

## **PARTICLEBOARD WITH LOW FORMALDEHYDE EMISSION. MECHANICAL STRENGTH AND RESISTANCE TO WATER**

**Gabriela-Mariana BALEA (PAUL)**

PhD student – Transilvania University of Braşov-Faculty of Wood Engineering

Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania

E-mail: [gabriela.balea@unitbv.ro](mailto:gabriela.balea@unitbv.ro)

**Camelia COŞEREANU**

Prof. dr. – Transilvania University of Braşov-Faculty of Wood Engineering

Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania

E-mail: [cboieriu@unitbv.ro](mailto:cboieriu@unitbv.ro)

### **Abstract:**

*The present paper shows the research conducted for the assessment of magnesium lignosulfonate as a potential binder for the particleboard manufacturing. Magnesium lignosulfonate (15 wt.%) in a pure state (as powder) was used first as binder for particleboard manufacturing, and was considered as reference for the next investigations, where the lignosulfonate was gradually modified by oxidation with hydrogen peroxide, than by addition of crosslinking agents, such as diphenylmethane diisocyanate (PMDI) in shares between 1% and 3% of the dry particles weight and glucose (15% of the lignosulfonate content). Mixed beech wood (30%) and spruce wood (70%) particles were used in the single mat configuration of the particleboard. Mechanical properties, formaldehyde emission, water absorption and thickness swelling were investigated for the manufactured panels in the laboratory conditions. The results showed that the oxidation process of lignosulfonate and addition of PMDI and glucose have positive impact on lowering formaldehyde emission and improving mechanical properties requested by EN 312 (2004) standard. Water absorption and thickness swelling tests performed on the samples cut from the experimental panels have shown their low resistance to water, recommending them to indoor use.*

**Key words:** particleboard; magnesium lignosulfonate; mechanical properties; formaldehyde emission; water absorption, thickness swelling.

### **INTRODUCTION**

Effective adhesives are recommended to be used in the production of wood-based composites, at a competitive price, and 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. The upper limit of formaldehyde emissions set by CARB (California Air Resources Board) for particleboard panels is 0.09 ppm (<https://www.regulations.gov/document/EPA-HQ-OPPT-2016-0461-0001>). Such regulation established the allowable limits of formaldehyde emissions at a level with 10 to 20 times lower than those existed 30 years ago (Mantanis *et al.* 2018) and in a few years the limits could be lowered and forcing thus the producers to adopt alternative methods in particleboard manufacturing.

Nowadays the researchers are focused on studying several methods to reduce the formaldehyde emissions in the wood-based panel industry, and they include the addition of amines in the recipe of urea-formaldehyde adhesive (Boran *et al.* 2011), the treatment of covering the surfaces of the panels with paints, varnishes, use of alternative adhesives: phenol formaldehyde (PF), PMDI, biomass-based adhesives (Athanassiadou *et al.* 2009), or application of veneer or synthetic foils (Duan *et al.* 2015). The most effective method to be applied for the reduction of formaldehyde emission is the use of scavengers (Boran *et al.* 2012, Bertaud *et al.* 2012; Costa *et al.* 2014). Bio-scavengers are environmentally friendly solutions to reduce formaldehyde emissions from panels and include substances, such as tannin, lignin, starch, and soy protein. Bio-scavengers are natural materials, they can be found in abundance, have a relatively low cost and are environmentally friendly (Imam *et al.* 1999). An alternative solution to reduce the formaldehyde content of adhesives is to replace formaldehyde with other chemicals with similar reactions. These substances include: glyoxal, dimethoxyethanol, isocyanates, mono- and di-saccharides, glucose, sucrose, epoxy resins, citric acid, lignin, tannin, soy, etc. These substances promote the formation of intermolecular, covalent or ionic bonds between polymer chains and they are named crosslinking agents (Solt *et al.* 2019). One of these substances is glyoxal, which (Mansouri *et al.* 2011) has been used it in the production of wood-based panels (particleboard and plywood), in the composition of the natural adhesive consisting of 50% lignin and glyoxal (0.5%). All panels have met the requirements of the standards in force regarding the mechanical strengths, while being completely environmentally friendly. 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. PMDI was subsequently added to this resin in proportions of 4%, 6% and 8%. According to the results of this research, the addition of PMDI accelerated the gel time, reduced the water absorption and significantly increased the mechanical strength of the panels. Sugars (glucose and fructose) which have primary and secondary groups of alcohol could be crosslinking agents, as few investigations show (Solt *et al.* 2019). Furfuryl alcohol can be used in the composition of adhesives, having the ability to crosslink with various monomers. Also, citric acid and maleic anhydride have the ability to crosslink chains with alcohol groups and can catalyze many chemical reactions (Solt *et al.* 2019).

The use of bio-adhesives prepared from natural raw materials, such as lignin, starch, soy or tannin is more and more recommended in particleboard manufacturing. The studies conducted in the last years were focused especially on three biopolymers: lignin, starch and plant proteins, but lignin seems to be the most used one in the experimental researches and industrial trials to manufacture particleboards. Lignin was used as a partial replacement of phenol (Da Silva *et al.* 2017, Antov *et al.* 2020a) up to 40 wt.%. Research work has been also done to improve the reactivity of lignin as the substitute of phenol in PF resin synthesis by modifying the chemical structure of lignin and increasing its reactivity by hydroxymethylation (Malutan *et al.* 2008, Hu *et al.* 2011, Aro and Fatehi 2017) and by oxidation (Hemmilä *et al.* 2013, Klapiszewski *et al.* 2017, Fernandes *et al.* 2019), hydrogen peroxide being considered to be an environmentally friendly oxidant (Junghans *et al.* 2020).

Contribution of lignosulfonates as adhesives in manufacturing engineered wood panels is presented in several papers (Akhtar *et al.* 2011, Ghorbani *et al.* 2016, Aro and Fatehi 2017). Recent research works (Antov *et al.* 2020b, Antov *et al.* 2020c) have shown that magnesium lignosulfonate (15% wt. reported to wood) is a suitable adhesive for obtaining eco-friendly fibreboards with satisfactory mechanical and physical properties. This fact constitutes the starting point of the present research on studying the possibility of using magnesium lignosulfonate (15% wt. reported to wood) as adhesive base for particleboard manufacturing.

## OBJECTIVE

The present paper aims to evaluate the mechanical properties, formaldehyde emission and resistance to water of particleboard made with magnesium lignosulfonate-based adhesives, using several methods to improve the reactivity of this natural adhesive, such as chemical modification by oxidation with hydrogen peroxide, and addition of PMDI and glucose, as cross-linkers.

## MATERIAL, METHOD, EQUIPMENT

Raw materials were supplied by Kastamonu particleboard manufacturer (Romania), and contained mixed beech (30%) and spruce (70%) wood particles at a moisture content of around 10%, with a bark percentage of 5% of the total amount. The granulometric analysis of the particles (coarses and fines) was performed using the Retsch vibratory sieve shaker machine, made in Germany. For coarse particles, the vibratory sieve shaker was equipped with five sieves placed from top to the bottom starting with the sieve with the largest meshes and ending with the finest sieve. For this first determination, sieves with mesh sizes, in mm, of 4.00 x 4.00, 3.15 x 3.15, 2.00 x 2.00, 1.25 x 1.25 and 1.00 x 1.00 were used. In order to analyze the fine particles in terms of size distribution, they were screened with the same vibratory sieve shaker, using sieves with mesh sizes, in mm, of 1.00 x 1.00, 0.80 x 0.80, 0.53 x 0.53, 0.40 x 0.40 and 0.16 x 0.16. Three samples from each type of particles were selected, each weighing 25 g. The particles were screened for 10 minutes at a frequency of 60 oscillations/min and then collected from each sieve. The participation rate of the particles, both for the coarse and fine particles are presented in Table 1.

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 1.25mm x 1.25mm (almost 40%), while for the fine particles the majority ones were collected in the sieve with 1.00mm x 1.00mm mesh size. Therefore, for a control on the particleboard structures, the particles collected from the sieve with mesh sizes of at least 1.25mm x 1.25mm were considered coarse particles, while for the fine ones, the minimum particle sizes should be either those collected in the sieve with meshes of 0.53mm x 0.53mm, and the largest in the sieve with meshes of 1.00mm x 1.00mm.

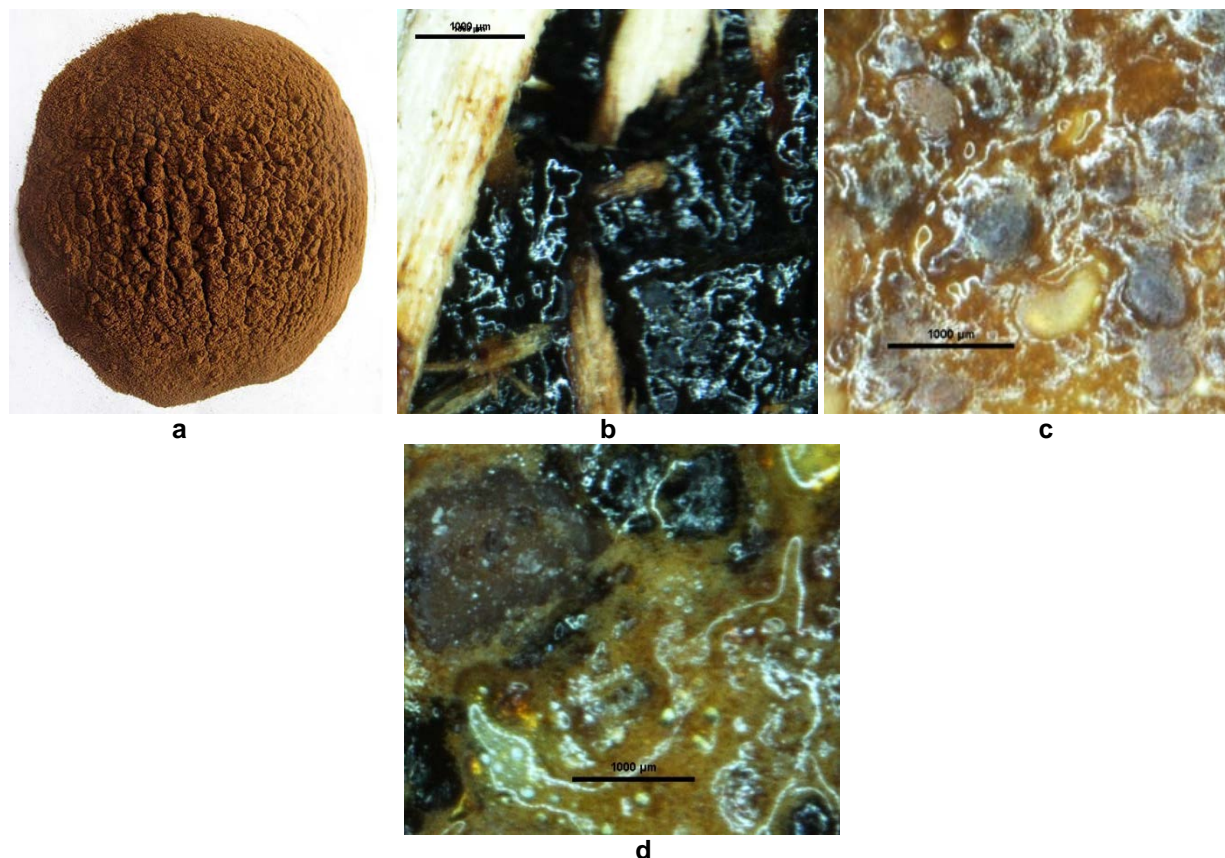
Table 1

*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	<b>Coarse particles</b>				-	-	-	Dust (not used)			
					<b>Fine particles</b>						

The sizes of both coarse and fine particles were measured and used as input data for the structure of the experimental particleboard. Thus, for coarse particles the length ranges between 3.7mm and 34.1mm, the width between 0.9mm and 10.6mm, and the thickness between 0.1mm and 4.1mm. For fine particles, the maximum measured length was of 19.5mm, the maximum measured width was of 1.7mm and the maximum measured thickness was of 1.6mm.

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 (Fig. 1a). The appearance of magnesium lignosulfonate is in the form of a yellowish-brown powder and it is obtained by the process of purification, evaporation, chemical treatment and drying of the black liquor, which is the by-product resulting from the pulp and paper production process.



**Fig.1.**

**Magnesium lignosulfonate Lignex MG (Sappi Biotech GmbH, Düsseldorf, Germany); a – pure state; b – oxidized state (22.5x magnification); c – oxidized state and 1% PMDI addition (22.5x magnification); d - oxidized state with addition of PMDI (1%) and glucose (22.5x magnification).**

The characteristics of pure magnesium lignosulfonate (Lignex MG), as set out in the data sheet issued by the manufacturer, are as follows: dry matter content:  $93 \pm 2\%$ ; magnesium content:  $6 \pm 1\%$  min; pH (10% solution):  $5.5 \pm 1\%$ ; bulk density:  $400\text{kg/m}^3$ ; ignition temperature:  $530^\circ\text{C}$ ; insolubility in water: 1% max; moisture content: 7% max.

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 2 and the characteristics of the resulted adhesive are presented in Table 3. The image from Fig. 1b shows the colour modification of the magnesium lignosulfonate under the oxidation process, which turned it into a dark brown colour. Images from Fgs. 1b, 1c and 1d were taken using the stereo microscope NIKON SMZ 18-LOT2 (Nikon Instruments, Tokyo, Japan).

Table 2

**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)

Table 3

**Characteristics of the adhesive obtained by oxidation of magnesium lignosulfonate**

Characteristic	Value
Solid content	57%
pH	8.9%-9%
Flow time through the viscometric cup STAS $\Phi 6$ mm	16 s
Adhesive reactivity on sand bath at $160^\circ\text{C}$	3 min 15 s

The adhesive based on oxidized magnesium lignosulfonate was prepared, as follows: magnesium lignosulfonate powder was mixed with distilled water, gradually added, until the lumps disappeared. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was then added, homogenizing the mixture well, then sodium hydroxide (NaOH) was added and the pH of the mixture was measured using the electronic pH meter AD12. The amount of NaOH was set in the recipe to reach a pH = 9. After preparing the adhesive, its flow time was determined by the STAS  $\Phi 6$  mm viscometer cup.

As found in the literature from the field, PMDI is considered crosslinking agent, having the role of favouring the formation of intramolecular bonds between polymers (Solt *et al.* 2019). In order to investigate the contribution of PMDI addition to the reactivity of lignosulfonate, share rates of 1%, 2% and 3% of the dried particles weight was used in the oxidized recipe of the lignosulfonate-based adhesive. The addition of PMDI to the adhesive recipe changed the adhesive colour into yellow one, as seen in Fig. 1c.

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 to be added in the recipes with magnesium lignosulfonate (LIGNEX MG) modified by oxidation and the addition of 1% and 2% PMDI, respectively. The addition of glucose changed the colour of the adhesive into a combination of yellow-green-dark brown colours (Fig. 1d).

The single-mat configuration of the particleboard manufactured in the laboratory conditions had in its composition participation rates of 65% coarse wood particles and 35% fines, sorted as presented in Table 1. The target density set for particleboard panels was  $650\text{kg/m}^3$ . The participation rate of the magnesium lignosulfonate (solid content) in the panel composition was of 15% of the weight of dry wood particles. The codes assigned to the experimental panels are presented in Table 4. The code indicates the type of adhesive and its participation rate in the composition of the panel.

The panels were hot pressing 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  $200^\circ\text{C}$  and the dimensions of the plates are 450mm x 450mm (length x width). Beech wood frames with inner sizes of 420mm x 420mm x 50mm were used for mat formation. A melamine faced particleboard panel 18mm thick was used for pre-pressing the mat. The frame was placed on a 3mm 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, 16mm thick steel stops were used. At least two panels of each size and type of recipe were made.

Table 4

**Codes of the panels, adhesive type and proportion of adhesive**

Experiment panel code	Adhesive type	Adhesive ratio (based on the total weight of the particles)	PMDI ratio (based on the total weight of the particles)	Glucose ratio (based on the total weight of the lignosulfonate-solid content)
L15	Magnesium lignosulfonate powder	15%	-	-
LO 15	Oxidized magnesium lignosulfonate	15%	-	-
LO 15 P1	Oxidized magnesium lignosulfonate	15%	1%	-
LO 15 P2	Oxidized magnesium lignosulfonate	15%	2%	-
LO 15 P3	Oxidized magnesium lignosulfonate	15%	3%	-
LO 15 P1G	Oxidized magnesium lignosulfonate	15%	1%	15%
LO 15 P2G	Oxidized magnesium lignosulfonate	15%	2%	15%

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 2.5N/mm<sup>2</sup>. 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 and then cut into specimens for mechanical testing, for the determination of formaldehyde emission by gas analysis method, and for water immersion testing.

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.

During the test, the formaldehyde released from the samples is mixed with the room air. The air in which the formaldehyde was released was collected in a vessel with a constant volume of distilled water. The solution in which the formaldehyde is dissolved was subjected to the photometric analysis procedure using the Jenway spectrophotometer and then the formaldehyde emission was calculated. The solutions used in the analysis are stored in a thermostat, specially designed for this purpose.

Determination of thickness swelling and water absorption by immersion in water was performed in accordance with the standard SR EN 317: 1996. The 50mm x 50mm immersion test samples were cut from the experimental panels, after they were conditioned at a temperature of 20°C and 65% relative humidity for 24 hours. A water bath was used for the test. The test samples were immersed in water at a temperature of 20°C for 24 hours. An electronic calliper with an accuracy of 0.01 mm was used to measure the specimens, and an electronic balance with an accuracy of 0.01g was used for weighing them. The thickness measurement of each specimen was made at the point of intersection of the diagonals. The specimens were weighed and measured before the start of the test, at 2 hours and at 24 hours.

The results were calculated using equations (1) and (2)

$$A = \frac{m_i - m_f}{m_i} \times 100 \text{ [%]} \quad (1)$$

where: A is water absorption;

m<sub>i</sub> – initial weight of the sample, in g;

m<sub>f</sub> – final weight of the sample, in g (2 h or 24 h), in g.

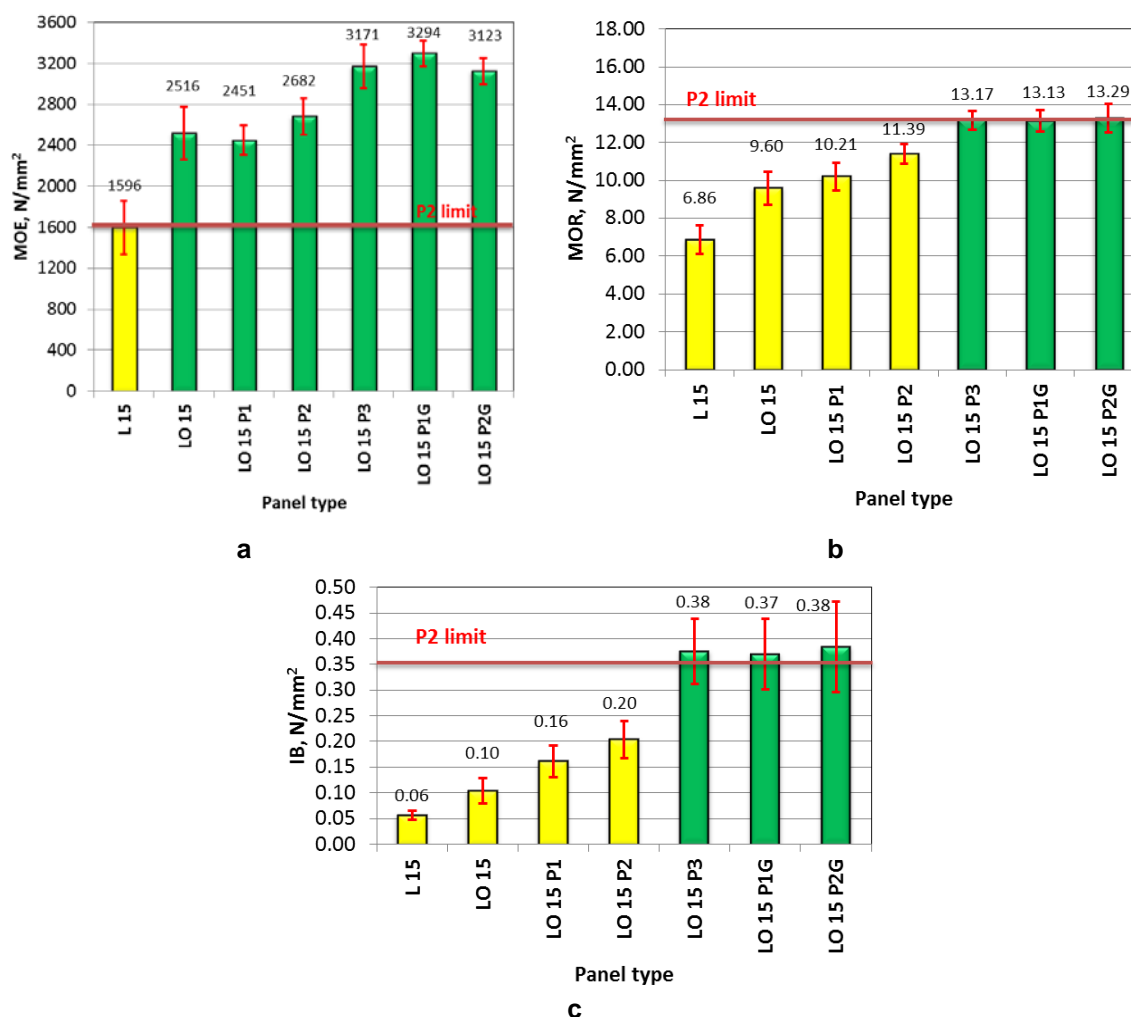
$$Gf = \frac{t_2 - t_1}{t_1} \times 10 \text{ [%]} \quad (2)$$

where:  $G_f$  is thickness swelling;  
 $t_1$ - the thickness of the test piece before immersion (mm);  
 $t_2$ - the thickness of the test piece after immersion (mm).

### RESULTS AND DISCUSSION

The results of the mechanical tests performed on the particleboard, such as MOR and MOE according to SR EN 310:1993 standard and internal bond (IB) perpendicular to the plane of the board according to SR EN 319:1993 standard are presented in the diagrams in Fig. 2 (a, b and c). The yellow coloured columns represent the values that not meet the allowable 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 addition of 3% PMDI (LO 15 P3), or 1% PMDI and glucose (LO 15 P1G) and 2% PMDI and glucose (LO 15 P2G).

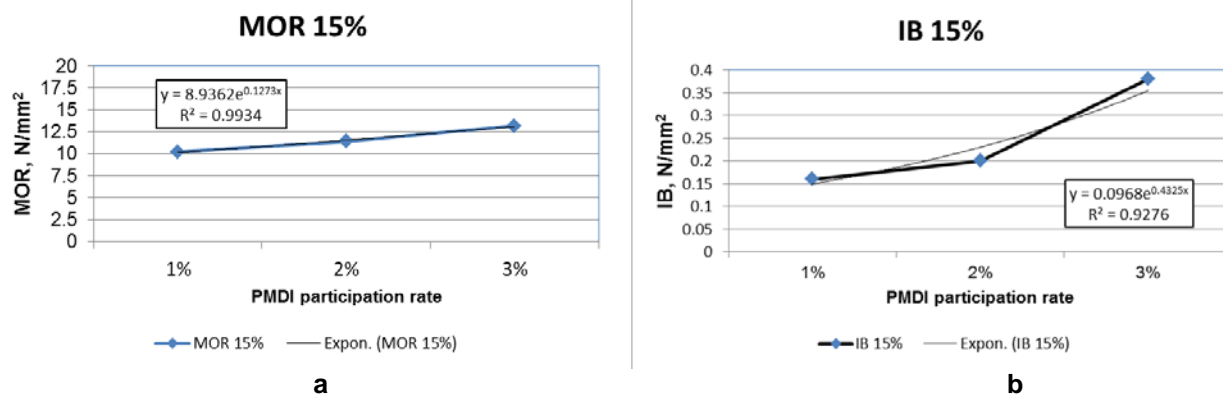


**Fig.2.**

**Results of the mechanical tests performed on the experimental particleboard made with magnesium lignosulfonate-based adhesives.**

As can be seen in Fig. 2a,b,c, 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%). It was noticed that the participation rate of 1% PMDI to the oxidized lignosulfonate-based adhesive in the composition of particleboard is not enough to achieve the desired mechanical performance. When increasing the participation rate of PMDI in the recipe to 2%, the mechanical performance increased, but again, not enough. Only the increase of this participation rate to 3% was effective for the mechanical performance of the panels.

Following the evolution of the mechanical performance of panels using the adhesive recipe based on magnesium lignosulfonate, it can be concluded that the participation of PMDI in the recipe has a positive influence on the reactivity of lignin, each additional percentage of PMDI bringing significant increases in IB and MOR, without great influence upon the modulus of elasticity (MOE). Performing the graphical analysis of the data regarding the increase of the mechanical properties (IB and MOR), it was observed that the values of these properties increase exponentially, as it results from the regression curves, depending on the percentage of PMDI (Fig. 3), with  $R^2 > 0.96$ .



**Fig. 3.**

**Variation of mechanical properties: IB (a) and MOR (b) depending on the participation rate of PMDI in the recipe.**

In order to reduce the percentage of PMDI from 3% to 1%, or 2%, the research continued by adding glucose (15% of the amount of lignosulfonate) to the recipes used in the panels LO 15 P1 and LO 15 P2. The results presented in Fig. 2 show that the addition of glucose in the composition of the adhesive has beneficial effects on the mechanical properties of the LO 15 P1G panel. Although the values are slightly above the lower limits stipulated by the SR EN 312 standard, this recipe can be considered as potential one for the manufacturing of environmentally friendly particleboard. The mechanical performance of the particleboard made with this recipe could be improved by adjusting the technological manufacturing process and especially the parameters of pressing process (pressing time and the pressure at the beginning of the process). Another direction of the research can be directed to the manufacture of three-layer particleboard and the modification of the particle sizes for the faces and core.

*Table 5*

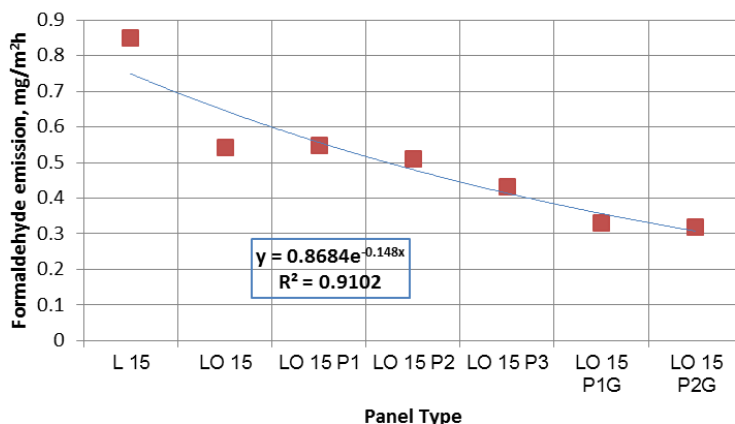
**Formaldehyde emission values for particleboard made with magnesium lignosulfonate modified by oxidation with  $H_2O_2$  and addition of PMDI and glucose**

Panel type	Formaldehyde emission, in $mg/m^2h$
LO 15 P1	0.547
LO 15 P2	0.509
LO 15 P3	0.433
LO 15 P1G	0.33
LO 15 P2G	0.32

From the economic point of view, the use of a lower amount of PMDI in favour of glucose is more advantageous, therefore the introduction of glucose as a crosslinking agent in the recipes can possibly be done in larger quantities, in order to use lower PMDI amount in the recipe (i.e. 1% of the weight of the dry particles), but these assumptions may be the objective of further research. From this point of view, it can be stated that the LO 15 P2G panel is more advantageous than that with 3% PMDI, namely LO 15 P3 panel.

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 5. The results from Table 5 show that the formaldehyde emission values are below the maximum limit imposed by the standard for emission class E1 ( $3.5mg/m^2h$ ). The differences occurred in formaldehyde emission can be determined by several factors related to: the wood raw material, the participation rate of coarse particles, the moisture content of wood particles, the degree of compression not identical for all panels, although the technological process was maintained constant for all panels. 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. Comparing the results, it can be noticed that the panels with the addition of PMDI and glucose (LO 15 P1G and LO 15 P2G) had the lowest formaldehyde emissions, and compared to those with magnesium lignosulfonate powder (L 15), the values were about 62% and 40% lower. An increase in amount of PMDI at 3% led to a decrease in formaldehyde emissions by approximately 20% for LO 15 P3 panel compared to those where only oxidized lignosulfonate was used (LO 15).



**Fig. 4.**

**Regression curves of variation of formaldehyde emission depending on the contribution of PMDI and glucose in adhesive recipes for panels with 15% 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. 4, the data are fitted to the regression curve with a coefficient of determination of  $R^2=0.91$ , 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). Several researchers (Costa 2013; Eom *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 15 P1G and LO 15 P2G panels. Formaldehyde emission values are much lower than the standardized limit specified for class E1 (3.5mg/m<sup>2</sup>h) (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: 0.397mg/m<sup>2</sup>h and 0.43mg/m<sup>2</sup>h respectively) (Salem *et al.* 2013).

Table 6 shows the immersion values for specimens made with modified magnesium lignosulfonate adhesive and the addition of PMDI and glucose. Those specimens that disintegrated after 2 hours of immersion and could no longer be measured and weighed have no values in the table.

*Table 6*

**Water absorption and thickness swelling**

Sample type	G <sub>f</sub> (2h), %	G <sub>f</sub> (24h), %	A (2h), %	A (24h), %
LO 15 P1	101	-	122	-
LO 15 P2	103	127	111	161
LO 15 P3	71	106	94	119
LO 15 P1G	96	136	147	194
LO 15 P2G	103	111	112	152

It can be seen from Table 6 that both the values of water absorption and thickness swelling are very high. Only the specimens with the addition of 3% PMDI and those with 1% and 2% PMDI and glucose withstood immersion in water for 24 hours.

The images of these specimens, after immersion, are shown in Fig. 5.



**Fig. 5.**  
**Samples after 24 hours of water immersion.**

It can be seen in the images in Fig. 5 that the water resistance of the experimental panels studied in this paper is very low. Future research can solve this problem by finding additives that reduce the hygroscopic properties of these panels.

## CONCLUSIONS

- The use of unmodified magnesium lignosulfonate (powder) as an adhesive in the composition of particleboard does not bring the mechanical performance required by standard 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 PMDI in the composition of particleboard adhesive 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 could be a solution to increase the reactivity of lignin in the presence of PMDI and improvement of the internal bond (IB) and the bending strength (MOR) of particleboard.
- 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), aiming to super E0 emission class.
- From the economic point of view, the variants with the lowest participation rate of PMDI (1%) and addition of glucose are more advantageous.
- The resistance to water of these adhesives is reduced, so they have to be used in dry environment. Further research could improve this drawback.

## REFERENCES

Akhtar A, Lutfullah G, Zahoorulah (2011) Lignosulfonate-phenolformaldehyde Adhesive: A Potential Binder for Wood Panel Industry, *J. Chem. Soc. Pak.* 33(4):535-538

- Antov P, Savov V, Neykov N (2020a) Sustainable Bio-Based Adhesives for Eco-friendly Wood Composites. A Review, *Wood Research* 65(1):51-62.
- Antov P, Jivkov V, Savov V, Simeonova R, Yavorov N (2020b) Structural Application of Eco-Friendly Composites from Recycled Wood Fibres Bonded with Magnesium Lignosulfonate, *Appl. Sci.* 10, 7526.
- Antov P, Mantanis GI, Savov V (2020c) Development of Wood Composites from Recycled Fibres Bonded with Magnesium Lignosulfonate, *Forests* 11, 613.
- Aro T, Fatehi P (2017) Production and Application of Lignosulfonates and Sulfonated Lignin, *ChemSusChem* 10, pp. 1861–1877.
- Athanassiadou E, Tsiantzi S, Markessini C (2009) Producing Panels with Formaldehyde Emission at Wood Levels. Available at <https://www.chimarhellas.com>
- Bertaud F, Tapin-Lingua S, Pizzi A, Navarette P, Petit-Conil M (2012) Development of green adhesives for fiberboard manufacturing, using tannins and lignin from pulp mill residues. *Cellulose Chemistry and Technology* 46(7-8):449-455.
- Boran S, Usta M, Gümüşkaya E (2011) Decreasing formaldehyde emission from medium density fiberboard panels produced by adding different amine compounds to urea formaldehyde resin. *Int. J. Adhes. Adhes* 31, pp. 674-678.
- Boran S, Usta M, Ondaral S, Gümüşkaya E (2012) The efficiency of tannin as a formaldehyde scavenger chemical in medium density fiberboard. *Composites: Part B* 43, pp. 2487-2491.
- Costa N (2013) Adhesive systems for low formaldehyde emission wood-based panels. Dissertation presented for the degree of Doctor of Philosophy in Chemical and Biological Engineering. Faculty of Engineering. University of Porto, Portugal. Available at: [https://www.researchgate.net/publication/260639431\\_Adhesive\\_systems\\_for\\_low\\_formaldehyde\\_emission\\_wood\\_based\\_panels](https://www.researchgate.net/publication/260639431_Adhesive_systems_for_low_formaldehyde_emission_wood_based_panels).
- Costa NA, Pereira J, Ferra J, Cruz P, Martins J, Magalha FD, Mendes A, Carvalho LH (2014) Formaldehyde emission in wood based panels: effect of curing reactions. *International Wood Products Journal* 5, pp. 146-150. Available at: <https://repositorio-aberto.up.pt/bitstream/10216/102727/2/93867.1.pdf>
- Da Silva MA, Dos Santos PV, Silva GC, Costa Lelis RC, Do Nascimento AM, Brito EO (2017) Using lignosulfonate and Phenol-Formaldehyde adhesive in particleboard manufacturing, *Scientia Forestalis* 45(115):423-433.
- Duan H, Qiu T, Guo L, Ye J, Li X (2015) The microcapsule-type formaldehyde scavenger: The preparation and the application in urea-formaldehyde adhesives. *Journal of Hazardous Materials* 293, pp. 46-53.
- Eom YG, Kim HJ, Kim JS, Kim SM, Kim JA (2006) Reduction of Formaldehyde Emission from Particleboards by BioScavengers. *J. Korean Wood Sci. Technol.* 34:29–41.
- Fernandes MRC, Huang X, Abbenhuis HCI, Hensen EJM (2019) Lignin oxidation with an organic peroxide and subsequent aromatic ring opening, *International Journal of Biological Macromolecules* 123:1044–1051.
- Formaldehyde Emission Standards for Composite Wood Products. Posted by the Environmental Protection Agency on Dec 12 (2016) Available online: <https://www.regulations.gov/document/EPA-HQ-OPPT-2016-0461-0001> (accessed on 31 July 2021).
- Ghorbani M, Liebner F, van Herwijnen HWG, Pfungen L, Krahofer M, Budjav E, Konnerth J (2016) Lignin Phenol Formal-dehyde Resoles: The Impact of Lignin Type on Adhesive Properties, *BioResources* 11(3):6727-6741.
- Hansen EL, Naerum L, Nissen P (2012) Method of Reducing the Formaldehyde Emission of a Mineral Fibre Product, and Mineral Fibre Product with Reduced Formaldehyde Emission. Patent BR112013013409A2, 14 June 2012.
- Hemmilä V, Trischler J, Sandberg D (2013) Lignin – an adhesive raw material of the future or waste of research energy, Brischke, C. & Meyer, L. (Eds.) Proc. 9th Meeting of the Northern European Network for Wood Science and Engineering (WSE), Hannover, Germany, September 11-12:98-103.
- Hu L, Pan H, Zhou Y, Zhang M (2011) Methods to Improve Lignin's Reactivity as a Phenol Substitute and as a Replacement for Other Phenolic Compounds: a Brief Review, *BioResources* 6(3):3515-3525.

Imam SH, Mao L, Chen L, Greene RV (1999) Wood Adhesive from Crosslinked Poly (Vinyl Alcohol) and Partially Gelatinized Starch: Preparation and Properties. *Starch* 51(6):225-229.

ISO 12460-3 (2015) Wood-based panels — Determination of formaldehyde release — Part 3: Gas analysis method. Standard revised by ISO 12460-3:2020. International Organization for Standardization, Geneva, Switzerland.

Junghans U, Bernhardt JJ, Wollnik R, Triebert D, Unkelbach G, Pufky-Heinrich D (2020) Valorization of Lignin via Oxidative Depolymerization with Hydrogen Peroxide: Towards Carboxyl-Rich Oligomeric Lignin Fragments, *Molecules* 25, 2717.

Klapiszewski L, Jamrozik A, Strzemieska B, Matykiewicz D, Voelkel A, Jesionowski T (2017) Activation of Magnesium Lignosulfonate and Kraft Lignin: Influence on the Properties of Phenolic Resin-Based Composites for Potential Applications in Abrasive Materials, *Int. J. Mol. Sci.* 18(6):1224.

Malutan T, Nicu R, Popa VI (2008) Contribution to the Study of Hydroxymethylation Reaction of Alkali Lignin, *BioResources* 3(1):13-20.

Mansouri HR, Navarrete P, Pizzi A, Tapin-Lingua S, Benjelloun-Mlayah B, Pasch H, Rigolet S (2011) Synthetic-resin-free wood panel adhesives from mixed low molecular mass lignin and tannin. *European Journal of Wood and Wood Products* 69(2):221-229.

Mantanis GI, Athanassiadou E, Barbu MC, Wijnendaele K (2018) Adhesive systems used in the European particleboard, MDF and OSB industries. *Wood Mater Sci Eng*, 13(2):104-116.

Salem MZM, Böhm M (2013) Understanding of formaldehyde emissions from solid wood: An overview. *Bioresources* 8(3):4775-4790.

Solt P, Konnerth J, Gindl-Altmutter W, Kantner W, Moser J, Mitter R, van Herwijnen HWG (2019) Technological Performance of formaldehyde-free adhesive alternatives for particleboard industries, *Int J Adhes Adhes*, 94:99–131.

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

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

SR EN 312 (2004) Particleboards. Specifications. 2004. European Committee for Standardization: Brussels, Belgium.

SR EN 317 (1996) Particleboards and fibreboards. Determination of swelling in thickness after immersion in water. European Committee for Standardization: Brussels, Belgium.

Xi X, Pizzi A, Delmotte L (2018) Isocyanate-Free Polyurethane Coatings and Adhesives from Mono- and Di-Saccharides. *Polymers* 10, 402. Doi:10.3390/polym10040402.

Younessi-Kordkheili H, Pizzi A (2018) Improving the physical and mechanical properties of particleboards made from urea-glyoxal resin by addition of pMDI. *Eur.J. Wood Prod* 76(6).