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INFLUENCE OF LIGNIN-BASED ADHESIVES UPON THE PROPERTIES OF PARTICLEBOARDS MADE FROM RAPE STRAWS

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Abstract:
The present paper investigates the physical and mechanical properties of the particleboard made from rape straws and lignin-based adhesives as bonding agents. Three receipts of lignin-based adhesives were prepared by hydroxyl methylation reaction. For the first one, lignin was treated by hydroxyl methylation with NaOH, formaldehyde was added for the second one and oxidation with H_2O_2 was applied for the third receipt. In the last variant, untreated lignin was used for particleboard manufacturing. Target density of the panels was of 600kg/m^3. Boards were hot pressed at a temperature of 180ºC, pressure of 2.5N/mm^2 and pressing time of 1min/mm. Physical (density, water absorption, and thickness swelling) and mechanical (modulus of elasticity, bending strength and internal bond strength) properties of the particleboards obtained in the laboratory conditions were tested, and the recorded values were compared to the limits imposed by SR EN 312: 2004 technical specifications. Particleboard made with lignin treated by hydroxyl methylation with NaOH as adhesive met the requirements of SR EN 312: 2004 for P1 panels. A good performance of internal bond property was recorded for the boards where lignin was treated by oxidation with H_2O_2. Pure lignin proved to have a poor adhesion to the rape straw particles. Unfortunately, the resistance to water for all panels was too low. Water absorption and thickness swelling recorded high values for all variants.

Key words: *particleboard; rape straws; physical properties; mechanical properties; lignin.*

INTRODUCTION

Rapeseed crops are widely cultivated in Romania nowadays for their application in biodiesel production, so rape straws represent an important agro-waste to be used as lignocellulosic resource to replace wood in particleboards' production, having similar chemical composition to hardwood (Dziurka *et al.* 2005, Szczepkowski *et al.* 2007).

Several researches on using rape straw to produce particleboards with synthetic resins were conducted in the last years (Kowaluk *et al.* 2007, Dziurka *et al.* 2015, Dukarska *et al.* 2017). The main drawback of using synthetic resins is their negative effect upon the human health. In this respect, new ecological adhesives are investigated to replace them in boards manufacturing applications, and one of them is lignin.

Lignin is one of the main components of wood and lignocellulosic materials, behaving as natural glue and having a thermoplastic structure. It gives mechanical support in the wood and it is a part of cellular structure. Lignin results as waste in the paper pulping process and it is usually burned as a fuel for energy. In the last years it was the subject of many research works that investigated the possibility of using lignin waste as an adhesive. The simplest way of using it as an adhesive is to use it as a partial replacement for phenol in PF resins in various percentages and P/F ratios (Mankar *et al.* 2012, Hemmilä *et al.* 2013, Klapiszewski *et al.* 2017).

A lot of research work was done for the treatment of lignin in order to obtain a better adherence of the lignin-based adhesives to the lignocellulosic particles (Malutan *et al*. 2008, Windsten and Kandelbauer 2008, Zhang *et al.* 2012, Klapiszewski *et al.* 2017). The modification of lignin through the hydroxyl methylation reaction was performed in alkaline medium, using NaOH solution (Malutan *et al.* 2008). Modified ammonium lignosulfonate and polyethylenimine were mixed and used as binder for particleboard manufacturing. Both maximum internal bond and bending strength were reached for a pressing time of 7min, a 20% binder ratio and for a temperature of 170ºC -180ºC (Yuan *et al.* 2014). Several receipts regarding hydroxyl methylation reaction of lignin using NaOH solution are the object of patent CN104245799A (2003). Lignin oxidized with hydrogen peroxide (H_2O_2) in the alkaline pH range recorded promising results (Hemmilä *et al.* 2013).

Other research works were focused on the treatment of rape straw particles, such as boiling in water or soaking in sodium hydroxide (NaOH) solution, in order to improve the adhesion of the particles to the resin (Částková *et al.* 2018).

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OBJECTIVE

The present paper investigates the performance of three types of lignin-based adhesives in particleboard manufacturing, using rape straw particles and treated lignin by hydroxyl methylation with single NaOH, both formaldehyde and NaOH and oxidation with H_2O_2. Untreated lignin was used as reference variant. The physical properties of water absorption (WA) and thickness swelling (TS) were determined after 24h of water immersion according to SR EN 317:1993 standard. The bending strength (BS) and modulus of elasticity (MOE) were determined according to SR EN 310:1993 standard, and internal bond (IB) perpendicular to the plane of the board was tested according to SR EN 319:1993 standard. The recorded values were compared to the limits imposed by SR EN 312: 2004 technical specifications.

MATERIAL, METHOD, EQUIPMENT

The experimental work presented in this paper was performed at the University of Teheran, in the frame of research laboratory of College of Agriculture and Natural Resources. Rapeseed straws used for boards manufacturing come from Iranian rapeseed crops. Rape straws were chopped using a hammer mill (Fig. 1c)

a. *b.* *c.*

Fig. 1.
Rape straws used as raw materials for particleboard manufacturing
a – rape straws (RS); b – rape straws prepared for chopping; c – hammer mill used for chopping the rape straws.

Both size and distribution of rape straw particles were analized after chopping. A sample with mass of 25g of rape straws was selected for this analysis. Particle size distribution represents the participation rate of particles with the same sizes into the sample. The particles were sieved for 10 minutes by oscillating screen method using large, medium and fine meshes (4x4, 3x3, 2x2,1x1 and 0.5x0.5mm).The particles collected from each sieve were afterwards weighed with an accuracy of 0,01 g, and the distribution of particle sizes was calculated with Equation 1.

$$c_d = \frac{m_s}{m_0} \times 100 \quad (\%) \qquad (1)$$

where: m_s is the mass of particles weighed from each sieve and m_0 is the mass of the initial sample (25 g).

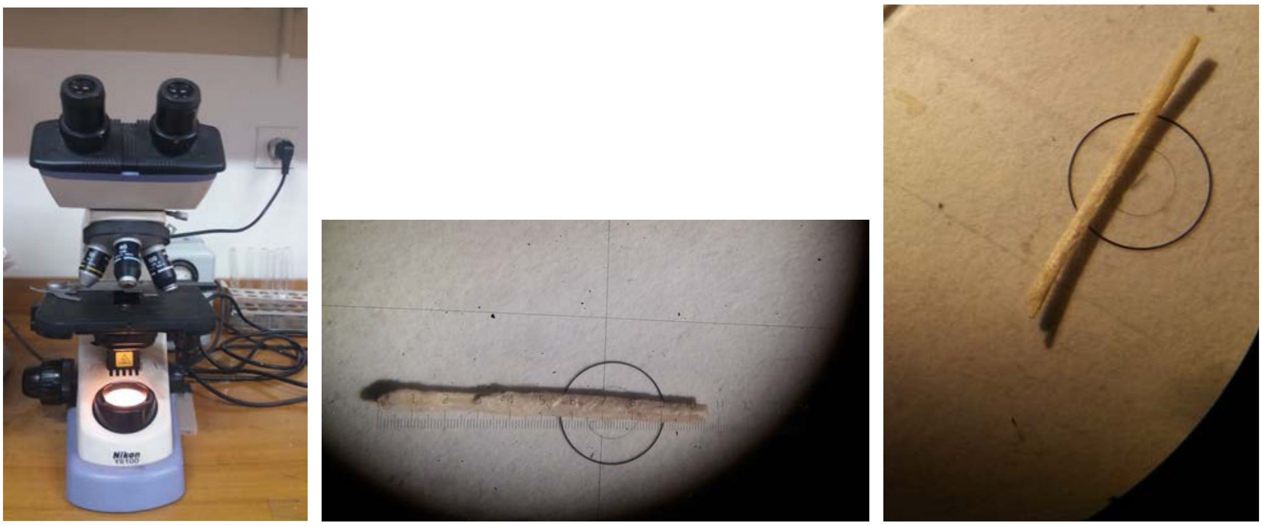


Fig. 2.
Microscope Nikon YS 100 and the method of measuring the length and width of particles.

Length, width and thickness of rape straw particles from each sieve were measured in order to establish the range of variation for these sizes. For this purpose, a Microscope Nikon YS 100 was used, with a 10x magnification (Fig. 2).

Moisture content of the rape straw particles was determined according to SR EN 322/1996 standard. Each sample was introduced in an oven at temperature of 103 (+/-2°C) and weighed successively with an accuracy of 0.01g until constant mass. Moisture content was calculated with Equation 2.

$$H = \frac{m_H - m_0}{m_0} \times 100 \quad (\%) \tag{2}$$

where: m_H is the initial mass of the sample, in g, and m_0 is the constant final weighed mass.

The lignin (Lignex Mg F) was provided by Sappi Biotech GmbH (Düsseldorf, Germany). The analytical data of this product are as follows: dry substance 92.7%, Magnesium 5.7%, insoluble substances 0.3%, pH-value 5.4%. Three receipts (A, B and C) were prepared so, to improve the adherence of these lignin-based adhesives to the rape straw particles. Untreated lignin (receipt D) has been used as reference.

In receipt A (Patent CN104245799A 2003) the lignin was treated by hydroxyl methylation with NaOH. Mixed water and NaOH were heated simultaneously from 60°C to 75°C for 1.5 hours, after which phenol and formaldehyde (37%) was added. Receipt B is based on the hydroxyl methylation reaction performed with formaldehyde 37% solution in alkaline medium (NaOH) and the pH of 9.7-9.9 (Patent CN104245799A 2003). Receipt C was obtained by oxidation of lignin with hydrogen peroxide (H_2O_2) and the addition of NaOH for increasing the pH to 9 (Hemmilä *et al.* 2013).

In the production of particle boards, 10% of the dry substance mass was used for the four types of lignin-based adhesives (Table 1). The final sizes (Length x Width x Thickness) of the single layer particleboards were 450mmx450mmx16mm and the target density was 600kg/m^3 (Fig. 3a). The press temperature was 180°C and the press factor was 1min/mm, whilst the pressure was 2.5N/mm^2. The press (Fig. 3b) used to manufacture the boards had the plates dimensions of 500mmx500mm and an automatic control of pressure and temperature.

Table 1

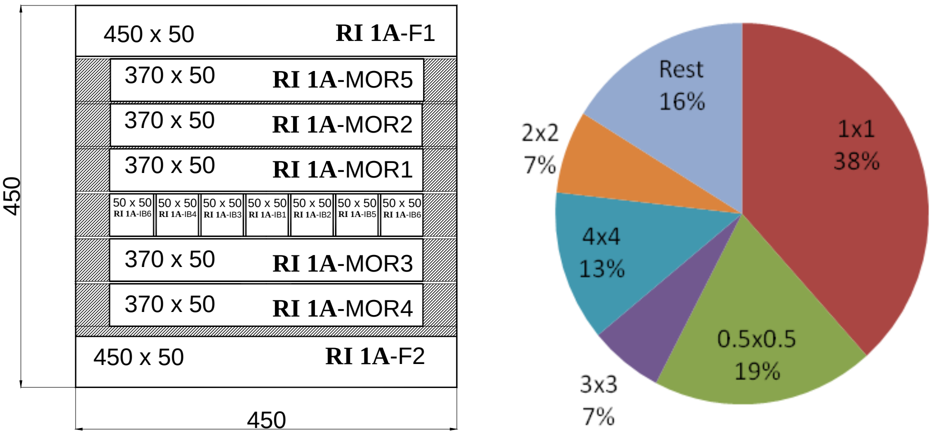
Particleboards design

No	Board code	Rape straw, in %	Adhesive proportion, in %			
			Receipt A	Receipt B	Receipt C	Receipt D (untreated)
1	**RI 1A**	100	10	-	-	-
2	**RI 1B**	100	-	10	-	-
3	**RI 1C**	100	-	-	10	-
4	**RI 1D**	100	-	-	-	10

a. b.

Fig. 3.
Single layer particleboard (a) and press used to manufacture the boards (b).

From each board, 5 samples were cut for bending strength (BS) and E-modulus (MOE) measurements and 5 samples for the internal bond (IB) measurements (Fig. 4a). The water absorption (WA) and thickness swelling (TS) tests were performed for 24 hours of immersion into distilled water at 20°C.



a. b.

Fig. 4.
a - samples cutting pattern; b - rape straw particles size distribution.

RESULTS AND DISCUSSION

The particles size distribution after screening with mesh sizes in the range from 0.5mmx0.5mm to 4mmx4mm is shown in Fig. 4b. The minimum and maximum sizes (length, width and thickness) of the particles collected in the sieves are shown in Table 2.

Table 2

Measured sizes of rape straws particles

Mesh size (mm x mm)	Length, in mm	Width, in mm	Thickness, in mm
0.5 x 0.5	1.2-8.6	0.5-0.8	0.7-1.0
1 x 1	2.3-11.5	0.7-1.3	0.7-1.0
2 x 2	5.1-12.5	2.1-2.8	0.7-1.0
3 x 3	8.5-13.4	3.2-3.9	0.7-1.0
4 x 4	10-14.4	4.1-4.6	0.7-1.0

The moisture content measured for rape straw particles was of 11.63%. The amount of adhesive solution used in the composition of particleboard structure was calculated as function of the rape straw

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moisture content experimentally determined. The results of the mechanical tests performed on the particleboard, such as BS 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. 5.

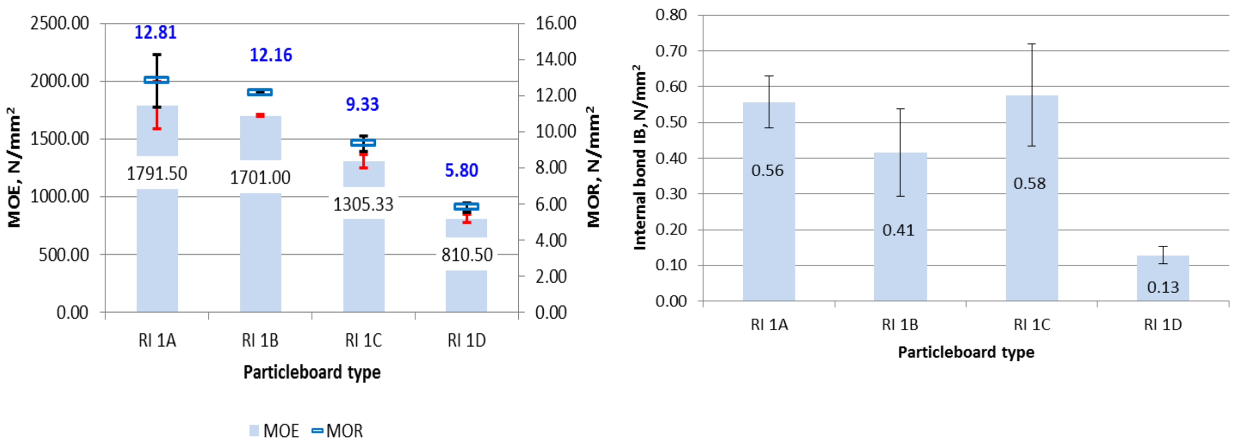

Fig. 5.
Results of the mechanical tests performed on the particleboard made with the four variants of lignin-based adhesives.

As expected, the boards glued with pure lignin showed poor mechanical properties compared to the boards glued with modified lignin-based adhesive. The performance of an adhesive is shown by the internal bond (IB) test that was better for the oxidized lignin samples than for those modified with hydroxyl methylation reaction. Instead, this receipt failed to MOE and BS (MOR) tests according to the limits imposed by SR EN 312:2004 for panels P1. All requirements of SR EN 312: 2004 were met by the boards manufactured with Receipts A and B, obtained by hydroxyl methylation with NaOH of lignin. The E modulus requirement was met by hydroxyl methylation lignin boards. Applying the lignin in a powder form in an aqueous suspension has a poor adhesion to the rape straw particles. Powdered lignin does not provide sufficient tackiness for the mat.

Fig. 6 shows the performance of the boards to the immersion into water for 24 hours, according to SR EN 317:1993 standard. For all boards, the results show high values both for WA and TS, which is the main drawback of using lignin-based adhesives.

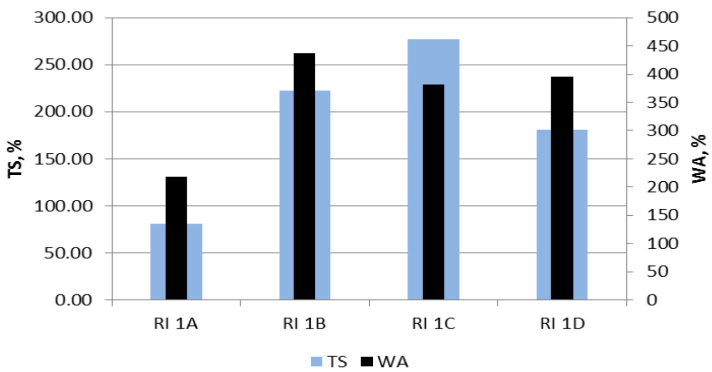

Fig. 6.
Results of immersion into water for 24 hours.

CONCLUSIONS

The results show that using lignin as an adhesive is possible in a modified form by oxidation with H_2O_2 and hydroxyl methylation with NaOH. In an unmodified form, lignin results in poor adhesion and too long a press time. The press factor of 1min/mm used in the experiments is high compared to that used in the particle board industry nowadays, so in applications where the press time is a critical factor, improved technology of this type of particleboard manufacture has to be tested. Further research on improving the water resistance of the particleboards glued with lignin-based adhesives has to be done.

REFERENCES

Částková T, Hýsek S, Sikora A, Schönfelder O, Böhm M (2018) Chemical and Physical Parameters of Different Modifications of Rape Straw (*Brassica napus* L.). BioResources 13(1):104 -114.

Dukarska D, Czarnecki R, Dziurka D, Mirski R (2017) Construction particleboards made from rapeseed straw glued with hybrid pMDI/PF resin. Eur. J. Wood Prod. 75(2):175-184. DOI: 10.1007/s00107-016-1143-x

Dziurka D, Mirski R, Łęcka J (2005) Properties of boards manufactured from rape straw depending on the type of the binding agent. Electronic Journal of Polish Agricultural Universities 8(3), article 5.

Dziurka D, Mirski R, Dukarska D, Derkowski A (2015) Possibility of using the expanded polystyrene and rape straw to the manufacture of lightweight particleboards. Maderas: Ciencia y Tecnologia. DOI: 10.4067/S0718-221X2015005000057

Hemmilä V, Trischler J, Sandberg D (2013) Lignin – an adhesive raw material of the future or waste of research energy?. In: Brischke, C. & Meyer, L. (Eds.) Proc. 9th Meeting of the Northern European Network for Wood Science and Engineering (WSE), Hannover, Germany, September 11-12, pp. 98-103.

Klapiszewski L, Jamrozik A, Strzemiecka B, Matykiewicz M, 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. 2017 Jun; 18(6):1224-1246.

Kowaluk G, Marchal R, Palubicki B, Frackowiak I, Beer P (2007) Some aspects of machining of particleboards produced from alternative lignocellulose raw materials. In: Proceedings of the 2nd International Scientific Conference Woodworking Technique, Zalesina, Croatia, pp. 277-282.

Malutan T, Nicu R, Popa VI (2008) Contribution to the study of hydroxymetylation reaction of alkali lignin. BioResources 3(1):13-20.

Mankar SS, Chaudhari AR, Soni I (2012) Lignin in phenol-formaldehyde adhesives. International Journal of Knowledge Engineering 3:116-118.

Patent CN104245799A (2003) Method for increasing the reactivity of lignin. Available at https://patents.google.com/patent/CN104245799A/en

Szczepkowski A, Nicewicz D, Koczoń P (2007) The relationship between tree health and chemical composition of beech (*Fagus sylvatica* L.) and oak (*Quercus robur* L.) wood of polish provenances. Acta Scientarum Polonorum Silvarum Colendarum Ratio et Industria Lignaria 6(3):77-88.

SR EN 310 (1993) Wood-based panels. Determination of modulus of elasticity in bending and of bending strength. Romanian Standardization Institute, Bucharest.

SR EN 312 (2004) Particleboards. Specifications. Romanian Standardization Institute, Bucharest.

SR EN 317 (1993) Particleboards and fibreboards. Determination of swelling in thickness after immersion in water. Romanian Standardization Institute, Bucharest.

SR EN 319 (1993) Particleboards and fibreboards. Determination of tensile strength perpendicular to the plane of the board. Romanian Standardization Institute, Bucharest.

SR EN 322 (1996) Wood based panels. Determination of moisture content. Romanian Standardization Institute, Bucharest.

Windsten P, Kandelbauer A (2008) Adhesion improvement of lignocellulosic products by enzymatic pre-treatment. Biotechnology Advances 26:379–386.

Yuan Y, Guo M, Liu F (2014) Preparation and evaluation of green composites using modified ammonium lignosulfonate and polyethylenimine as a binder. BioResources 9(1):836-848

Zhang Y, Yang DQ, Wang XM, Feng M, Brunette G (2012) Process for fungal modification of lignin and preparing wood adhesives with the modified lignin and wood composites made from such adhesives. Patent: WO 2012/113058 A1.