxidized magnesium lignosulfonate15%	LO 15
Oxidized magnesium lignosulfonate 20%	LO 20
International Standards Organization	ISO
Panel with 15% lignin, 1% PMDI and 15% glucose	LO 15 P1
Panel with 20% lignin content, 1% PMDI and 15% glucose	LO20 P1
Panel with 15% lignin, 2% PMDI and 15% glucose	LO15 P2
Panel with 20% lignin content, 2% PMDI and 15% glucose	LO20 P2
Panel with 15% lignin, 3% PMDI and 15% glucose	LO15 P3
Panel with 20% lignin content, 3% PMDI and 15% glucose	LO20 P3
Panel with 15% lignin, 1% PMDI and 15% glucose	LO15P1G
Panel with 20% lignin content, 1% PMDI and 15% glucose	LO 20 P1G
Panel with 15% lignin, 2% PMDI and 15% glucose	LO 15 P2G
Panel with 20% lignin content, 2% PMDI and 15% glucose	LO 20 P2G
Parts per million	ppm
Parts per billion	ppb
Particleboard	PB
General particleboards, used in dry environment (according to SR EN 312:2004)	P1
Panels used for joints, including furniture, used in dry environments, (according to SR EN 312:2004)	P2

Detailed name	Abbreviation used in the thesis
Medium density fiber boards	MDF
Oriented strand board	OSB
Fiber board panel	PFL
Glued laminated timber	Glulam
Laminated veneer lumber	LVL
Formaldehyde	CH_2O
Volatile organic compounds	VOCs
Polymeric diphenylmethane diisocyanate	PMDI
Phenol-formaldehyde resins	PF
Melamine formaldehyde resin	MF
Urea-formaldehyde resins	UF
X-ray analysis	XDR
Vertical density profile of the composites	VDP
Internal bond (tensile perpendicular to the faces of panel)	IB
Modulus of elasticity	MOE
Modulus of rupture (bending strength)	MOR
Fourier-transform infrared spectroscopy	FTIR
State standard	STAS
Romanian European Standard	SR EN
Research and Development Institute of Transilvania University Brașov	ICDT
European Union	UE
International Agency for Research on Cancer	IARC
European Chemicals Agency	ECHA
Dynamic Micro Chamber	DMC
Cell and Laboratory Emission Cell	FLEC
California Air Resources Board	CARB
European Panel Federation	EPF

INTRODUCTION

The topic of this doctoral thesis is to study an important field of current research, namely, the replacement of synthetic adhesives with bio-adhesives with low formaldehyde emission.

The thesis is structured in six chapters, starting from the current state of research on the development of lignocellulosic composites with low formaldehyde emissions and which is the starting point in establishing the direction of research.

Chapter 1 entitled "Current state of research on low formaldehyde lignocellulosic composites" summarizes the extensive documentation on the results obtained by other researchers regarding bio-adhesives and their application for composites with low formaldehyde emission.

The study presents data on formaldehyde emission and its allowable values, as well as the most used standardized methods for determining formaldehyde emission. Alternative ways to reduce formaldehyde emissions are also presented, such as the replacing of formaldehyde with other chemicals with similar reactions, by addition of amines and scavengers like tannin, lignin, starch or soy proteins.

The conclusions of current research are presented at the end of Chapter 1, and they constitute the starting point for establishing the objectives of this doctoral thesis.

Chapter 2 entitled "The objectives of the doctoral thesis" presents the general objective with regard to the manufacture of particleboard with low formaldehyde emission and the specific objectives related to the preliminary study on the chemical modification of magnesium lignosulfonate, selection of chemically modified adhesive, improvement of recipes and establishment of optimal recipes for lignin-based bio-adhesive, manufacture the particleboard in the laboratory conditions and determination of their emission of formaldehyde by the gas analysis method.

Chapter 3 entitled "Preliminary research on the modification of magnesium lignosulfonate" presents the preliminary research on increasing the reactivity of magnesium lignosulfonate using two methods, namely hydroxymethylation and oxidation and the FTIR analysis of magnesium lignosulfonate which was used as a raw material for bio-adhesives. The three adhesive recipes were prepared and particleboard panels were made in the laboratory conditions. Internal bond strength of the panels was determined. The comparison of the obtained results led to the choice of the recipe for the preparation of the lignin-based adhesive for further experimental work.

Chapter 4 entitled "Experimental research on the manufacturing and testing of particleboard made with adhesive based on magnesium lignosulfonate modified by oxidation with H_2O_2" presents the objectives set for the panels manufacturing, investigation of raw material and adhesive and microscopic analysis of the structure of particleboard. The panels were tested in order to determine the internal bond strength (IB) and the modulus of elasticity/ bending strength (MOE/ MOR).

Formaldehyde emission was determined by the gas analysis method and it was found that by the oxidation process of the magnesium lignosulfonate, the formaldehyde emission decreases.

Chapter 5 entitled "Experimental research on the production and testing of particleboard made with adhesive based on magnesium lignosulfonate modified by oxidation with H_2O_2 and the addition of crosslinking agents" is an important chapter of this thesis and consists in improving the adhesive recipe by addition of crosslinking agents.

The research conducted in this chapter included FTIR analysis of new improved adhesives obtained by adding crosslinking agents and testing the mechanical performance of the particleboard panels manufactured in the laboratory conditions with these adhesive types.

A first solution was identified to improve mechanical performance by using polymeric diphenyl methane diisocyanate (PMDI) in proportions ranging from 1% to 3%. The microscopic analysis of the structures of the panels and the determination of the density profile along the thickness of the panels were also taken into account. The formaldehyde emission of the panels was also determined by gas analysis method. It was noticed that lower values were obtained by the addition of PMDI and glucose as crosslinkers. The results of the study in this chapter offer new solutions for improving the mechanical strength of particleboard made with bio-adhesive based on magnesium lignosulfonate, by using crosslinkers such as PMDI and glucose.

Chapter 6 entitled "General conclusions. Original contributions. Dissemination of results. Further research directions" presents the results obtained in the experimental research performed in order to fulfil the proposed objectives, the original contributions to knowledge by this doctoral thesis, the way of disseminating the results and the open paths for further research work.

The research conducted in this doctoral thesis has shown that there are possibilities to manufacture particleboard with adhesives based on magnesium lignosulfonate and having low formaldehyde emission, and also with good mechanical performance according to the standard SR EN 312: 2004 requirements for indoor panels.

Chapter 1. Current state of research on low formaldehyde lignocellulosic composites

1.1. Formaldehyde and permissible limits

Wood emits and contains volatile organic compounds (VOCs), including formaldehyde. The emission of formaldehyde from wood increases when wood is processed, but formaldehyde is mostly released in the manufacturing process of wooden based boards (particleboard and fibreboard).

Formaldehyde emission is the amount of formaldehyde released from wood panels in a certain volume of air or a certain amount of water in a specified period of time. The standardized methods used to determine formaldehyde emissions are:

- Chamber method (reference method): with chamber capacities of 0.225 m^3, 1 m^3, 22 m^3, 40 m^3 (EN 717-1:200/ ISO 12460-1:2007; ASTME 1333:2014; ASTM D 6007:2014, JIS A 1901:2015, JIS A 1911:2015, ISO 12460-2:2018)

- Gas analysis method (derived method) – (EN 717-2:1995/ ISO 12460-3:2015, UNI EN ISO 12460-3: 2021) (http://www.cosmob.it/en/2021/03/11/formaldehyde-new-version-of-the-gas-analysis-test-method-uni-en-iso-12460-32021/

- Flask method (EN 717-3:1996; AWPA:1991)

- Desiccator method (ASTM D 5582:2014, JIS A 1460:2001, JAS-MAFF 235:2016, JAS MAFF 233:2001, AS/ NZS 4266.16:2004; ISO 12460-4:2016)

Test methods can be divided into three categories (Young, 2004):

a. Reference methods: - the chamber method that simulates a standard indoor environment;

b. Certification methods used in particular for the certification of products intended for sale (perforator and desiccator methods).

c. Quality control methods used for fast and regular production control (i.e., flask method, gas analysis and others, based on specialized devices such as Dynamic Micro Chamber (DMC) and Cell and Laboratory Emission Cell (FLEC).

Table 1. Permissible limits of concentration and formaldehyde content for the 3 emission classes (1980- 1989)

Emission class	The concentration of formaldehyde determined by the chamber method, in ppm	Formaldehyde concentration determined by the perforator method, in mg / 100g dry plate
E1	≤ 0.1	≤10
E2	0.1 – 1.0	10-30
E3	1.0 – 2.3	30 – 40

1.2. Solutions to reduce formaldehyde emission

Adhesives have been always of interest to the wood panel industry. For these wood-based products, it is desired to use effective adhesives, at a competitive price, with the lowest possible formaldehyde emissions. Due to formaldehyde emissions, it has been shown that formaldehyde-based adhesives are not environmentally friendly products, so solutions must be found to modify or replace them.

Bio-scavengers are environmentally friendly solutions to reduce formaldehyde emissions from panels and include substances, such as:

- Tannin,

- Lignin,

- Starch,

- Soy protein.

1.2.1. Use of amines as additives in adhesive resins

In urea-formaldehyde resins can be added additives called scavengers, which bind to urea-formaldehyde and aim to reduce formaldehyde emissions. The addition of five types of amines resulted in a decrease in the formaldehyde content of the boards, but to the detriment of water absorption and thickness swelling of the panels. (Boran *et al.*, 2011). It was found that the addition of hexamine greatly reduced the emission of formaldehyde, but slightly reduced the mechanical strength of the panels, but within the acceptable limits (Pizzi *et al.*, 1996).

1.2.2. Use of amino plastic resins (CHIMAR)

The Greek company CHIMAR HELLAS has developed innovative technologies to reduce the formaldehyde emission of wood-based panels, up to the level of the Japanese emission class, F ***, class E0 and "super E0", or the level of emission of solid wood. In addition to very low formaldehyde emissions, panels made with CHIMAR adhesives have acceptable water and mechanical resistance. Adhesives are based on petrochemical resins, to which formaldehyde scavengers from natural resources are added: bio-oils, tannin, soy or lignin (Papadopoulou, 2009).

In the production of MDF and particleboard, using Chimar resin, low formaldehyde emissions were obtained through the use of amino plastic resins. There was no need to change production parameters or equipment settings for MDF and particleboard production, and no loss of productivity or a significant increase in the production cost were recorded.

1.2.3. Tannin-based adhesives

Tannins are polyphenols of vegetable origin, with a substantial concentration in the bark of trees, which are divided into two categories: hydrolysable tannins and condensed tannins. Condensed tannins account for more than 90% of the total commercial tannin production (Pizzi, 2013).

Tannins are water, alcohol and acetone soluble compounds and are of particular interest in the preparation of adhesives, due to the presence of phenolic groups, with reactivity similar to that of phenols.

Tannins used in the production of adhesives for wood products reduce their formaldehyde emissions (Neimsuwan *et al.*, 2017).

1.2.4. Addition of silicon nano-dioxide (SiO_2)

FTIR analysis of urea-formaldehyde resin with the addition of silicon nano-dioxide revealed that these nanoparticles create hydrogen bonds with UF resin. The low cost and low amount of nanoparticles that improve the performance of UF resin, as well as the simple technology, are the advantages of this promising solution for obtaining mechanically efficient panels and reducing harmful formaldehyde emissions (Roumeli *et al.*, 2012).

1.2.5. Lignin-based adhesives

Lignin is found as a component of the cell wall in all cereals, and the lignin content of plant stems varies between 15% and 40%. Lignin protects plants against biological attack and acts as a permanent adhesive, tying the cells together in the plant stems and thus giving the stems the necessary rigidity and strength. Industrial lignin is a residual product, obtained from the industrial process of pulp and paper manufacturing, as a result of the chemical separation of cellulose from lignin.

In the process of making lignin-based adhesives, lignin is often combined with synthetic resins such as phenol formaldehyde (PF) resins and/ or urea formaldehyde (UF) resins, in order to reduce the cost of production and formaldehyde emissions.

The most used methods for increasing reactivity are hydroxymethylation (Malutan *et al.*, 2008; Aro and Fatehi, 2017) and oxidation (Hemmilä *et al.*, 2013; Klapiszewski *et al.*, 2017; Fernandes *et al.*, 2019; Hu *et al.*, 2011). Oxidation of lignin has been described as a way to weaken the structure of lignin, making it more susceptible to depolymerisation (Fernandes *et al.*, 2019) and a good procedure to improve the properties of lignin (Hu *et al.*, 2011).

Other research works has shown that the process of lignin phenolisation involves a long reaction time, high temperatures and a low percentage of lignin participation. Thus, for the phenolisation of ammonium lignosulfonate, the optimal conditions are represented by a temperature of 120 °C, for 160 minutes and a percentage of lignosulfonate participation of maximum 30% (Alonso *et al.*, 2005).

1.2.6. Protein extracts adhesives.

In an effort to develop low-formaldehyde-adhesives, some researchers prepared adhesives with protein extract from *Rhodotorula rubra* (Núñez-Decap *et al.*, 2018).

Soy protein adhesives have been used in several applications to manufacture particleboard or plywood, but it has been noticed that they have both low water resistance and high viscosity. Thus, several researchers have obtained adhesives based on soy protein, but with modest performance (Fapeng *et al.*, 2017). Soy protein, in other studies, was mixed with lignin to improve the water resistance of the adhesive and it was observed that lignin, with smaller particle sizes, increased the water resistance of the adhesive (Pradyawong *et al.*, 2017).

1.2.7 Low formaldehyde emission UF adhesives

The major disadvantage of these adhesives is their low water resistance and formaldehyde emissions, which can sometimes exceed the E1 level, the maximum level allowed for indoor products. Some research works have investigated the reduction of formaldehyde emissions of UF adhesives by various methods: changing the preparation recipe, by adding different formaldehyde scavengers, but also by changing the technological parameters of pressing process (time, temperature, pressure). At the laboratory level, it was found that the urea: formaldehyde molar ratio of 1: 0.7 provides an acceptable balance between formaldehyde emission and mechanical strength of the panels (Pizzi *et al.*, 1994a).

1.2.8. Reduction of formaldehyde emissions with the addition of nano-clay (Closite Na +)

Some researchers have shown that the addition of nano-clays contributes to the improvement of the mechanical strength of some particleboard with lignin-based adhesives (Younesi-Kordkheili *et al.*, 2015).

Another study (Ismita *et al.*, 2018) investigated the role of nano-clay (Closite Na+) in reducing formaldehyde emissions from particleboard. Closite Na+ was added in various concentrations and it was observed that by the addition of Closite Na+ there was a visible reduction in formaldehyde emissions from the panels. Particles resulted from bamboo stalks were used as raw material and they were dried to a moisture content of 6%.

Closite Na+ nano-clay was added to UF resin in proportions of 1%, 3% and 5%. The percentage of participation of UF resin was 10% of the mass of dry particles. The desiccator method was used to determine formaldehyde emission. The results of the study showed that the use of Closite Na+ in bamboo particleboard reduces the emission of formaldehyde.

1.2.9. Use of crosslinking agents in the manufacture of particleboard

Crosslinking agents are substances that promote the formation of intermolecular, covalent or ionic bonds between polymer chains (Solt *et al.*, 2019).

One method of reducing formaldehyde emissions is to replace formaldehyde with substances with similar reaction mechanisms. One of these substances is glyoxal. (Mansouri *et al.*, 2011).
Another crosslinking agent widely used in the field of wood-based composites is PMDI. Several researchers (Younessi-Kordkheili and Pizzi, 2018) made particleboard using adhesive based on urea resin and glyoxal addition, synthesized in weak acid conditions.

1.3 Conclusions on methods to reduce formaldehyde emissions

- The permissible values for particleboard to be in the formaldehyde emission class E1 must be less than 0.1 ppm (EN 717-1: 2004 – chamber method) and 3.5 mg/m^{2}h (EN 717-2:1995 – gas analysis method).
- In order for the panels to meet the Super E0 emission classes (corresponding to the emission class F ****), for which the value determined by the chamber method is 0.04 ppm, using the gas analysis method, the measured value must be below 1.4 mg/m^{2}h.
- Formaldehyde emission values measured for several solid wood species (beech, fir, spruce, oak and pine) indicate values between 0.114 mg/m^{2}h – 0.431 mg/m^{2}h for wood moisture content above 50% and values between 0.034 mg/m^{2}h – 0.086 mg/m^{2}h for wood moisture content below 10%. The species that recorded the highest emission values in the wet state were oak and fir, and pine and fir in dry condition. The lowest values, in both situations, were recorded by the beech wood.
- Methods for reducing formaldehyde emissions from particleboard include the use of bio-adhesives (as plant extract, wood biomass, plant and animal proteins, etc.), the use of formaldehyde scavengers from natural resources in petrochemical resins (bio -oils, tannin, soy or lignin), the use of crosslinking agents, which promote the formation of intermolecular, covalent or ionic bonds between polymer chains (glyoxal, PMDI, sugars, furfuryl and furfuryl alcohol, citric acid, maleic anhydride, etc.)
- Lignin-based bio-adhesives and lignosulfonates occupy an important place in research on reducing the formaldehyde emission of particleboard panels. There is a lot of research done to increase the reactivity of lignin, as it has been proven that its reactivity is low in its pure state. The most used methods are: oxidation, phenolation, hydroxymethylation. Lignin is also used as a substitute for phenol in phenol-formaldehyde resin, with good substitution results of up to 20%-30%, according to research in the literature.
- There are few studies related to the use of magnesium lignosulfonate in the manufacture of bio-adhesives for particleboard. Recent research work on the use of this lignosulfonate in the manufacture of MDF panels has favourably appreciated with relation to its potential in the manufacture of wood-based panels.

Chapter 2. The objectives of the doctoral thesis

The general objective of the doctoral thesis is the manufacture of particleboard with low formaldehyde emission, using for this purpose magnesium lignosulfonate as raw material for bio-adhesives. The panels thus made must meet the requirements of mechanical strengths imposed by the European Standard SR EN 312: 2004 for the jointed panels (including furniture) used in dry environments (type P2).

The research conducted in this doctoral thesis took into account the following specific objectives:

- Preliminary study on the chemical modification of magnesium lignosulfonate in order to increase its reactivity, applying two methods: oxidation and hydroxylation.
- Selection of the chemically modified adhesive with the greatest potential in the manufacture of particleboard, using three variants of adhesive to manufacture particleboard in the laboratory conditions, testing the panels for internal bond strengths and comparing the results.
- Improving recipes by adding crosslinking agents: PMDI (1%, 2% and 3%) and glucose (15% of solid lignin content).
- Determination of formaldehyde emission by the method of gas analysis according to ISO 12460-3: 2015 (revised ISO 12460-3: 2020), and comparison of the results with permissible limits for formaldehyde emissions of class E1 and Super E0 (F***, F****).
- Determination of the modulus of elasticity (MOE) and bending strength (MOR) according to the standard SR EN 310: 1996 and the tensile strength perpendicular to the panel faces - internal bond (IB) according to SR EN 319: 1997 and comparing the results with the requirements of standard SR EN 312: 2004.
- Establishment of optimal lignin-based bio-adhesive recipes for low formaldehyde emission particleboards with mechanical performance within permissible limits, according to SR EN 312: 2004, for P2 type panels - jointed panels (including furniture) used in dry environment (type P2).

The implementation strategy of these objectives is presented schematically in Fig. 1.

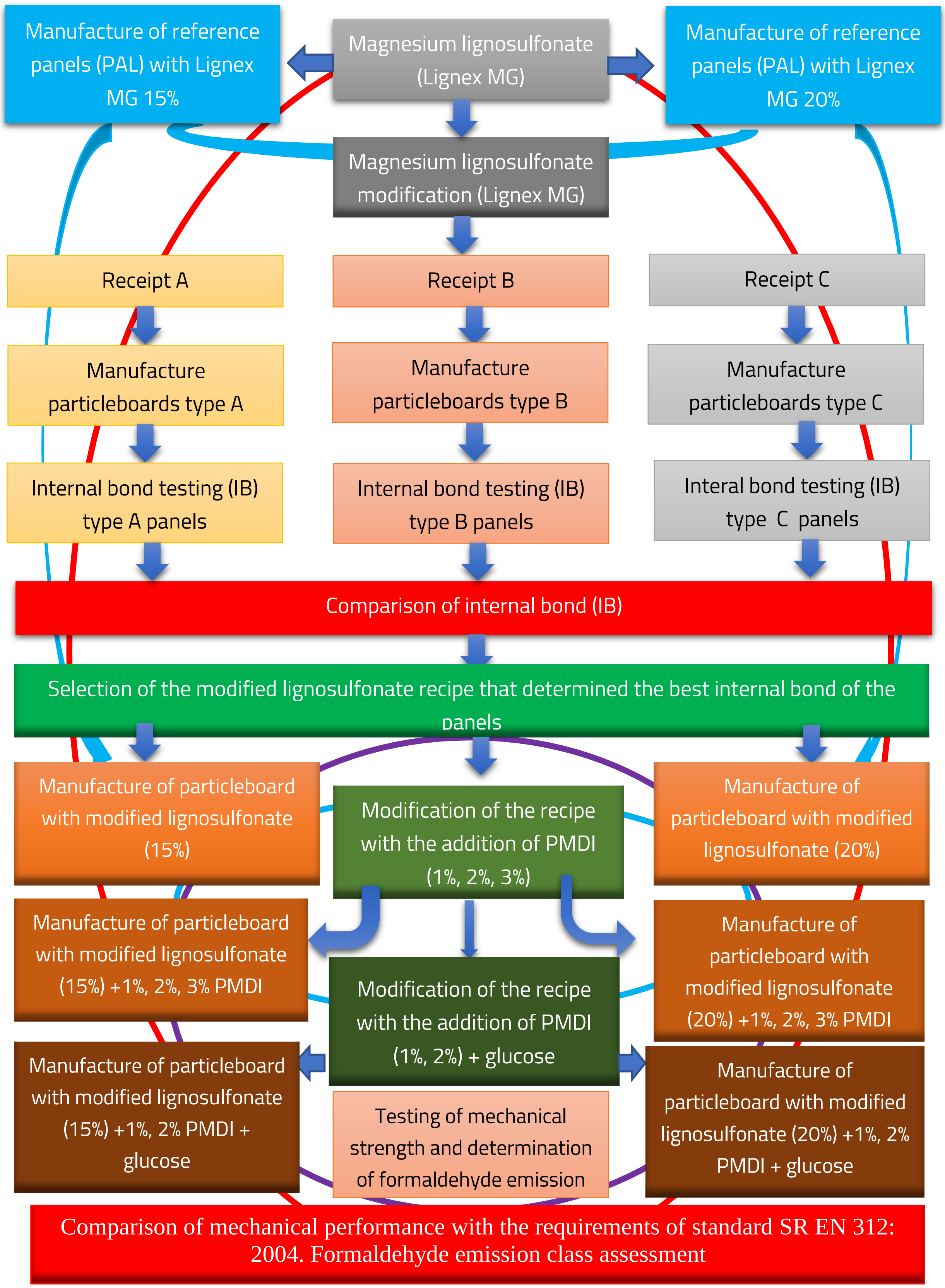


Fig. 1. Strategy for fulfilling the thesis objectives

Chapter 3. Preliminary research on the modification of magnesium lignosulfonate

3.1. The objective of the research

Preliminary research aimed to increase the reactivity of magnesium lignosulfonate through its chemical modification, using two methods: hydroxymethylation and oxidation and three recipes, noted with A, B and C. The first two recipes (adhesives A and B) were based on two methods of hydroxymethylation of lignin taken from the literature (Patent CN104245799A, 2003; Malutan *et al.*, 2008), and the third recipe (Hemmilä *et al.*, 2013) was based on H_2O_2 oxidation of lignin.

From the three adhesives, only one was selected, balancing both the resistance to internal bond of the single layer particleboard made with the three recipes of adhesives in identical laboratory conditions, and the degree of difficulty of the method of preparation of the adhesive.

3.2. Characteristics of unmodified magnesium lignosulfonate

Magnesium lignosulfonate (Lignex MG) was used for the preparation of the bio-adhesives for experimental particleboard manufacturing. Lignex MG was provided by Sappi Biotech GmbH (Düsseldorf, Germany), in unmodified condition, as powder.

3.2.1. Characteristics of Lignex MG

The characteristics of magnesium lignosulfonate (Lignex MG), as set out in the data sheet issued by the manufacturer, are as follows:

- dry matter content: 93 ± 2%
- magnesium content: 6 ± 1% min
- pH (10% solution): 5.5 ± 1%
- bulk density: 400 kg / m^3
- ignition temperature: 530˚C
- insolubility in water: 1% max
- moisture content: 7% max

3.2.2. FTIR analysis

Fourier-transform infrared spectroscopy (FTIR) analysis was conducted for three presentation forms of magnesium lignosulfonate, as follows: original powder provided by the manufacturer and powder mixed with water and dry in two ways: crosslinked state (oven dried) and air dried at room temperature. The crosslinking of lignosulfonate was performed at 160 ˚C for 15 min. This process was performed using the laboratory oven (Binder ED 115, Tuttlingen, Germany). For crosslinked and air dried magnesium lignosulfonate, sample preparation involved mixing the powder (10 parts) with water (1 part), and the mixture was then applied as a film to the microscope slides. One slide was left at room temperature for 5 days and the other was placed in the laboratory oven for crosslinking.

The comparative spectra of magnesium lignosulfonate powder, air-dried adhesive prepared from magnesium lignosulfonate powder and water (10 to 1) and crosslinked adhesive at 160 °C for 15 minutes are are similar in terms of absorption bands, indicating a similar chemical structure. There are some differences in the relative intensities of the absorption bands in the range 1600 cm^{-1} - 1000 cm^{-1} compared to the –OH absorption at 3400 cm^{-1} (with quasi-constant intensity due to the normalmin-max spectra). The present water in the analysed samples contributes to the absorption at 3400 cm^{-1}. These differences could be related to different water content in the three types of samples.

For the crosslinked adhesive, the absorption at 1332 cm^{-1} is better highlighted. In conclusion, it can be said that similar spectra indicate a physical binding mechanism, based mainly on the thermoplastic character of lignin (Fig. 2).

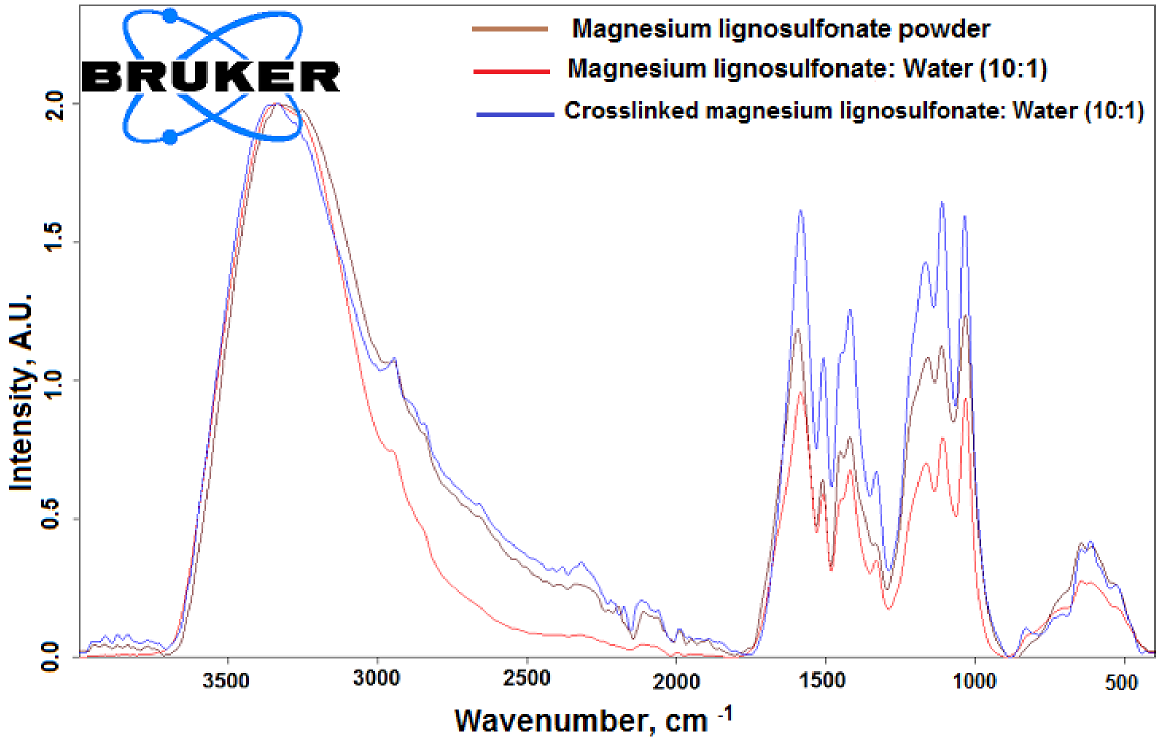


Fig. 2. Graphs obtained in FTIR spectroscopic analysis for lignosulfonate powder (brown line), lignosulfonate powder mixed with water and dried at room temperature (red line) and lignosulfonate powder mixed with water, crosslinked at 160 ° C for 15 min. (blue line)

3.3. Experimental research on the modification of magnesium lignosulfonate

In order to increase the reactivity of magnesium lignosulfonate, the most used methods in the literature are hydroxymethylation (Malutan *et al.*, 2008; Aro *et al.*, 2017) and oxidation (Hu *et al.*, 2011; Hemmilä *et al.*, 2013; Fernandes *et al.* 2019).

The purpose of this research was to select the method and recipe for chemical modification of magnesium lignosulfonate, in order to obtain an appropriate binder to be used in the composition of single-mat particleboard, which completely replaces the classic urea-formaldehyde adhesives and give the acceptable mechanical strength to the panels.

This research was conducted in the laboratory of the Faculty of Natural Resources at Tehran University in Iran. The internal bond of the panels was chosen for comparison (according to SR EN 319 - 1997), which best expresses the adhesion between the glued wood particles.

Thus, three recipes for increasing the reactivity of magnesium lignosulfonate were chosen from the literature:

Receipt A: hydroxymethylation of lignin (US Patent Application, 2019);

Receipt B: hydroxymethylation of lignin (Malutan *et al.*, 2008);

Receipt C: oxidation of lignin (Hemmilä *et al.*, 2013).

These three adhesive recipes were used to manufacture, in the laboratory conditions, single layer particleboard with a target density of 600 kg/m^3 and dimensions of 450 mm x 450 mm x 16 mm after pressing the panels.

The single-mat configuration of the particleboard was obtained using as raw material beech wood particles with sizes ranging between 8.6 mm - 13.5 mm for length, 0.5 mm - 2.4 mm for width and 0.5 mm - 1.4 mm for thickness.

The wood particle sizes were measured using a Nikon YS100 microscope, made in China, with an accuracy of 0.01 mm.

3.3.1. Preparation the adhesive with recipe A

For the preparation of the adhesive with recipe A, the following substances were used:

Water 836 g

NaOH 50% 584 g

Magnesium lignosulfonate 1270 g

Phenol 39 g

Formaldehyde 37%

Water and NaOH were mixed and heated. The lignin was slowly dispersed into the water mixture, and the temperature was raised to 60 °C. When all the lignin was dispersed, the temperature was raised to 75 °C for 1.5 hours. Following this process, lignin became alkaline and could be used as an adhesive in the following composition: 38 g of phenol (90%) was mixed with 105 g of alkaline lignin, after which 79 g of formaldehyde (37%) was added gradually. NaOH was used as a catalyst. The temperature was kept below 75 °C. Thereafter, the temperature was raised to 85 °C - 90 °C until the viscosity of the formed composition was about 415 cps (viscosity was measured at 25 °C).

The solid content of the adhesive thus obtained was 45.2%.

3.3.2. Preparation the adhesive with recipe B

For recipe B, the modification of lignosulfonate was used by a hydroxymethylation reaction. A 37% concentration formaldehyde solution was used in an alkaline medium using a 3% (w/w) NaOH solution. Thus, the lignosulfonate was mixed with 100 ml of 3% NaOH solution corresponding to a NaOH/ lignosulfonate ratio equal to 0.08 (w/w). The temperature of the resulting mixture was 25 °C, and the measured pH was 9.7. The hydroxyl methylation of lignin was performed by adding a 37% formaldehyde solution, using a CH_2O/lignosulfonate ratio of 0.258 (w/w), at room temperature. After that, the temperature was first raised to 50 °C and then gradually to 90 °C. The total reaction time was 3 hours. The solid content of the adhesive thus obtained was 48.3%.

3.3.3. Preparation the adhesive with recipe C

For this recipe, the lignin was oxidized with 30% hydrogen peroxide (H_2O_2) and the final H_2O_2 content was 5.7% based on the weight of the resin. NaOH was used to raise the pH to 9.

The recipe was as follows:

Magnesium lignosulfonate	316 g
Hydrogen peroxide 30%	24 g
Distilled water 1	69 ml
Sodium hydroxide 50%	50 ml

The solid content of the adhesive thus obtained was 56.5%:

3.4. Conclusions on the recipes of chemical modification of magnesium lignosulfonate

Single-layer particleboard panels were produced in the laboratory conditions, as explained in sub-chapter 3.3., where the three recipes of adhesives were used. After conditioning the panels, the test specimens were cut and subjected to mechanical testing protocol, according to SR EN 319:1997, in order to determine the internal bond (IB) strength. The Instron universal testing machine was used for this test. Six specimens cut from each panel were tested for IB and the results were afterwards compared.

The comparison of the results of the internal bond of the particleboard made with magnesium lignosulfonate modified by hydroxymethylation (recipe A and recipe B) and oxidation (recipe C) is presented in Fig. 3 and it is presented as percentages comparison between the results. According to these results, the oxidation process of lignosulfonate with H_2O_2 produced an adhesive (recipe C) with better impact on the results of the internal bond compared to the other two adhesives.

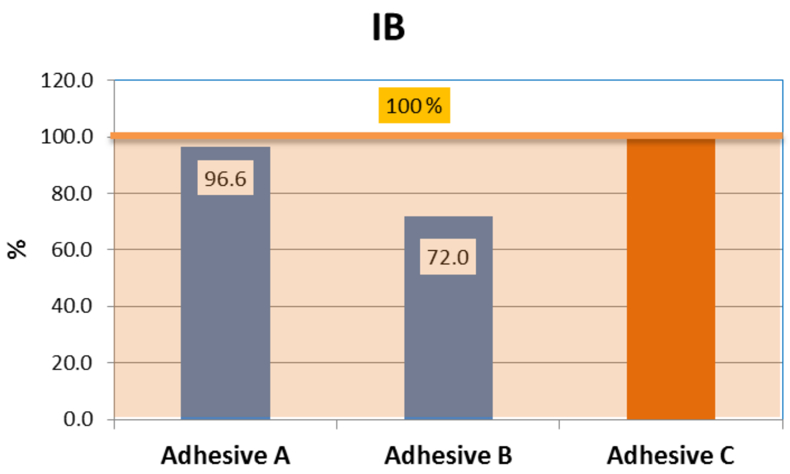


Fig. 3. Comparison of the results of internal bond, determined for experimental panels for which the three types of adhesives were used

It can be seen that the adhesive with recipe C proved a good adhesion to the wood particles, the binding process in the structure of the manufactured panel with this adhesive conducting to the highest value of the internal bond (considered 100% for the comparison), very close to that obtained with recipe A (96.6% of the IB obtained for panels made with adhesive C).

Having also the advantage of a better adhesion between the wood particles of the particleboard panels, as demonstrated by the IB test, the selected recipe to continue the research is recipe C, obtained by reactivating magnesium lignosulfonate by the oxidation process with hydrogen peroxide.

Chapter 4. Experimental research on the manufacturing and testing of particleboard made with adhesive based on magnesium lignosulfonate modified by oxidation with H_2O_2

4.1. The objectives of the research

The objectives set to manufacture and test the particleboard made with adhesive based on magnesium lignosulfonate modified by oxidation with H_2O_2 were:

- Procurement of the wood particles used in the industrial production process of particleboard, their gravimetric analysis and the determination of their moisture content;
- Establishing a target density of experimental particleboard, similar to that of the industrial manufactured particleboard made with urea-formaldehyde adhesives;
- Use of recipe C for the oxidation of magnesium lignosulfonate with hydrogen peroxide, in order to obtain the necessary bio-adhesive to manufacture the experimental single-layer particleboards;
- Manufacture in the laboratory conditions of single-layer particleboard, with the use of bio-adhesive in a proportion of 15%, respectively 20% based on the weight of the dry wood particles; these percentages have been established based on previous research (Hemmilä *et al.*, 2013), showing that a 10% participation rate of the reactivated lignin by oxidation in the composition of particleboard is not enough to achieve the required mechanical performance;
- Investigate the mechanical strengths of the panels: modulus of elasticity (MOE) and bending strength (MOR), according to EN 310: 1993, tensile strength perpendicular to the panel faces, or internal bond (IB) according to EN 319: 1993 and comparison of results with limits imposed by standard EN 312: 2004 for P2 type panels, intended for jointed panels, including furniture and for indoor use;
- Analysis of the density profile on the panel thickness, or vertical density profile (VDP);
- Fourier transform infrared spectroscopy (FTIR) of the lignosulfonate-based adhesive;
- Microscopic analysis of the structure of particleboard, for which the lignosulfonate bio-adhesive was used.

4.2. Investigation of raw material and adhesive

4.2.1. Granulometry and wood particles sizes

In order to manufacture the experimental single-layer particleboard with low formaldehyde emission, wood particles provided by the company Kastamonu Romania S.A. (particleboard manufacturer) were used. Wood particles were a mixture of beech species (30%) and softwood species (70%). Of the total amount, 5% were represented by the bark (Lengyel, 2018).

The moisture content of the wood particles was determined at the moment of receiving them from the supplier, in accordance with EN 322:1993. The average moisture content of three determinations was 6.8%.

The granulometric analysis of the particles (coarses and fines) was performed using the Retsch vibratory sieve shaker machine, made in Germany, from the endowment of the chemistry laboratory of the Faculty of Furniture Design and Wood Engineering - Transilvania University of Brașov.

The participation rate of the particles, both for the coarse and fine particles are presented in Table 2.

Table 2. The participation rate of the particles collected in the sieves, in %

Types of particles		Sieve mesh size, in mm								
	4.00 x 4.00	3.15 x 3.15	2.00 x 2.00	1.25 x 1.25	1.00 x 1.00	0.80 x 0.80	0.53 x 0.53	0.40 x 0.40	0.16 x 0.16	Waste
Coarse	4.8%	2%	28%	38.4%	15.2%	-	-	-	-	11.6%
Fines	-	-	-	-	50.4%	12%	18%	11.6%	6.4%	1.6%
The role in the particleboard structure	Coarse particles				-	-	-	Dust (not used)		
					Fine particles					

The analysis of the participation rate of the particles fractions showed that a large share belonged to the particles collected in the sieve with meshes of 1.25 mm x 1.25 mm (almost 40%), while for the fine particles the majority ones were collected in the sieve with 1.00 mm x 1.00 mm mesh size. Therefore, for a control on the PB structures, the particles collected from the sieve with mesh sizes of at least 1.25 mm x 1.25 mm were considered coarse particles, while for the fine ones, the minimum particle sizes should be either those collected in the sieve with meshes of 0.53 mm x 0.53 mm, and the largest in the sieve with meshes of 1.00 mm x 1.00 mm.

Measurements on the length and width of the chips (Fig. 4) were performed in AutoCAD, and the thickness was measured with an electronic calliper with an accuracy of 0.01 mm. In this way, intervals of dimensional variation were established for each pile of particles obtained in the sieves used in the experimental research.

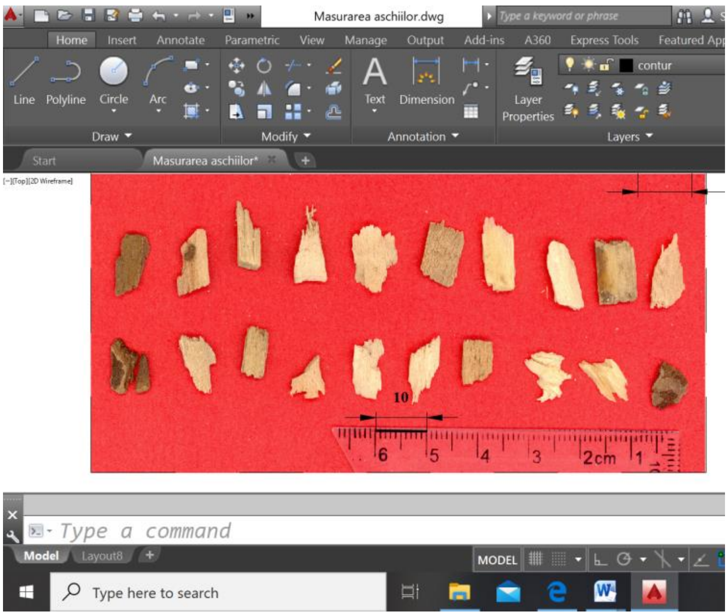


Fig. 4. Scale 1: 1 adjustment in AutoCAD of the scanned image to measure chip size (length and width)

The centralized data are presented in Table 3, as dimensional ranges of the length, width and thickness of the particles for each fraction obtained in the sieves used for the analysis.

Table 3. Dimensional ranges of the particles collected in each sieve

Sieve mesh size mm^2	Size range, mm		
	Length	Width	Thickness
4.00 x 4.00	7.6 - 25.8	4.1-10.6	0.2-4.1
3.15 x 3.15	6.1 - 18	4.1- 5.7	0.4-3.1
2.00 x 2.00	4.2 - 34.1	1.1 - 5.2	0.2-1.8
1.25 x 1.25	3.7 - 25.6	0.9 - 3.4	0.1-1.6
1.00 x 1.00	2.4 - 19.5	0.5 - 1.7	0.2-0.9

Depending on the measurements presented in Table 3, the dimensions of coarse and fine particles are established, as input data for the structure of experimental particleboard manufactured in the laboratory conditions. Thus, for coarse particles the length ranges between 3.7 mm and 34.1 mm, the width between 0.9 mm and 10.6 mm, and the thickness between 0.1 mm and 4.1 mm.

For fine particles, the maximum measured length is 19.5 mm, the maximum measured width is 1.7 mm and the maximum measured thickness is 1.6 mm.

4.2.2. Characteristics of oxidized modified magnesium lignosulfonate

In order to increase the reactivity of magnesium lignosulfonate, the oxidation process was used, based on the preparation recipe used by other researchers (Hemmilä *et al.*, 2013). The participation rates of the hydrogen peroxide, distilled water and sodium hydroxide, relative to the amount of magnesium lignosulfonate, are shown in Table 4.

Table 4. Recipe for the preparation of the adhesive resulting from the oxidation of magnesium lignosulfonate

Material	**Quantity in the recipe**
Magnesium lignosulfonate	460 g
Hydrogen peroxide 30%	35 g (7.6% from the amount of magnesium lignosulfonate)
Distilled water	246 ml (53.5% from the amount of magnesium lignosulfonate)
Sodium hydroxide 50%	66 ml (14.3% from the amount of magnesium lignosulfonate)

In the preparation of the adhesive resulting from the oxidation of magnesium lignosulfonate, a low viscosity and adhesive agglomerations in certain areas of the manufactured panel resulted in the previous experiment presented in Chapter 3. In order to allow a better spread of the adhesive within the whole number of particles, the receipt was modified by adding distilled water. The distilled water was added to the recipe, so as to obtain a flow time of 16 s through the viscosity cup STAS Φ 6 mm, at a temperature of 20 °C. At the same time, because the results of the mechanical test of resistance to internal bond were not within the acceptable limits, the participation rate of hydrogen peroxide increased from 5.7% to 7.6%, as seen in Table 4. The characteristics of the resulted adhesive are presented in Table 5.

Table 5. Characteristics of the adhesive obtained by oxidation of magnesium lignosulfonate

Characteristic	Value
Solid content	57%
pH	8.9%-9%
Flow time through the viscosity cup STAS Φ6 mm	16 s
Adhesive reactivity on sand bath at 160 ˚C	3 min 15 s

4.3. Manufacture and testing of particleboard with adhesive based on unmodified magnesium lignosulfonate and modified by oxidation

The single-mat configuration of the particleboard had in its composition participation rates of 65% coarses and 35% fines, sorted according to the selection presented in subchapter 4.2.1. The target density set for particleboard panels was 650 kg/m^3, close to the density of the particleboard manufactured with UF resin by Kastamonu SA Romania, an important PB manufacturer.

The codes assigned to the experimental panels are presented in Table 6. The code indicates the type of adhesive and the proportion of its participation in the composition of the panel.

Table 6. Codes of the panels, adhesive type and proportion of adhesive

Experiment panel code	Adhesive type	Adhesive ratio (of the total mass of the particles) in %
L15	Magnesium lignosulfonate powder	15%
L20	Magnesium lignosulfonate powder	20%
L50	Magnesium lignosulfonate powder	50%
LO 15	Oxidized magnesium lignosulfonate	15%
LO 20	Oxidized magnesium lignosulfonate	20%

4.3.1. Methods and equipment used for particleboard manufacturing and testing

Hot pressing of panels was performed using the press from the Laboratory of composite materials within the Faculty of Furniture Design and Wood Engineering. This press has the possibility of heating the plates up to a temperature of 200 °C and with the dimensions of the plates of 450 mm x 450 mm (length x width).

Beech wood frames with inner sizes of 420 mm x 420 mm x 50 mm and 420 x 180 x 50 mm respectively, were used for mat formation. A melamine faced particleboard panel 18 mm thick was used for pre-pressing the mat. The frame was placed on a 3 mm thick steel sheet, covered with heat-resistant paper. After pre-pressing the mat, the frame and the cover were removed and heat-resistant paper and a new steel sheet were used for the top of the mat. In order to maintain the thickness of the panel during pressing, 16 mm thick steel stops were used. At least two panels of each size and type of recipe were made.

The adhesive and wood particles were mixed mechanically (with a hand mixer) for 10 minutes. The mixture was then placed in the wooden frame and pre-pressed manually with the pre-pressing panel. After that, the frame was removed and the mat was hot pressed in the laboratory press at 180 ˚C for 16 minutes at a pressure of 2.5 N/mm^2. After being removed from the press, the panels were conditioned at a temperature of 20 °C and a relative humidity of air of 65% for 7 days, then cut into specimens for mechanical testing, vertical density profile (VDP) and for the determination of formaldehyde emission by gas analysis method.

Determination of bending strength (MOR) and modulus of elasticity (MOE)

The bending strength test was conducted according to the SR EN 310: 1996 standard and consists in applying a load in the middle of a test piece supported on two fulcrums (Fig. 5), with the help of a special device from the Zwick/ Roell Z010 universal testing machine.

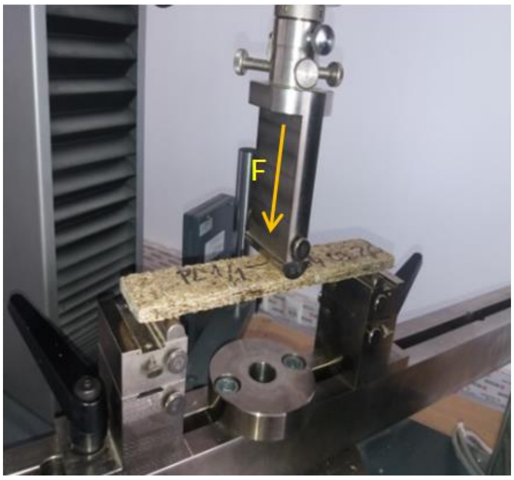


Fig. 5. Bending strength test

Determination of the internal bond (IB) or tensile strength perpendicular to the panel faces

This test was conducted according to standard SR EN 319: 1997 and the specimens were subjected to a uniformly distributed tensile stress, until breaking (Fig. 6). The tensile strength perpendicular to the panel faces is determined as a ratio between the maximum load and the squared specimen surface. The specimens had 50 mm x 50 mm square shape and before testing they were conditioned at a moisture content U = 65 (+/- 5) % and a temperature of T = 20 (+/- 2) °C.

Fig. 6. Internal bond test

Formaldehyde emission was determined by the gas analysis method in the chemistry laboratory, located at the Faculty of Furniture Design and Wood Engineering, and the results were compared with the limits imposed for formaldehyde emissions by standard ISO 12460-3: 2015. The method consists in exposing a test piece for a period of 4 hours, at a temperature of 600 °C in a closed space, respectively the Timber test chamber, New Zealand manufacturer (Fig. 7).

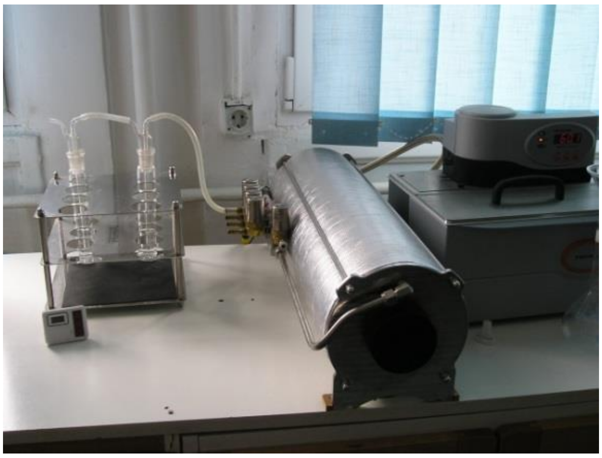


Fig. 7. Equipment for the determination of formaldehyde emission by the gas analysis method (Timber test chamber)

The determination of the formaldehyde emission by the gas analysis method involves several work phases:
- Sampling and cutting of test pieces to a length of 400 (±1) mm and width of 50 (±1) mm;
- Conditioning of the test pieces at a temperature of (20 ±2) °C and a relative humidity of air of (65 ±5) %;
- Each specimen was wrapped tightly, immediately after cutting, and stored in an environment with constant temperature;
- For testing, the specimens were sealed on the edge with high temperature resistant self-adhesive foil (≥ 60 °C);
- The determination of formaldehyde emission was performed no later than 72 hours after sampling.

The test samples, measuring 400 mm x 50 mm x 16 mm and sealed with aluminium tape, were placed in a closed room where the conditions (temperature, relative humidity of less than 3% and air flow of (60 ± 3) L/h and pressure between 1000 Pa and 1200 Pa) were checked during the test. After four hours of testing, the concentration of formaldehyde in the water was determined photometrical.

Formaldehyde emission (in mg/m^{2}h) was calculated based on this concentration, sampling time and exposed sample area. The tests were performed on two replicates, using two different samples for each type of panel, and the average value obtained was compared with the minimum value of 3.5 mg/m^{2}h, classified as emission class E1, according to the European standard.

Variation of the density profile of the panels along their thicknesses, or vertical density profile (VDP)

This test was conducted with the help of X-ray equipment, DPX 300 (IMAL, Italy), located at the laboratory of the Research-Development Institute of Transilvania University of Brașov.

For the test, square specimens with the side of 50 (+/-1) mm were cut. The dimensions of the specimen were measured using the apparatus of the equipment, and the specimens were then weighed on the EU-C-LCD 2002 scale, produced by Gibertini, Italy. These two apparatuses belong to equipment DPX 300.

After measuring and weighing the test piece, it was inserted inside the apparatus in order to determine the density profile using X-rays.

Microscopic analysis of the particleboard structure

The microscopic investigation was performed on the NIKON SMZ 18-LOT2 stereo microscope (Nikon Instruments, Tokyo, Japan), with 30x and 180x magnification (Fig. 8).

The microscopic investigation was performed on the edges of the samples prepared for testing the vertical density profile of the panel. The purpose of microscopic investigation was to analyse the interface between wood particles and adhesive, while observing structural defects that could affect the mechanical properties of the panels. Microscopic analysis is a complementary test to VDP investigation, providing additional information about the core structure of the panels, which usually has a lower density and which may influence the mechanical properties and especially internal bond (IB) of the particleboard.

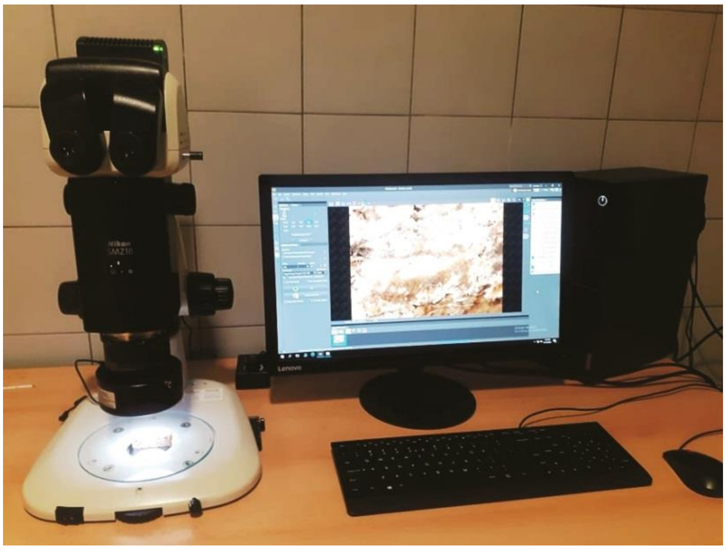


Fig. 8. NIKON SMZ 18-LOT2 stereo microscope, used for microscopic analysis of the panels' structure

4.3.2. Mechanical test results

As proved by the FTIR analysis, the adhesion with particleboard, in case of using lignosulfonate in powder state, was achieved due to the thermoplastic character of lignin. It can be seen from the results shown in Fig. 9, that with the increase of the participation rate of lignosulfonate in the composition of particleboard, the mechanical properties of the panels improved, but the values obtained for MOR and IB are below the minimum limits imposed by the SR EN 312: 2004 standard, both for P1 type panels (generally used panels in dry environments), as well as for P2 type panels (with application for interior joints, including furniture and used in dry environment).

There is a large increase in the modulus of elasticity for panels with a lignosulfonate content of 50%, which shows that this type of panels has high rigidity. The limits imposed by the standard SR EN 312: 2004 for panels of type P1 and P2 with a thickness of 16 mm are presented in Table 7.

Table7. Imposed limits of mechanical properties for the panels P1 and P2 (SR EN 312:2004)

Panel type	Application	MOE (N/mm^2)	MOR (N/mm^2)	IB (N/mm^2)

P1	General purpose, used in dry environment	-	11.5	0.24
P2	Interior joints, including furniture, used in dry environment	1600	13.0	0.35

As can be seen in Figs. 9, the mechanical properties of the particleboard improved for the case when magnesium lignosulfonate modified by oxidation was used as adhesive.

Higher increase was recorded for the modulus of elasticity (MOE), more than 50% increase was calculated both for participation rates of lignosulfonate of 15% and 20%, respectively.

It has been also noticed that for lignosulfonate participation rate of 20% of the dry particles weight, in the variant where lignosulfonate modified by oxidation was used as adhesive, the mechanical performance of the panels was similar to that of the particleboard where the unmodified lignosulfonate powder was used for a 50% participation rate (with a small difference between internal bond results). Compared to the modulus of elasticity (MOE) of the panels with 50% lignosulfonate powder, the panels with oxidized lignin (both with 15% and 20% participation rate) recorded lower values (almost half of L 50 value), which indicates a higher elasticity of those panels.

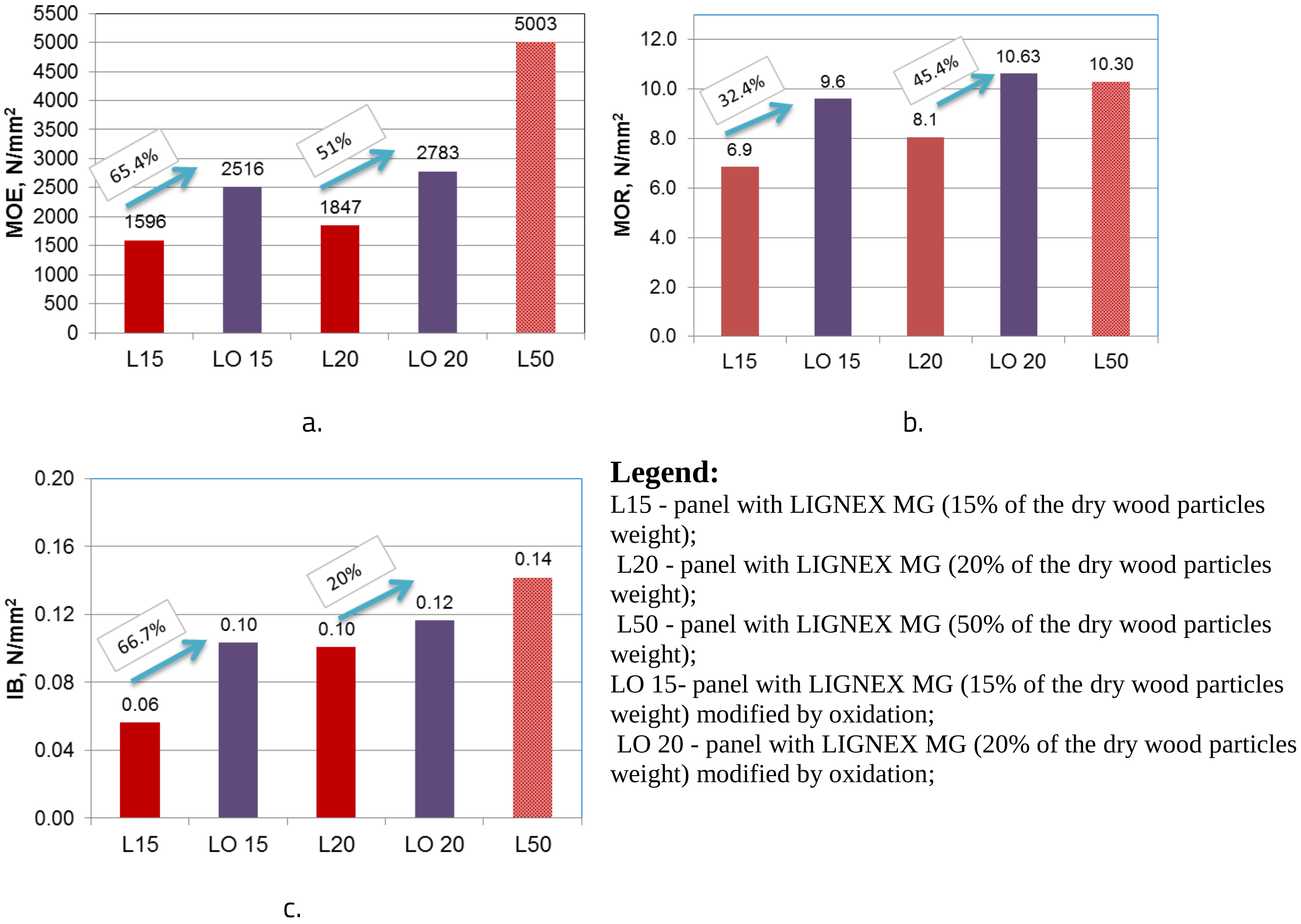


Fig. 9. Comparison between the mechanical properties of the panels made with unmodified lignosulfonate and chemically modified by oxidation lignosulfonate.

4.3.3. Density profile along the thickness of the particleboard made with unmodified and oxidized magnesium lignosulfonate (VDP)

Studies on the vertical density profile (VDP) of the particleboard (Gamage *et al.*, 2009) have shown that for relatively high MOE and MOR results, the maximum peak density of the profile must record more than 900 kg/m^3 and the average density of the core must be higher than 600 kg/m^3. In addition, it has been concluded that the technological process is very important in "modelling" this profile.

Panels obtained with shorter pressing times have the maximum density peak closer to the panel surface. As the pressing time increases, the maximum peak density moves towards the core.

Also, a high initial pressure and a short closing time of the press has as result panel faces with high density and core with low density, while a lower initial pressure and a longer closing time of the press, produces a more uniform density along the panel thickness.

It has been also found that the moisture content of the wood particles in the core increases the thickness swelling of the panel and reduces the average density of the panel. Based on these considerations, it can be said that the experimental particleboards studied in this doctoral thesis belong to the category of those with long pressing time (16 min), so the maximum peak density is moved towards the core, as can be seen in Fig. 10.

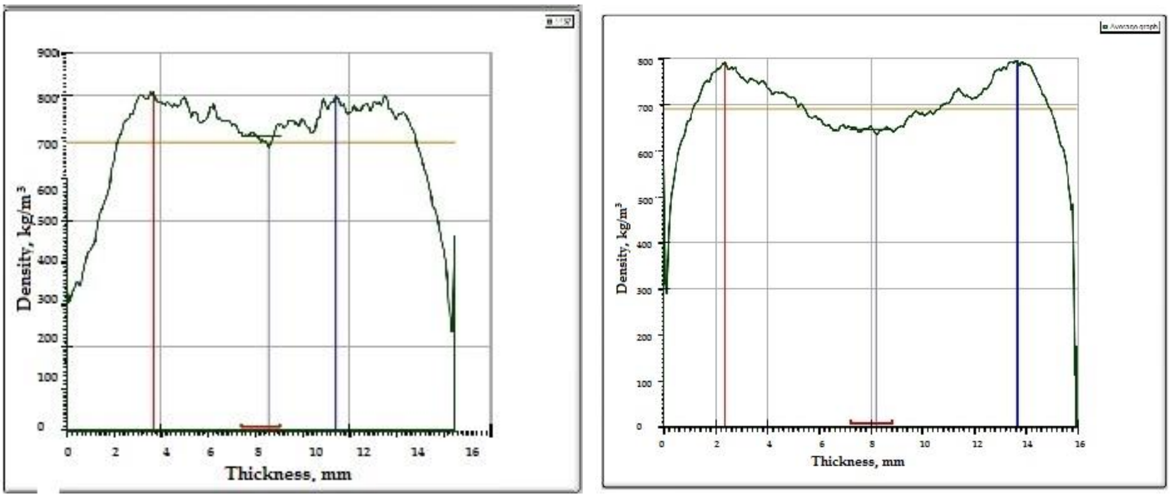


Fig. 10. Density profile for panels made with magnesium lignosulfonate (LIGNEX MG) chemically modified by oxidation; a. 15% participation rate; b. 20% participation rate (selection).

Analysing VDPs in Fig. 10 it can be noticed that for adhesive prepared by oxidized magnesium lignosulfonate, the pressing technology with a pressing time of 16 min seems to be unfavourable to the maximum density peak, which is located at 3 mm-4 mm from surfaces of the panels with 15% adhesive and approx. 2 mm for panels with 20% adhesive.

Changing the technology in this case, by reducing the pressing time and proceed with higher pressure at the beginning of the pressing process, may improve the VDP of the particleboard by moving the maximum peak density closer to the surfaces, which would positively influence the mechanical performance of the panel.

4.3.4. Microscopic analysis of the structure of panels made with unmodified and oxidised magnesium lignosulfonate

The microscopic analysis was performed for the panels with adhesive prepared from chemically modified magnesium lignosulfonate by oxidation, in order to better observe the adhesion of the resin to the wood particles. Fig. 11 presents the images taken by 30x magnification of the particleboard edge. The images in Fig. 11 show numerous small gaps situated both in the core of the panel and close to its faces.

a. b.

c.

Fig. 11. Images with 30x magnification of the panel LO 15 edge; a. middle area; b) edging; c. centre with gap measurements.

4.3.5. Formaldehyde emission of the particleboard made with unmodified and oxidized lignosulfonate

Table 8 presents the results of the determinations of the formaldehyde emission of the panels made with 15% and 20% participation rate of unmodified magnesium lignosulfonate powder (L 15 and L 20 respectively), and also for panels made with adhesive obtained by oxidation of lignosulfonate (LO 15 and L 20), with the same participation rate as previous ones.

Table 8. Formaldehyde emission of the panels made with unmodified lignosulfonate (L 15 and L 20) and modified one by oxidation (LO 15 and LO 20)

The analysed characteristic	Panel type			
	L 15	LO 15	L 20	LO 20
Formaldehyde emission, in mg/m^2h, determined by the gas analysis method	0.850	0.541	0.789	0.616

The results of the determinations of formaldehyde emission show that these panels are below the E1 emission class limit of 3.5 mg/m^2h and are very close to the values determined for solid wood (Salem and Böhm, 2013), values corresponding to the ultra-low emission class (E0).

4.3.6. Conclusions on formaldehyde emission and mechanical performance of particleboard made with H_2O_2 oxidized magnesium lignosulfonate as adhesive

- The use of magnesium lignosulfonate LIGNEX MG as powder and with thermoplastic characteristics as adhesive, conducted to the production of particleboard with poor mechanical performance that did not meet the requirements of SR EN 312: 2004, neither for general purpose panels (P1) nor for panels used for jointing in dry environment (P2).
- The process of oxidation of magnesium lignosulfonate with hydrogen peroxide (H_2O_2) and addition of sodium hydroxide (NaOH) to a basic pH = 9, brought improvements in the mechanical performance of the panels, but not enough.
- The vertical density profile (VDP) of the experimental particleboards presented in this chapter showed that the maximum density peak is situated at 2 mm-3 mm distance to the panel faces, which explains the weak mechanical strengths. Further research will be able to establish a proper technology to improve this profile when using oxidized lignosulfonate as adhesive in particleboard production, reaching a maximum density closer to the panel faces, by reducing pressing times and applying higher pressure at the beginning of the pressing process.
- Formaldehyde emissions determined for particleboard made with unmodified magnesium lignosulfonate (L 15 and L 20), but also for those with chemical modification of lignosulfonate by oxidation (LO 15 and LO 20) resulted into the ultra- low, or Super E0 emission class, corresponding to Japanese F**** formaldehyde emission class.
- It has been observed that through the oxidation process of magnesium lignosulfonate used as adhesive, the emission of formaldehyde also decreases in the particleboard.

Chapter 5. Experimental research on the production and testing of particleboard made with adhesive based on magnesium lignosulfonate modified by oxidation with H_2O_2 and the addition of crosslinking agents

5.1. The objective of the research

- Improving the adhesive recipe by adding crosslinking agents recommended by the literature (Solt *et al.*, 2019): polymeric diphenyl methane diisocyanate (PMD)I and glucose;
- Gradual increase of the percentage of PMDI participation rate in the oxidized lignosulfonate recipe, starting with 1% of the dry wood particles, until reaching the limits imposed for P2 type panels by the standard SR EN 312: 2004, for MOE, MOR and IB;
- Improving recipes with low percentage of participation rate of PMDI by adding glucose, in order to increase the reactivity of the lignin in the composition. The participation rate of glucose is 15% of the amount of magnesium lignosulfonate;
- Investigating the mechanical properties of the panels manufactured with the new recipes and comparing the results;
- Determining the vertical density profile (VDP) of the panels and interpreting the results;
- Microscopic analysis of the structure of the edges of the experimental panels, by 30x and 180x magnification;
- FTIR spectroscopic analysis of the samples extracted from particleboard panels manufactured in laboratory conditions with the new recipes;
- Determination of formaldehyde emission for panels made with the new recipes.

5.2. Manufacturing and testing particleboard with oxidized modified magnesium lignosulfonate with H_2O_2 and crosslinking agents (PMDI and glucose)

The investigation of adhesives and the influence of crosslinking agents used in the present research, respectively PMDI and glucose, was conducted on four directions:
- particleboard manufacturing in the laboratory conditions with the new adhesive recipes;
- testing the mechanical performance of the panels;
- FTIR spectroscopic analysis of the adhesives extracted from the experimental particleboard panels made in this stage. This analysis was performed on samples extracted from the panels;
- microscopic analysis of the structure on the panels edges, conducted on the specimens cut for the internal bond test (IB) and for the density profile.

5.2.1. Recipes for the preparation of adhesives based on magnesium lignosulfonate modified by oxidation with H_2O_2 and the addition of crosslinking agents (PMDI and glucose)

As found in the literature from the field, besides PMDI, sugars are considered crosslinking agents, having the role of favouring the formation of intramolecular bonds between polymers (Solt *et al.*, 2019). Sugars are carriers of primary and secondary alcohol groups, which can theoretically generate crosslinking reactions.

The results of the incorporation of sugars in adhesives with and without formaldehyde emission were investigated by researchers (Belgacem and Gandini, 2003), based on the reaction of their controlled transformation into furan. Furan resins can be used in combination with formaldehyde, urea, phenols and casein, bringing a positive contribution to the adhesion capacity of lignocellulosic particles.

Glucose is a monomer carrying four groups of secondary alcohol and one group of primary alcohol. Some researchers have used it in the preparation of polyurethane adhesives (Xi *et al.*, 2018).

The adhesive preparation recipes from this stage of the experimental research will verify the hypothesis of using sugars (respectively glucose) as crosslinking agents. A proportion of 15% addition of glucose from the amount of magnesium lignosulfonate (solid content) was established.

The addition of glucose will be used in recipes with magnesium lignosulfonate (LIGNEX MG) modified by oxidation and the addition of 1% and 2% PMDI. The codes and composition of the panels manufactured in laboratory conditions at this stage of the research are presented in Table 9.

Table 9. Codes of the panels, composition and proportion of adhesive

Experiment panel code	Proportion of the total mass of the chips, in %		Proportion of the mass of LIGNEX MG, in %
	LIGNEX MG modified by oxidation (substance content)	PMDI	Glucose
LO 15 P1	15%	1%	-
LO 20 P1	20%	1%	-
LO 15 P2	15%	2%	-
LO 20 P2	20%	2%	-
LO 15 P3	15%	3%	-
LO 20 P3	20%	3%	-
LO 15 P1G	15%	1%	15%
LO 20 P1G	20%	1%	15%
LO 15 P2G	15%	2%	15%
LO 20 P2G	20%	2%	15%

5.2.2. Particleboard manufacturing in the laboratory conditions

Wood particles provided by particleboard manufacturer company, Kastamonu S.A. Romania were used in the following proportion:

- 65 % coarse particles;
- 35 % fine particles.

The particles with a moisture content of about 10% were mixed together with prepared adhesive, in order to obtain a single-mat configuration of the particleboard. The density set as an objective was 650 kg/m^3, a density which is similar to that of particleboard with UF resin manufactured at Kastamonu SA Romania.

Beech timber panel frames measuring 420 mm x 420 mm x 16 mm and 420 mm x 180 mm x 16 mm were used for mat formation. These dimensions allow the obtaining of specimens for the physical and mechanical tests of the panels. For the second type of frame, the recipe for preparing the adhesives was adapted to the particles weight. The adhesive was prepared before the formation of the mat.

The participation rate of magnesium lignosulfonate (solid content) was 15% and 20% of the total weight of the dry wood particles. For the recipes in which the addition of glucose was introduced, the glucose was dissolved in the distilled water in the recipe and introduced into the mixture of lignosulfonate, hydrogen peroxide and sodium hydroxide.

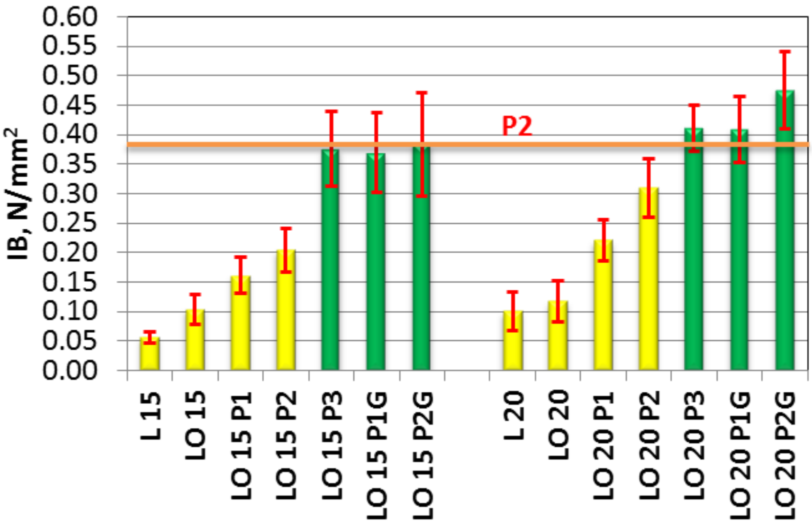
The wood particles and the prepared adhesive were mixed mechanically for 10 min, than PMDI was introduced into the mixture and homogenized with the mixture for another 5 min. The mixture was then placed into the frames and manually pre-pressed. After pre-pressing the mat, the forming frame was removed. Two steel sheets were used for the contact with the press plates. Heat-resistant paper sheets covered the formed mat of the particleboard before introducing the mat between the two metal sheets and hot pressing. The mat was hot pressed at 180 °C for 16 minutes, under a pressure of 2.5 N/mm^2. After being removed from the press, the panels were conditioned for 7 days at a temperature of 20 °C and the relative humidity of air of 65%.

After conditioning, the samples were cut from the experimental panels and tested for the mechanical properties, density profile and formaldehyde emission. At least two replicates of each panel were manufactured for testing and experimental investigations.

5.2.3. Mechanical testing results

In order to compare the mechanical properties of all particleboard panels which use magnesium lignosulfonate LIGNEX MG as the raw material for the adhesive, the results of the conducted investigations on the mechanical properties were centralized and exemplified in the diagram presented in Fig. 12. The yellow-coloured columns represent the values that not meet the permissible limits, and those coloured in green are the ones that have exceeded the lower limits imposed for the mechanical properties by the standard SR EN 312: 2004.

The results presented in these graphs show that the particleboard that met the conditions imposed for panels P2 type with application in dry environment for jointed panels (including furniture), are those with adhesive participation rate of 15% and 20% based on the weight of dry wood particles and addition of 3% PMDI (LO 15 P3 and LO 20 P3), or 1% PMDI and glucose (LO 15 P1G and LO 20 P1G) and 2% PMDI and glucose (LO 15 P2G and LO 20 P2G).



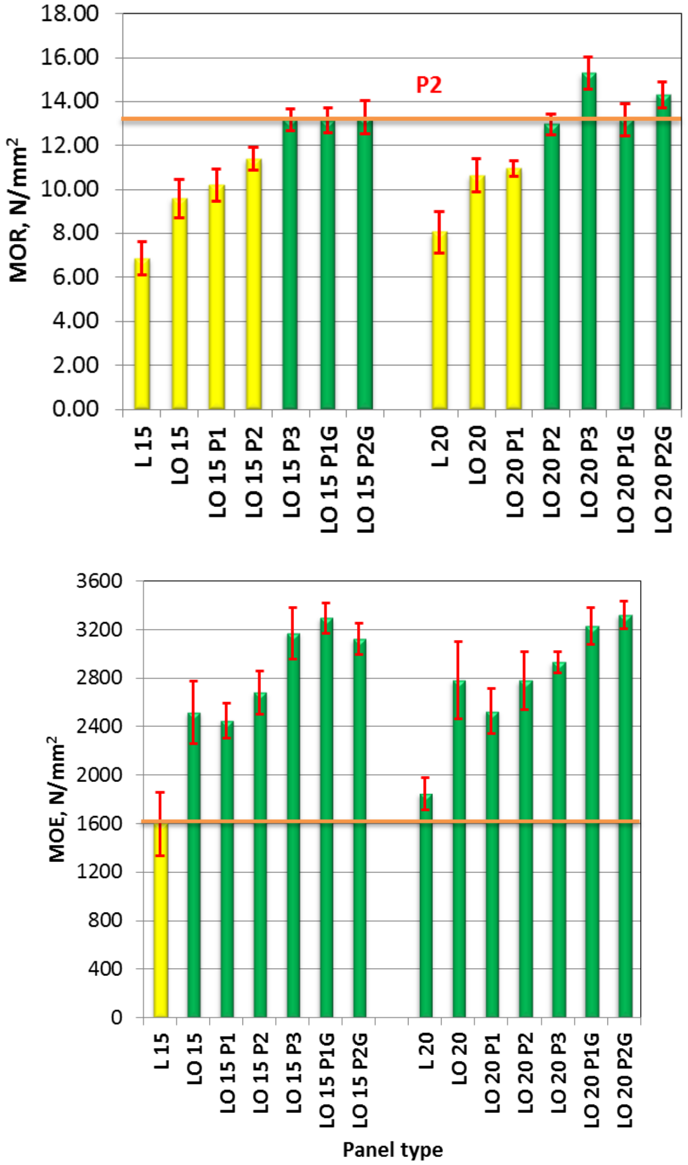


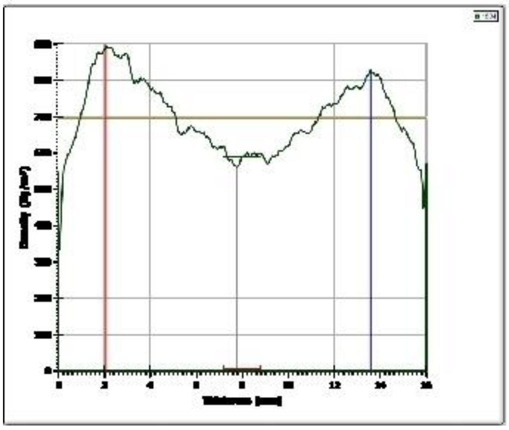
Fig. 12. Centralization of results for the mechanical properties (IB, MOR and MOE) of magnesium lignosulfonate adhesive panels LIGNEX MG

5.2.4. Vertical density profile (VDP) of the particleboard panels made with addition of crosslinking agents

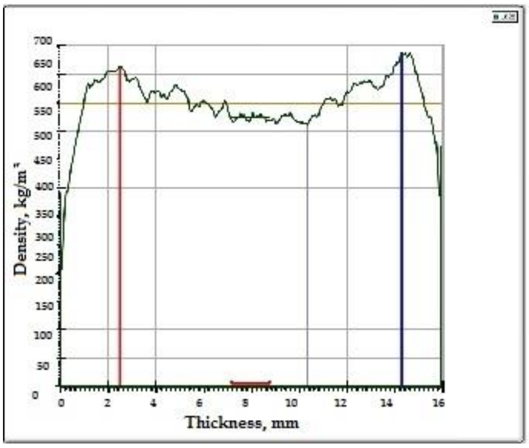
As a general remark after analysing the vertical density profiles of the experimental particleboard manufactured and tested in the present phase of the research, it was noticed that with the increase of PMDI participation rate in the composition and with the addition of glucose, the difference between the densities recorded for core and faces decreased and also the distance between the peak of maximum density and the panel faces became smaller, which indicates better mechanical performance of those panels.

This was also demonstrated by the results of mechanical tests, where a significant increase in internal cohesion (IB) was observed for panels with higher addition of PMDI and glucose.Major differences in the density profile between the panels with 15% adhesive and those with 20% adhesive (Fig. 13) were not observed, the only difference is the deeper profile in the middle area (core) for those with lower adhesive content.

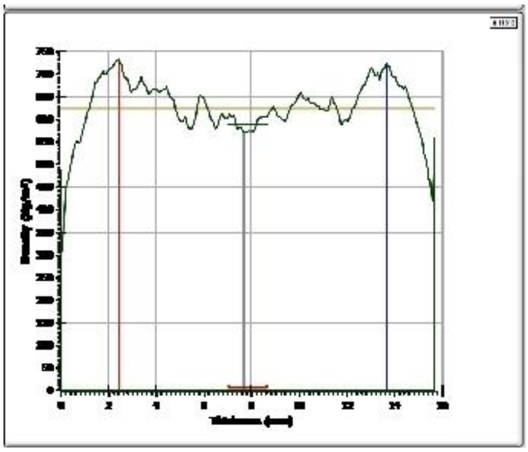
In conclusion, the density profile along the thickness of the panel is a good tool to anticipate the particleboard behaviour at mechanical stresses, having also the advantage of being a non-destructive test.



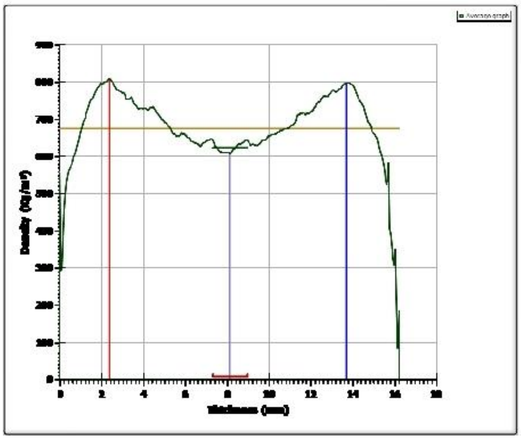
a.



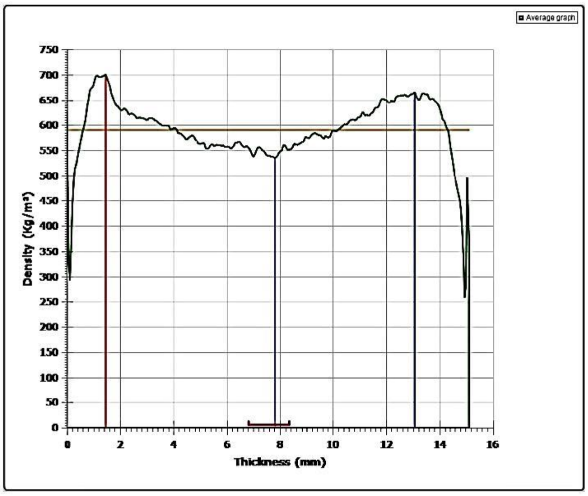
b.



c.



d.

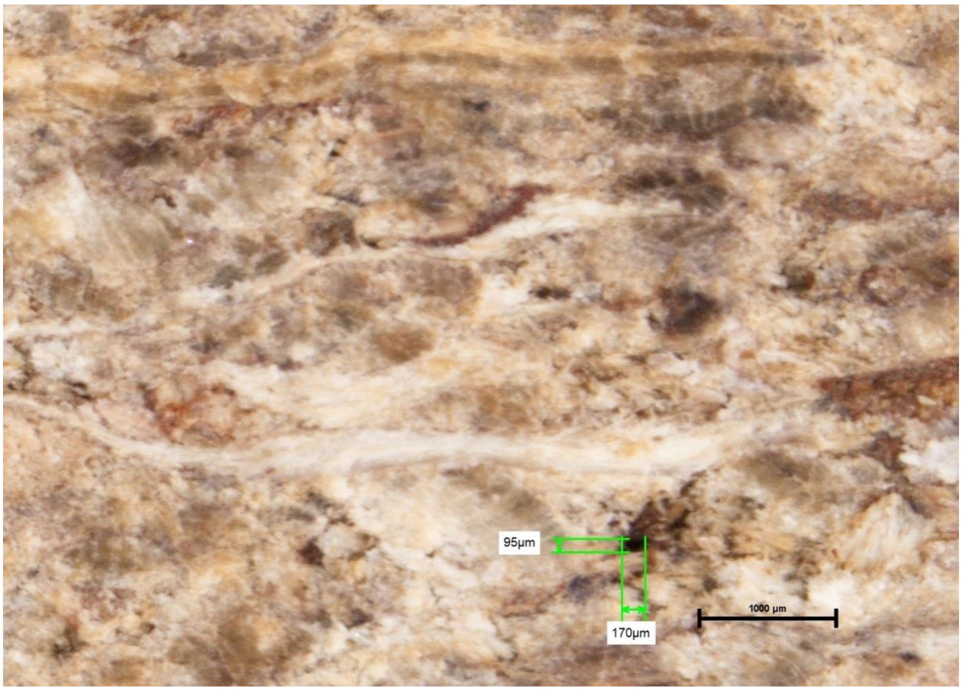


e.

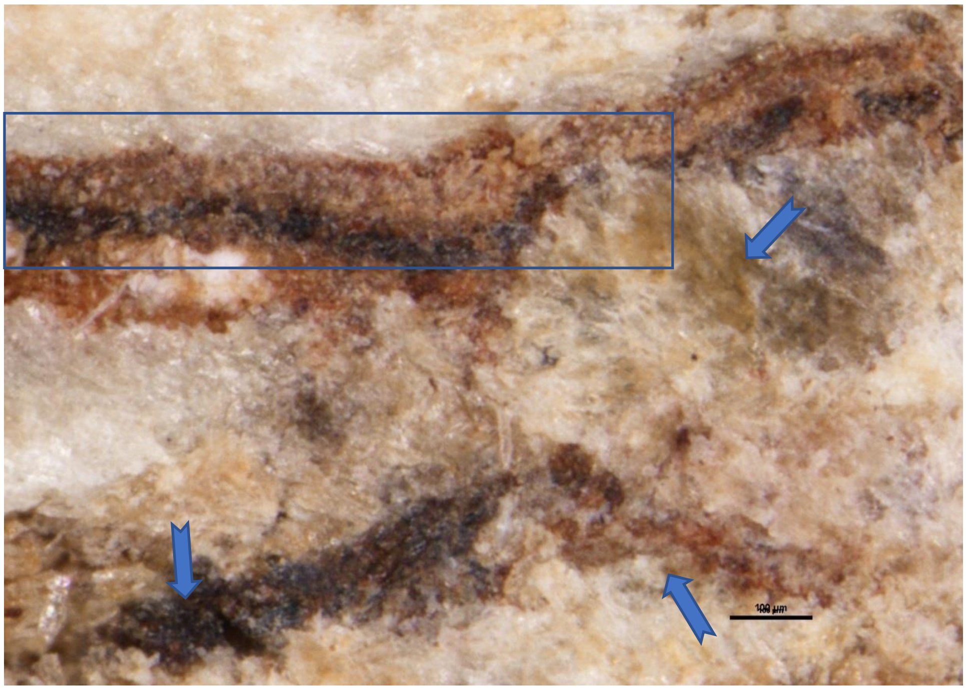
Fig. 13. Density profile for panels made of magnesium lignosulfonate (LIGNEX MG F) chemically modified by oxidation, in proportion of 20%; a. with the addition of 1% PMDI; b. with the addition of 2% PMDI; c. with the addition of 3% PMDI; d. with the addition of 1% PMDI and glucose; e. with the addition of 2% PMDI and glucose.

5.2.5. Microscopic analysis of the panel structure

Microscopic analysis with the Nikon SMZ18 stereo microscope was performed for particleboard made with adhesive prepared from chemically modified magnesium lignosulfonate by oxidation, to which 1%, 2% and 3% PMDI were gradually added, then glucose for the recipes with 1% and 2 % PMDI.



a.



b.

Fig. 14. Images with 30x magnification taken on the edge of the panel (LO 15 P2G); a. core; b. wood particle-adhesive interface (180x magnification).

The microscopic analysis of the structure of these panels was done by 30x image magnification, and for the interface areas between the adhesive and the wood particles an image magnification of 180x was applied. The specimens used for the microscopic analysis had the sizes of 50 mm x 50 mm, and were the samples prepared for the internal bond test and for the VDP test.

Both the core and the edging areas were carefully examined under the stereo-microscope and the significant areas with gaps or adhesive agglomerations were noticed and were highlighted by recording the images with both 30x and 180x magnifications.

The yellow-transparent colour of the adhesive is noticeable at the contact areas between the wood particles. The area marked in blue rectangle highlights the agglomeration of adhesive inside the gap structure. The brown-transparent colour of the adhesive can be observed, the colour indicating the larger amount of accumulated adhesive in that area.

Gaps were observed at the macroscopic level between the glued wood particles in all structures. Those with glucose used as crosslinking agent had smaller and rare gaps, and for structures with 3% PMDI (LO 15 P3 and LO 20 P3) the presence of these gaps was extremely rare. If for the structures made with 1% PMDI (LO 15 P1 and LO 20 P1), gaps with lengths of 894 µm and 634 µm were measured, for those with 2% PMDI (LO 15 P2 and LO 20 P2) these dimensions proved to be smaller: gaps of 443 µm and 225 µm were measured. For the structures with 1% PMDI and glucose addition (LO 15 P1G and LO 20 P1G), the dimensions of the gaps of 327 µm x 136 µm, respectively 171 µm x 75 µm were measured, and for the panels with 2% PMDI and glucose (LO 15 P2G and LO 20 P2G) a more compact structure was observed (Fig. 14), measuring gaps of 170 µm x 95 µm for the panel variant with 15% adhesive. As a general observation, it was noticed that the distribution of gaps along the thickness of the panel was concentrated on the core area for the majority of the panels. There are also densified areas at 2 mm - 4 mm distance from the panel faces, where these gaps are much rare, or even absent.

In Fig. 15, two examples are presented (for the panel LO 20 P1 - left and LO 20 P2 - right), where the edging of the panel corresponding to one of the faces is marked with a blue arrow. By analogy with the vertical density profile (VDP) of the panels, these densified areas correspond to the maximum density peaks, generally located at the experimental panels studied in this chapter at 2 mm - 4 mm distance from the edging of the faces.

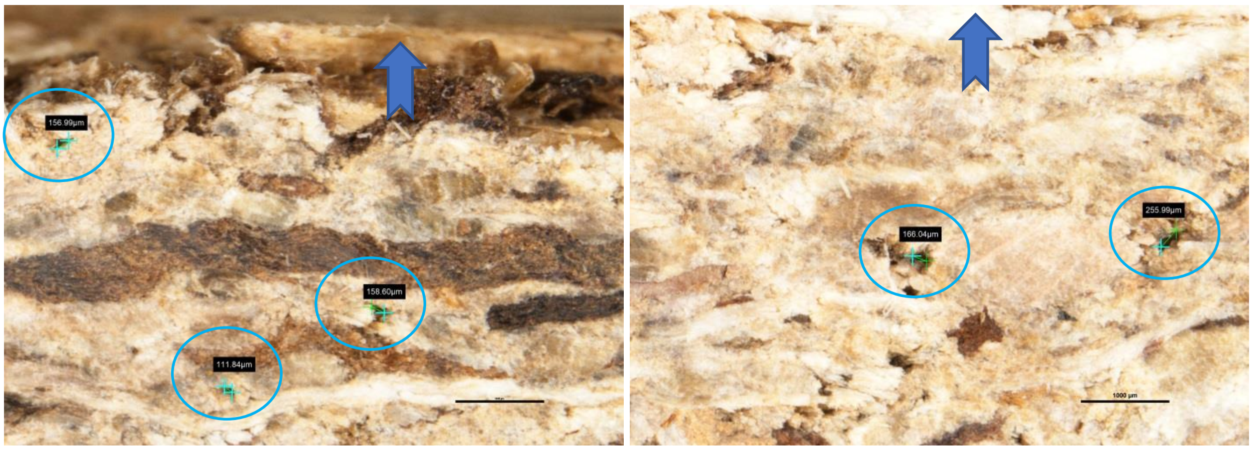


Fig. 15. Locating the gaps on the thickness of the LO 20 P1 (left) and LO 20 P2 (right) panels in relation to their faces (edging).

5.3. FTIR analysis of magnesium lignosulfonate-based adhesives modified by oxidation with H_2O_2 and addition of PMDI and glucose

Fourier spectroscopic analysis (FTIR) was performed on samples extracted from the experimental panels, from the areas with adhesive agglomerations observed during the microscopic analysis. Experimental panels with a higher percentage of adhesive (20%) were used for this analysis. The structural modifications were compared with those of the adhesive resulting from lignosulfonate powder mixed with water (10: 1) and crosslinked (L20 Ad L1-R). The modifications highlighted by FTIR analysis are presented in Fig. 16.

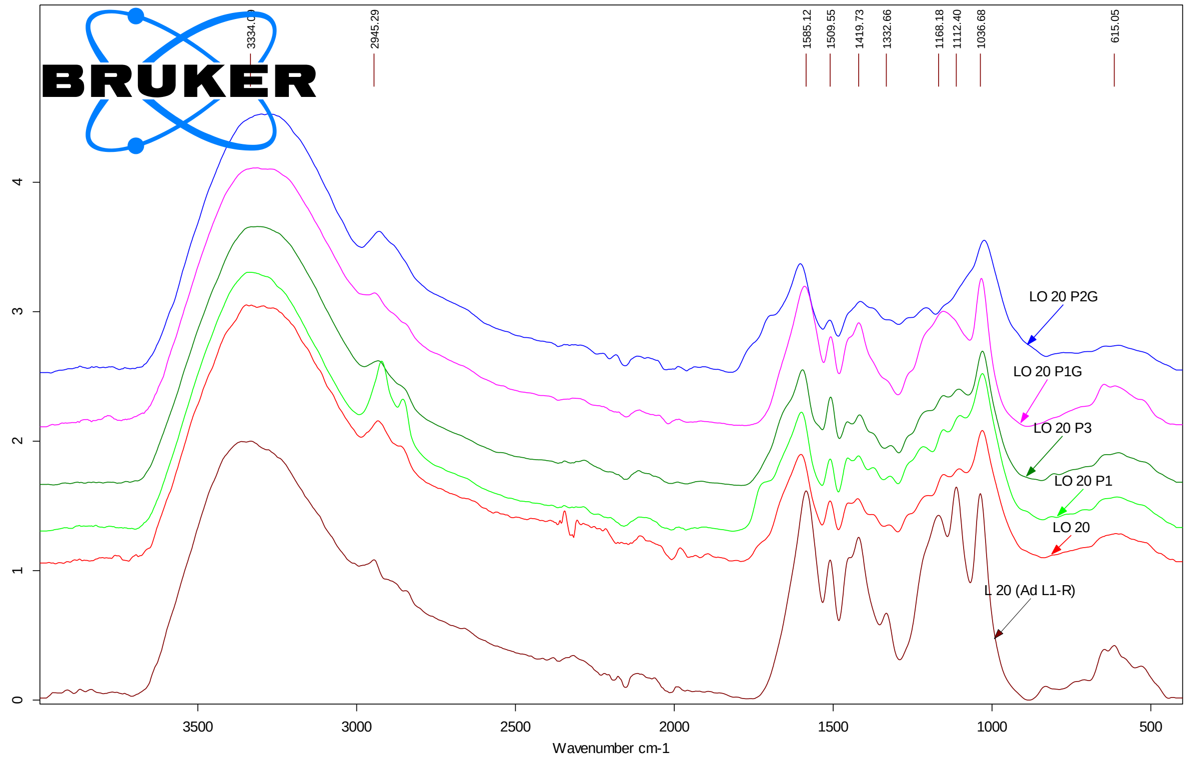


Fig. 16. FTIR analysis in the bands between 400 cm^{-1} and 4000 cm^{-1}

Structural changes were observed due to the addition of glucose as a crosslinking agent to oxidized lignin (LO 20 P1G, LO 20 P2G) (Fig. 60), such as: increase of the absorption band 1422 cm^{-1}, increase of the band 1152 cm^{-1}, which also accumulates absorption at 1220 cm^{-1}.

For LO 20 P1G, a shoulder at the absorption band of 1760 cm^{-1}, a small peak at 1700 cm^{-1} (carbonyl group in the urethane structure), decreased skeletal vibration of lignin at 1515 cm^{-1} and increased absorption at 1216 cm^{-1}, which is characteristic of urethane structures.

All structural changes suggest the involvement of glucose and lignin in crosslinking with PMDI.

5.4. Formaldehyde emission of particleboard made with magnesium lignosulfonate adhesive modified by oxidation with H_2O_2 and addition of PMDI, and glucose

The results of the formaldehyde emissions obtained for the panels made with modified lignosulfonate adhesive obtained by oxidation and addition of PMDI and glucose, are presented in Table 10.

Table 10. Formaldehyde emission values for particleboard made with magnesium lignosulfonate modified by oxidation with H_2O_2 and addition of PMDI and glucose

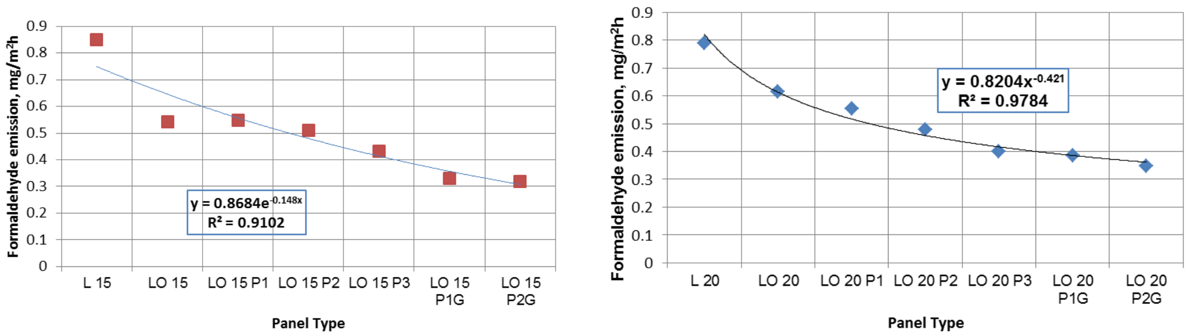
Particleboard with 15% adhesive		Particleboard with 20% adhesive	
LO 15 P1	0.547	LO 20 P1	0.553
LO 15 P2	0.509	LO 20 P2	0.477
LO 15 P3	0.433	LO 20 P3	0.401
LO 15 P1G	0.33	LO 20 P1G	0.386
LO 15 P2G	0.32	LO 20 P2G	0.347

The results from Table 10 show that the formaldehyde emission values are below the maximum limit imposed by the standard for emission class E1 (3.5 mg/m^2h).

For panels with 15% adhesive in the composition, the formaldehyde emission was 6.4 times up to 10.9 times lower than the acceptable value for emission class E1, the lowest values being recorded for the panels with high participation rate of PMDI and glucose.

For panels with 20% adhesive in the composition, the formaldehyde emission was 6.3 times up to 10 times lower than the acceptable value for emission class E1, the lowest values being also recorded for high participation rate of PMDI and glucose.

A comparison between all the experimental panels studied in this doctoral thesis, the data on formaldehyde emission were centralized in the graphs in Fig. 17.



a. b.

Fig. 17. Regression curves of variation of formaldehyde emission depending on the contribution of PMDI and glucose in adhesive recipes; a. for panels with 15% adhesive; b. for panels with 20% adhesive

Due to the superior moisture tolerance of PMDI, it was not necessary to dry the wood particles at levels lower than 4%, the moisture content of the wood particles varied between 10% and 15%, which is ideal for gluing (Costa, 2013). The high moisture content facilitates the rate of hydrolysis and transport of formaldehyde from the particle board (Eom *et al.*, 2006). As shown in Fig. 17, the data are fitted to the regression curve with a coefficient of determination of R^2 = 0.91, and R^2 = 0.97 respectively), which indicates a good correlation between the amount of formaldehyde released and the PMDI, respectively PMDI-glucose ratio.

The decrease in formaldehyde emissions by increasing PMDI and glucose participation rates could be explained by the short time of curing the adhesive film formed by PMDI on the particle surfaces, which can prevent the release of formaldehyde from the surface of wood particles (Eom *et al.*, 2006). This theory is supported by the microscopic images, which showed the good adhesion at the interface between wood particles.

Several researchers (Costa, 2013; Eom *et al.*, 2006; Kim *et al.*, 2006), reported that substances with hydroxyl groups contribute both to the high internal bond of the lignocellulosic panels and to the low formaldehyde emission of the wooden based composites (Hansen *et al.*, 2012).

Based on this theory, D-glucose, which has hydroxyl groups in its composition, can thus reduce the emission of formaldehyde, as proved by the results obtained for LO 20 P1G and LO 20 P2G panels. Formaldehyde emission values are much lower than the standardized limit specified for class E1 (3.5 mg/m^2h) (EN 13986: 2004 + A1: 2015). More than that, the values recorded for formaldehyde emission are close to those of some natural wood species (Douglas, fir and oak: 0.397 mg/m^2h and 0.43 mg/m^2h respectively) (Salem *et al.*, 2013)

5.5. Conclusions on formaldehyde emission and mechanical performance of particleboard made with adhesive based on magnesium lignosulfonate modified by oxidation with H_2O_2 and addition of crosslinking agents (PMDI and glucose)

- The use of unmodified magnesium lignosulfonate (powder) as an adhesive in the composition of particleboard does not bring the mechanical performance required for general purpose panels (type P1) or jointed panels, including furniture, used in dry environment (panels type P2), according to SR EN 312:2004.
- Oxidation of magnesium lignosulfonate with hydrogen peroxide at the environment temperature (20 °C) and bringing the mixture, using NaOH, to a basic pH = 9, did not attend the necessary improvements for the panels to reach the required mechanical performance.
- The contribution of polymeric diphenyl methane diisocyanate (PMDI) in the composition of particleboard made with adhesive based on magnesium lignosulfonate modified by oxidation with H_2O_2 had a good influence on the mechanical performance required for these panels, only for a participation rate of PMDI of 3% of the weight of the dry wood particles.
- The addition of glucose to the structures with 1% and 2% PMDI content, has improved the internal bond (IB) and the bending strength (MOR) of particleboard, with values above the minimum limits imposed by SR EN 312: 2004. Thus, the addition of glucose could be a solution to increase the reactivity of lignin in the presence of PMDI.
- Structural changes resulting from FTIR analysis of all modified lignosulfonate-based adhesives by oxidation with H_2O_2 and addition of PMDI and glucose suggest the involvement of glucose and lignin in crosslinking with PMDI.

- Both the microscopic analysis of the panel structure and the vertical density profile determination indicate densified areas, which correspond to the maximum density peaks, generally located in the experimental panels studied in this chapter at 2 mm - 4 mm distance to the panel faces.
- The values of formaldehyde emissions obtained in the experiment for particleboard made with magnesium lignosulfonate-based adhesives are close to those of some natural wood species (fir, Douglas and oak), and they were 6.3 to 10.9 times lower than the permissible limit value for E1 formaldehyde emission class of 3.5 mg/m^2h, aiming to super E0 emission class.
- Three types of adhesives studied in the present research had positive results in the manufacture of particleboard with acceptable mechanical properties and "zero" formaldehyde. These adhesives are based on magnesium lignosulfonate modified by oxidation with hydrogen peroxide (7.5%) in the presence of NaOH until reaching pH = 9. The participation rates of these adhesives in particleboard composition are 15% or 20% based on the weight of the dry wood particles. The recipes of the three variants of adhesives include the following participation rates of the crosslinking agents:

  1. Addition of 3% PMDI (based on the weight of the dry wood particles) in the composition of the adhesive.

  2. Addition of 1% PMDI (based on the weight of the dry wood particles) and 15% glucose (based on the lignosulfonate weight).

  3. Addition of 2% PMDI (based on the weight of the dry wood particles) and 15% glucose (based on the lignosulfonate weight).
- From the economic point of view, the variants with the lowest participation rate of PMDI (1%) and addition of glucose are more advantageous.
- A participation rate of lignosulfonate of 15% in the particleboard composition is sufficient to meet the mechanical performance imposed by SR EN 312:2004 standard, but safer values, well above the limits imposed by the standard were recorded for a participation rate of lignosulfonate of 20%.

Chapter 6. General conclusions. Original contributions. Dissemination of results. Further research directions.

6.1. General conclusions

The present doctoral thesis had as main objective the research on the possibility to obtain lignocellulosic panels with low formaldehyde emission. The theoretical study of the literature in the field has created a direction of research in approaching the thesis subject, proposing the use of lignin, a natural resource and by-product of the pulp and paper industry and the second most abundant biopolymer after cellulose, as raw material to prepare bio-adhesives for particleboard manufacturing.

The studies on the use of lignin have shown that its reactivity in the natural state is low, so various methods have been investigated in order to increase its reactivity, including hydroxymethylation and oxidation.

Preliminary research used to select the appropriate method to increase lignin reactivity, choosing between hydroxymethylation and oxidation, considered two hydroxymethylation recipes and one oxidation recipe (taken from the literature in the field) for the preparation of binder with increased reactivity of lignin. LIGNEX MG magnesium lignosulfonate, supplied by Sappi Biotech GmbH in Stockstadt, Germany, was used for the experimental research.

The two recipes based on the hydroxymethylation of lignin were more difficult to prepare than that based on oxidation, the last one having an advantage this case, favouring the selection of the final recipe for further research in the doctoral thesis. The adhesives prepared by the three methods were used in the manufacture of PB panels, from which test pieces were cut and mechanical tests of internal bond were performed.

Due to the good results obtained with oxidized modified lignin and given the advantage of ease of preparation, this method was chosen for further research. Although the oxidation recipe did not give the desired results for the mechanical performance of the panels, the improved recipes with the addition of crosslinking agents such as PMDI and glucose had a positive effect in this regard. In the literature they are also included in the category of scavengers, with the role of reducing formaldehyde emissions.

In the experimental research, in order to meet the proposed objective of the doctoral thesis, particleboards with magnesium lignosulfonate participation rates of 15% and 20% respectively, calculated based on the weight of dry wood particles, were manufactured in the laboratory conditions using adhesive recipes modified gradually by oxidation of lignosulfonate, addition of PMDI (1%, 2% and 3%) and glucose (15% based on the lignosulfonate weight). The experimental panels were tested for mechanical properties according to SR EN 310: 1993 for the determination of bending strength (MOR) and modulus of elasticity (MOE) and SR EN 319: 1993 for the determination of internal bond (IB).

The results were compared with the limits imposed by the European standard SR EN 312:2004 for P2 boards, with application in dry environment as jointed panels, including furniture. In addition to the mechanical strengths, the density profile of the panels was investigated, their structure was analysed microscopically and the formaldehyde emission was determined by the gas analysis method.

The general conclusions of the research conducted in the present doctoral thesis are, as follows:

- The use of magnesium lignosulfonate LIGNEX MG in its original state as powder with thermoplastic characteristics, has led to the production of particleboard panels with poor performance in terms of mechanical strengths, which do not meet the requirements of SR EN 312: 2004, neither for general purpose panels (P1) nor for panels with application in dry environment as jointed panels, including furniture (P2).
- The process of oxidation of magnesium lignosulfonate with hydrogen peroxide (H_2O_2) in the presence of sodium hydroxide (NaOH) in order to reach a basic pH (= 9), brought improvements in the mechanical performance of the panels, but not enough.
- The emissions of formaldehyde determined for particleboard made with unmodified magnesium lignosulfonate (L 15 and L 20), but also for those with chemical modification of lignosulfonate by oxidation (LO 15 and LO 20) and addition of crosslinking agents (PMDI and glucose) can be included in Super 0 formaldehyde emission class.

- Increasing the reactivity of magnesium lignosulfonate by oxidation process with H_2O_2 has as result the decrease of formaldehyde emission in the particleboard, compared to the situation where lignosulfonate powder was used as an adhesive.
- The contribution of polymeric diphenyl methane diisocyanate (PMDI) as additive in the adhesive recipe had as result the improvement of the mechanical performance, but the panels met the requirements of SR EN 312: 2004 only for a participation rate of 3% of the weight of the dry wood particles.
- The addition of glucose has improved the internal bond (IB) and bending strength (MOR) of the particleboard made with PMDI addition of 1% and 2% in the adhesive recipes. These panels (LO 15 P1G, LO 15 P2G LO 20 P1G LO 20 P2G) are possible variants of particleboard with low formaldehyde emission and good mechanical performance.
- Structural changes resulted from FTIR analysis of all lignosulfonate-based adhesives modified by oxidation with H_2O_2 and crosslinked with the addition of PMDI and glucose suggest the involvement of glucose and lignin in crosslinking with PMDI.
- Both the microscopic analysis of the panels structures and the vertical density profile (VDP) graphs indicated densified areas, which correspond to the maximum peaks along the panel thickness density profile, generally located at the experimental panels in this study at 2 mm - 4 mm distance to the faces of the panel. According to the literature in this field, this profile can be changed by adjusting the pressing technology and bringing the densified area closer to the panel faces, which leads to increased mechanical strengths.
- The formaldehyde emission values obtained for all experimental panels in this study are close to those of some natural wood species (fir, Douglas and oak), recording values of 6.3 to 10.9 times lower than the permissible limit value of 3.5 mg/m^{2}h (corresponding to E1 class of formaldehyde emission), due to the addition of PMDI and glucose.
- There are three variants of adhesives that had positive results in the manufacture of particleboard with acceptable mechanical properties and "zero" formaldehyde. The adhesive is based on recipes prepared with magnesium lignosulfonate modified by oxidation with hydrogen peroxide (7.5%) in the presence of NaOH to bring the pH to 9 and with a participation rate of the adhesive in the composition of the panel of 15% or 20% (based on the weight of the dry particles). The three adhesive recipes include the addition of crosslinking agents, as follows:

  1. Addition of 3% PMDI (based on the weight of the dry wood particles) in the composition of the adhesive.

  2. Addition of 1% PMDI (based on the weight of the dry wood particles) and 15% glucose (based on the lignosulfonate weight).

  3. Addition of 2% PMDI (based on the weight of the dry wood particles) and 15% glucose (based on the lignosulfonate weight).
- From the economic point of view, the variants with the lowest participation rate of PMDI (1%) and addition of glucose are more advantageous.
- A participation rate of lignosulfonate of 15% in the particleboard composition is sufficient to meet the mechanical performance imposed by SR EN 312:2004 standard, but safer values, well above the limits imposed by the standard were recorded for a participation rate of lignosulfonate of 20%.

6.2. Original contributions

- Comparison of the methods to increase the lignosulfonate reactivity, namely oxidation and hydroxymethilation and selection of the most appropriate one for the research conducted in the thesis.
- The gradually development of original recipes (14 recipes) and preparation of adhesives based on magnesium lignosulfonate, using crosslinking agents and formaldehyde scavengers identified in the literature.
- Elaborate the experimental method to identify the appropriate adhesive recipes to be used in order to obtain particleboard with low formaldehyde emission and good mechanical performance.
- Establish the technology and manufacture in the laboratory conditions of experimental particleboard (over 70 panels), using the original adhesive recipes.
- Based on the experimental research strategy and performing mechanical strengths tests, determining the vertical density profile (VDP), conducting microscopic analysis of the panel structure, FTIR analysis and determining the formaldehyde emission by the gas method, six particleboard structures with magnesium lignosulfonate - based adhesives have met the mechanical performance required for jointed panels, including furniture, with application in dry environment and with formaldehyde emissions close to those of solid wood. These particleboard structures are, as follows:

LO 15 P3 - particleboard made with adhesive based on oxidized magnesium lignosulfonate (LIGNEX MG) (15% of the weight of the dry wood particles) and addition of 3% PMDI;

LO 20 P3 - particleboard made with adhesive based on oxidized magnesium lignosulfonate (LIGNEX MG) (20% of the weight of the dry wood particles) and addition of 3% PMDI;

LO 15 P1G - particleboard made with adhesive based on oxidized magnesium lignosulfonate (LIGNEX MG) (15% of the weight of the dry wood particles), addition of 1% PMDI and glucose (15% of the lignosulfonate weight);

LO 20 P1G - particleboard made with adhesive based on oxidized magnesium lignosulfonate (LIGNEX MG) (20% of the weight of the dry wood particles), addition of 1% PMDI and glucose (15% of the lignosulfonate weight);

LO 15 P2G - particleboard made with adhesive based on oxidized magnesium lignosulfonate (LIGNEX MG) (15% of the weight of the dry wood particles), addition of 2% PMDI and glucose (15% of the lignosulfonate weight);

LO 20 P2G - particleboard made with adhesive based on oxidized magnesium lignosulfonate (LIGNEX MG) (20% of the weight of the dry wood particles), addition of 2% PMDI and glucose (15% of the lignosulfonate weight).

These particleboard panels were manufactured based on the original recipes of adhesives and the technology proposed by the author of the thesis.

6.3. Dissemination of results

The results of the research conducted in this doctoral thesis were disseminated by publishing an ISI Web of Knowledge indexed article in the journal Applied Sciences, with an impact factor of 2,679, an article in the Pro Ligno journal, BDI indexed, and a participation in an international conference and one article accepted for publication in Pro Ligno journal, vol. 17, no.4.

The titles of the articles are, as follows:

1. Balea Paul, G., Timar, M.C., Zeleniuc, O., Lunguleasa, A., Cosereanu, C. (2021). Mechanical Properties and Formaldehyde Release of Particleboard Made with Lignin-based Adhesives, Applied Sciences 11, 8720. DOI: https://doi.org/10.3390/app11188720
2. Balea (Paul), G.M., Coșereanu, C. (2019). Influence of lignin-based adhesives upon the properties of particleboards made from rape straws, Pro Ligno 15 (1), pp. 49-54.
3. Balea (Paul), G.M., Coșereanu, C., Pourtahmasi, K. (2019). Lignin based adhesive for particleboard manufacturing and formaldehyde emission. Proceedings of the International Conference "Wood Science and Engineering in the Third Millennium", ICWSE, Brașov, 2019.
4. Balea (Paul), G.M., Coșereanu, C. Particleboard with low formaldehyde emission. Mechanical strength and resistance to water. Accepted for publication in Pro Ligno 17 (4) journal.

The author of the doctoral thesis is the first author of all published manuscripts.

6.4. Further research directions

- Improving the vertical density profile (VDP) of the panels by adjusting the technological parameters of pressing: reducing the pressing time, increasing the pressure at the beginning of the process, reducing the closing time of the press, in order to move the maximum density peaks of the panel as close as possible to the panel faces;

- Use the recipes of bio-adhesives developed in this doctoral thesis on three-layer particleboard structures in order to verify their potential use for these most used structures in the industry sector;

- Verification of the adhesive recipes developed in this doctoral thesis in the industrial sector, in order to validate the results on a larger scale;

- Investigation of water absorption and thickness swelling of the particleboard that uses the adhesive recipes from the present research by immersion in water for 2 hours and 24 hours and extend the application of the panels for outdoor application;

- Investigate the use of other types of lignins (Kraft, ammonium lignosulfonate, etc.) in the preparation of adhesives with the recipes developed in this doctoral thesis and test them for possible application as binders for particleboard and MDF;

- Investigate the possible use of adhesive recipes developed in the present research for wood fibreboard and MDF.

- Continuation of research conducted in the present doctoral thesis with investigations on veneered particleboard and various types of joints specific to the construction of furniture.

- Studies and research on the technological machinability of these panels, including cutting, milling, sanding, etc.

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Rezumat (RO/EN)

Teza de doctorat intitulată ”Cercetări privind realizarea unor compozite ligno celulozice cu emisie scăzută de formaldehidă” abordează un domeniu important al cercetărilor actuale în domeniul adezivilor bio cu emisie scăzută de formaldehidă. Rezultatele acestei cercetări aduce beneficii din punct de vedere al emisiilor de formaldehidăși utilizează materiale naturale în compoziția adezivilor.

Obiectivul general al tezei de doctorat îl constituie realizarea de plăci din așchii de lemn cu emisie scăzută de formaldehidă,

În urma cercetărilor efectuate, se poate trage concluzia că utilizarea lignosulfonatului de magneziu Lignex MG în obținerea de panouri din așchii de lemn nu a dus la obținerea performanțelor mecanice conform standardului SR EN 312: 2004 cu adaosul de glucoză s-a îmbunătățit simțitor coeziunea internă (IB) și rezistența la încovoiere (MOR) a structurilor cu 1% și 2% PMDI, la valori peste limitele minime impuse de SR EN 312:2004, deci poate fi o variantă de mărire a reactivității ligninei în prezența PMDI.

Valorile emisiilor de formaldehidă obținute pentru toate panourile din acest studio sunt apropiate de cele ale unor specii naturale de lemn (brad, Douglas și stejar), acestea au valori de 6.3 până la 10.9 ori mai mici decât valoarea limită admisibilă de 3.5 mg/m^{2}h, datorită adiției de PMDI și glucoză iar din punct de vedere economic, variantele cu adiție de glucoză sunt mai avantajoase.

Short summary

The doctoral thesis entitled "Research on the development of low-formaldehyde lignocellulosic composites" addresses an important area of current research in the field of low-formaldehyde bio-adhesives. The result of this research brings benefits in terms of formaldehyde emissions and uses natural materials in the composition of adhesives.

The general objective of the doctoral thesis is the production of particleboards with low formaldehyde emission, using for this purpose magnesium lignosulfonate. The particleboard must meet the mechanical strengths requirements imposed by the European standard SR EN 312: 2004 for the panels designed for jointing (including furniture) use in dry environment (type P2).

With the research done, it can be concluded that the use of Lignex MG magnesium lignosulfonate in manufacturing particleboard panels did not lead to mechanical performance according to SR EN 312: 2004 but with addition of glucose in the adhesive recipes has mproved the internal bond (IB) and bending strength (MOR) of the structures for PMDI participation rates of 1% and 2% (based on the weight of the dry wood particles), at values above the minimum limits imposed by SR EN 312: 2004. The addition of glucose in the adhesive recipes could be a variant of increasing the reactivity of lignin in the presence of PMDI.

The formaldehyde emission values obtained for all panels in this study are close to those of some natural wood species (fir, Douglas and oak), having values of 6.3 to 10.9 times lower than the permissible limit value of 3.5 mg/m^{2}h, due to the addition of PMDI and glucose. From the economic point of view, the variants with addition of glucose instead of PMDI are more advantageous.