



Novel kraft-lignin-based adhesives for the production of particleboards

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ABSTRACT

Lignin is produced worldwide in pulp mills and is currently mainly used for energy recovery. Because of its chemical properties, one possible utilisation is the production of lignin-based materials. Currently, developed lignin-based adhesives are based mainly on lignosulfonate instead of kraft lignin since lignosulfonate is more reactive than kraft lignin. However, worldwide substantially more kraft lignin is produced. The presented research deals with the development of resin chemically modified with kraft lignin up to 40% (w/w) content of kraft lignin. The synthesis of adhesives is described, and developed adhesives are characterised. Namely, viscosity, mechanical properties of resins and results of differential scanning calorimetry are presented. Furthermore, the developed kraft-lignin-based adhesives were used for the production of particleboards. Pre-pressing in a cold press followed by hot pressing in a laboratory press was used for the production of particleboards. The physical (thickness swelling, moisture uptake, vertical density profile), as well as mechanical (internal bonding, modulus of rupture, modulus of elasticity in three-point bending) properties of particleboards, were evaluated. The results clearly show that kraft lignin can be used for the production of lignin-based adhesives for the production of particleboards.

1. Introduction

Lignin is, after cellulose, the second most abundant polymer of amorphous phenolic structure in nature [1,2]. The majority of lignin comes from the paper industry, where it is taken as a by-product and serves as a source of thermal energy, and only units of percent are used for other value-added applications [3]. Annual production of kraft lignin is estimated at 55 million tons [4]. The attractiveness of lignin as a substitute in wood adhesives lies in its natural origin, phenolic nature, high availability and low cost [5,6].

Kraft lignin comes from the kraft pulping process, which is the most common method of pulp production for papermaking [7]. Many studies have looked into the use of kraft lignin for the preparation of phenol-formaldehyde (PF), urea-formaldehyde (UF), epoxy (EP) or polyurethane (PU) based resins [8–10]. The use of these resins can be found in the production of particleboards and OSB [11–13], fibreboards [14], plywood [15,16] or paper-based laminates [17,18]. Other uses of lignin

are the production of plastics, carbon fibres, pharmaceutical applications or depolymerisation into other valuable chemical products [19].

Particleboards (PB) are produced from wood particles and an adhesive, when under the influence of temperature and pressure, the adhesive is activated and the wood material is joined in a solid board with the required physical and mechanical properties [20]. The predominant type of adhesive used for PB production is urea-formaldehyde resins (90–92 % of European PB production) [21].

The widespread use of urea-formaldehyde (UF) resins in the production of composite materials is based on their properties (cheap raw materials, high reactivity, excellent adhesion to wood, low curing temperature and short pressing time compared to other resins) [22]. The disadvantage of UF resins is low water resistance [23] and high formaldehyde emissions when using UF resins in wood panels [24,25], which decrease over time but do not decrease to zero in the long term [26].

The release of formaldehyde into the ambient air can lead to health problems [27–29]. From the point of view of carcinogenic effects for

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humans, formaldehyde is classified in group 1, i.e. it is a human carcinogen [30].

The reduction of formaldehyde emissions in UF resins has become the main direction of their research. Phenols are an important scavenger of formaldehyde, so they are added to UF resins in the production of DTD [31]. The reduction of formaldehyde emissions is the main reason for interest in the possibility of using lignin as a phenolic component in connection with UF resins [32].

Therefore, the addition of lignin to UF resins will increase the environmental performance, among other things, it gives the products higher moisture resistance, higher thermal stability, while achieving the same or even slightly higher mechanical properties as untreated UF [33–35].

The aim of this study is to observe the effect of kraft lignin as an additional component in UF resins on the properties of the modified resins and properties of PB bonded with these resins. The subsequent use of the developed resins for the production of PB will bring us knowledge about the interaction of resins with wood to form a compact board and their effect on the mechanical and physical properties of the produced PB. Our vision was to create a UF resin modified with kraft lignin, the production of which would be simple even on an industrial scale.

2. Materials and method

2.1. Materials

2.1.1. Urea-formaldehyde resin

For the preparation of lignin-urea-formaldehyde resin, Diakol F resin (Chemcol U 100) with the addition of Diakol R 60 hardener (Diakol Strážske, s.r.o., Slovakia) for cold gluing of wood in the woodworking and furniture industry was used. The hardener is added to the UF resin in a ratio of 100:4.

2.1.2. Black liquor

Black liquor from hardwood from Mondi (Mondi SCP, a.s., Slovakia) was used for the preparation of kraft lignin, from which kraft lignin from hardwood was subsequently isolated (2.2.1 Lignin precipitation and characterization).

2.1.3. Wood particles

Wood chips from the company DDL Lukavec (Lukavec, Czech Republic) were used for the production of the test PB, which are intended for the production of the middle layer of the three-layer PB.

2.2. Methods

2.2.1. Lignin precipitation and characterization

Lignin was precipitated from hardwood black liquor using a 2 M solution of sulfuric acid (H₂SO₄). The initial pH of the black liquor was 12, and acid addition was terminated at pH 2, when the reaction proceeded at 80 °C with constant stirring. After reaching the required pH, the solution with precipitated lignin was filtered under reduced pressure. The resulting filter cake was mixed in distilled water and filtered again. This procedure was repeated three times. The washed lignin was subsequently dried at a temperature of 60 °C, the dry lignin was crushed in the next step on a knife mill to the required fraction.

Determination of the molecular weight of lignin

Molecular weight was determined using gel permeation chromatography Waters e2695 Separation, detector differential refractometer 2414 (Waters, USA). Two PLgel Mixed 300 × 7.5 mm columns (Agilent Technologies, USA) were used for separation. The mobile phase was dimethyl sulfoxide with 0.1 M LiBr, with a flow rate of 0.5 ml/min. The column was calibrated to pullulan standards.

Determination of lignin particle size

The particle size of lignin was determined by laser diffraction Analysette 22 COMPAC (Fritsch, Germany). The sample was dispersed in

water using an ultrasonic bath for 30 min.

2.2.2. Adhesives manufacturing

The urea-formaldehyde (UF) resin used was Diakol F (Chemcol U 100), a white liquid with a viscosity of 1000 to 2000 mPa.s, with a dry matter content of at least 65 % and a resin pH of 8. This resin contains a maximum of 1.5 % of free formaldehyde.

After weighing the UF resin and the given amount of lignin, which was calculated on the basis of the dry matter of the resin and lignin, the mixture was mixed in the beaker using an anchor stirrer at 300–500 revolutions per minute (depending on the viscosity) for 10 min. For better dispersion of lignin, a Yellow line DI 25 basic disperser (IKA, Germany) was also used at 4000 – 5000 revolutions per minute (depending on the viscosity) for 5 min. The individual resins were then poured between two Teflon-coated metal plates with a 4 mm thick spacer wire. Here the resins were cured at laboratory temperature for 48 h. After curing, individual test specimens were cut from the resin plates. Furthermore, individual variants of resins were used for the production of PB.

2.2.3. Adhesives characterisation

Viscosity of resins

The two-plates model was chosen to measure the viscosity of the resins. The measurements were carried out on a Malvern Kinexus lab + rheometer (Malvern, UK). The measurements were carried out at 25 °C. A shear rate of 10 s⁻¹ was used to compare the shear viscosity results.

Impact bending strength by the Charpy method

Five test samples with dimensions of 80 × 10 × 4 mm (according to the standard ČSN EN ISO 179 [36]) were prepared to measure the impact bending strength (IBS) of the resins. The measurement was performed on a PIT 501 J Charpy hammer (Wance, China) using a 4 J hammer. The distance between the supports was set at 62 mm. The IBS was calculated according to the formula:

$$IBS(kJ/m^2) = \frac{A_n}{b \cdot h} \cdot 10^3$$

where A_n is the energy consumed to break through the sample in J, b is the width of the sample in mm and h is the thickness of the sample in mm.

Hardness of resins

The Shore hardness, which is based on the tip impression method, was used to measure the hardness. A type D tip was used to measure the resistance against the tip being pushed into the sample (indenting body 35° cone, test load 44.45 N). The samples were measured after 48 h of preparation on plates with a thickness of 4 mm.

Bending strength of resins

Prepared samples with dimensions of 80 × 10 × 4 mm were placed in a beam in a Shimadzu AGS-X (Shimadzu, Japan) blasting machine. It was a three-point bending method with a support distance of 64 mm, according to the ČSN EN ISO 178 [37] standard. The bending strength was calculated according to the formula:

$$BS(MPa) = \frac{3 \cdot F_{max} \cdot l}{2 \cdot b \cdot t^2}$$

where F_{max} is the maximum force achieved on the sample in N, l is the distance between supports (64 mm), b is the width, and t is the thickness of the sample in mm.

Tensile strength of resins

Measurements were made on a Shimadzu AGS-X blasting machine (Shimadzu, Japan). The distance between the clamping jaws was 100 mm. The dimensions of the samples were prepared according to ČSN EN ISO 527 [38] to 150 × 10 × 4 mm. The ultimate tensile strength was calculated according to:

$$MORTS(MPa) = \frac{F_{max}}{b \cdot h}$$

where F_{max} is the maximum force in N, b is the width of the sample in mm and h is the thickness of the sample in mm.

Compression strength of resins

Cylindrical test samples with dimensions of 15×10 mm were prepared for the test. The measurement was performed on a Shimadzu AGS-X blasting machine (Shimadzu, Japan). The ultimate compressive strength was calculated according to:

$$CS(MPa) = \frac{F}{S_0}$$

where F is the maximum compressive force in N and S_0 is the initial cross-section of the sample in mm^2 .

Tensile shear strength of resins

The tensile shear strength of the bonded joint (TSS) is determined by shear stress on a Shimadzu AGS-X (Shimadzu, Japan). Six samples with a glued area of 25×25 mm were prepared from each variant. Beech plywood was chosen as the adherent. After application of the resins, the samples were placed in a special preparation and loaded with a 4 kg weight. Curing was carried out at laboratory temperature for 48 h. The TSS was calculated according to:

$$TSS(MPa) = \frac{F}{S}$$

where F is the maximum force in N and S is the area of the bonded joint in mm^2 .

Moisture uptake of resins

The essence of the test is the increase in weight after placing the sample in water at laboratory temperature for 24 h. Ten samples of each variant for this test had dimensions of $50 \times 10 \times 4$ mm. The samples were conditioned for 24 h at a temperature of $50^\circ C$. The sample was weighed on an analytical balance before immersion in water and after 24 h in water. Finally, the percentage gain in weight was calculated:

$$MU(\%) = \frac{m_2 - m_1}{m_1}$$

where m_1 is the mass of the sample before immersion in water in g and m_2 is the mass of the sample after being removed from the water in g.

Thermomechanical analysis (TMA) of resins

This is a method based on measuring the change in sample dimensions depending on the temperature regime. The sample is placed in the beam and heated. A constant force (50 mN) is applied to the sample. Samples with a size of $5 \times 5 \times 4$ mm were used for the measurements. T_g was determined for individual concentrations of UF resin with lignin.

2.2.4. Particleboards manufacturing

For laboratory testing, single-layer PB bonded with lignin-urea-formaldehyde resin (0–40 % lignin content) with a thickness of 12 mm and dimensions of 600×600 mm with a target density of 650 kg/m^3 were produced.

First, the moisture content of wood chips and prepared adhesives was determined using a moisture analyzer MB – 23 (Ohaus®) to calculate the dry matter of the material. After weighing the required amount of material, the adhesive mixture was applied to the chips using a drum applicator with mixing arms. The resin content for all variants was chosen to be 8 % (dry adhesive/dry particles).

Chips with an applied adhesive mixture were then layered into a chip carpet. The layering was carried out by hand with evidence of even layering into a mold with a steel plate on the bottom. After layering, the mat was hand pressed to simulate pre-pressing and then a steel plate was added on top to prevent the PB from being baked to the press plates. This file was loaded into a hydraulic press.

The PBs were pressed with a pressure of 3.5 MPa at a temperature of

$140^\circ C$ for 5 min. After pressing, the outer steel plates were removed and the plates were conditioned at $20^\circ C$ and 60 % humidity for 96 h before being shaped into test specimens.

2.2.5. Particleboards characterisation

Moisture uptake and thickness swelling

To measure resistance to moisture, 20 samples with dimensions of 50×50 mm from each variant were prepared. The samples were first dried in an oven at $103^\circ C$ to constant weight to achieve absolute 0 % moisture. Thickness (t_0) and weight (m_0) were measured for the dried samples. Subsequently, the samples were placed in a container where water ($20^\circ C$) was added and the samples were left there for 24 h. After this time, the samples were taken out, placed on a mat, where they were left for 10 min to drain the water from the surface of the samples. Subsequently, the thickness (t_w) and weight (m_w) of the samples were measured, from which the thickness swelling (TS) and moisture uptake (MU) were calculated as a percentage according to the following formulas:

$$TS(\%) = \frac{t_w - t_0}{t_0} \cdot 100$$

where t_w is board thickness after taking samples from the water after 24 h, and t_0 is board thickness dried to 0 % moisture.

$$MU(\%) = \frac{m_w - m_0}{m_0} \cdot 100$$

where m_w is board weight after taking samples from the water after 24 h, and m_0 is board weight dried to 0 % moisture.

Vertical density profile

The vertical density profile (VDP) was carried out on a DPX300-LTE X-ray density analyzer (IMAL PAL GROUP, San Damaso, Italy). The measurement was carried out on four samples with dimensions of $50 \times 50 \times 12$ mm from each variant. For individual variants, the VDP values were averaged in order to obtain a density curve. The VDP curves of the individual variants were subsequently compared.

Bending strength and modulus of elasticity

Bending strength (MOR) and modulus of elasticity in bending (MOE) were measured according to the ČSN 49 0115 [39] standard using the three-point test method using a TT 2850 universal testing machine (TIRA, Schalkau, Germany). Ten PB samples with dimensions of $300 \times 50 \times 12$ mm were prepared from each variant. The distance of the supports (l) was set to 240 mm. Modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated according to the following formulas:

$$MOR(MPa) = \frac{3 \cdot F_{max} \cdot l}{2 \cdot b \cdot t^2}$$

where F_{max} is the maximum force achieved on the sample in N, l is the distance between supports (240 mm), b is the width, and t is the thickness of the sample in mm.

$$MOE(MPa) = \frac{l^3 \cdot (F_2 - F_1)}{4 \cdot b \cdot t^3 \cdot (a_2 - a_1)}$$

where l is the distance between supports (240 mm), F_1 is 10 % and F_2 is 40 % of the maximum load F_{max} given in N, b is the width and t is the thickness of the sample in mm, a_1 and a_2 is the deflection increment in the center of the length of the test specimen in mm (corresponding to $F_2 - F_1$).

Internal bonding

Internal bonding perpendicular to the plane of the plate (IB) was determined according to ČSN EN 319 [40]. Ten samples with dimensions of $50 \times 50 \times 12$ mm were prepared from each variant, for which the exact surface dimensions were measured and then these samples were glued using the two-component polyurethane glue Bison Power adhesive to the preparations to measure IB of the beech wood

board. Curing of the glue for the prepared samples took place for 24 h under constant pressure. The IB test was carried out on a TT 2850 universal testing machine (TIRA, Schalkau, Germany). The IB was calculated according to the following formula:

$$IB(MPa) = \frac{F_{max}}{a \cdot b}$$

where F_{max} is the maximum force achieved on the sample in N, a is the length and b is the width of the sample in mm.

Scanning electron microscopy (SEM)

SEM of the produced PB were performed using a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic) with a secondary electron detector operated at 15 kV acceleration voltage [41]. Samples for SEM were obtained from breached samples after the internal bonding test and during the microscopic sample preparation, they were sputtered by gold. Additionally, SEM of hardened adhesives was also conducted in order to monitor interaction between lignin particles and UF resin. The hardened adhesives without wood particles were cut by a blade in order to produce samples for SEM.

Formaldehyde content

Extraction perforator method was employed to estimate the formaldehyde content in all pressed particleboards. The test was carried out according to the EN ISO 12460-5 [42].

3. Results

3.1. Lignin characterization

Determination of the molecular weight of lignin

The following graph (Fig. 1A) shows the cumulative (blue) and differential (red) lignin molecular weight curves. Molecular weight is subject to error, due to comparison with a standard (pullulan).

The graph shows that the number average of M_n is roughly 540 g/mol, the mass average of M_w is around 2000 g/mol, and the center average was set at M_z of 10,000 g/mol. It is therefore an oligomer with a molar mass in the range of a few hundred to a thousand g/mol.

Determination of lignin particle size

A graph of the cumulative and distribution function of lignin particle size (Fig. 1B) can be formulated using the data in lignin). The Table 1 shows that 90 % of lignin particles are below 50 μm . The graph shows that the largest amount of particles has a size of around 30 μm .

3.2. Mechanical and physical properties of developed adhesives

Viscosity of resins

The results of viscosity measurements showed that with the addition

of lignin to UF resins, the shear viscosity increased from 1.56 Pa.s (R-UF0) to 250.3 Pa.s (R-UF40). An exponential increase in viscosity with increasing lignin addition was observed. The shear viscosity results for each resin type are shown in Table 2.

Impact bending strength by the Charpy method

The following graph (Fig. 2A) shows the dependence of the impact strength of the UF resin on the lignin content. It can be seen from the graph that with increasing lignin concentration, the Charpy impact strength decreases relatively little (0.057 kJ/m² (R-UF0) – 0.048 kJ/m² (R-UF20)) up to a lignin concentration of 20 % and does not significantly affect it. On the other hand, at a higher concentration, there will be a more significant reduction, namely at a value of 40 % of the lignin content by approximately half compared to the pure UF resin (0.028 kJ/m²).

Hardness of resins

Shore hardness tests were performed on UF resin samples with different lignin content. The samples were measured after 48 h of preparation on plates with a thickness of 4 mm. The commercial UF resin showed the highest hardness according to Shore (81.4), subsequently there is a slight decrease in hardness with the addition of 10 % lignin (74.4), with further addition of lignin the decrease is very slight and almost linear up to a concentration of 40 % (71.2). The addition of lignin does not significantly negatively affect the hardness of the measured mixtures. Fig. 2B shows the dependence of the Shore hardness on the lignin content of the UF resin.

Xu [43] for PF resin modified with alkaline lignin at a concentration of 40 %, on the contrary, achieved a slight improvement in Rockwell hardness for PF modified with lignin.

Bending strength of resins

The following graph (Fig. 2C) shows the dependence of the bending strength of the UF resin on the lignin content. The BS limit is very similar up to 30 % lignin content (17.94 – 15.95 MPa), the addition of lignin does not have a significant effect and the given mixtures show good properties in terms of BS. At a lignin content of 40 %, there is a significant decrease of BS to 10.13 MPa (about 40 %). From the dependence of the deflection at failure of the sample for UF resin, it emerged that with 10 % addition of lignin, it decreases by about 40 %. At 10 % and 20 % lignin content, the deflection values are similar, and then there is a gradual decrease in deflection with further addition of lignin. According to the data obtained, it can be observed that the amount of added lignin has an effect on the fragility of the adhesive samples. The drop in R-UF10 is due to measurement deviation. Deflection at failure in bending strength of individual resin variants can be found in Table 2.

Tejado [44] achieved similar results with PF resin with lignin addition of 25 % or 45 %. The decrease in strength at higher lignin content is attributed to the existence of low-reactivity zones in lignin that fail to

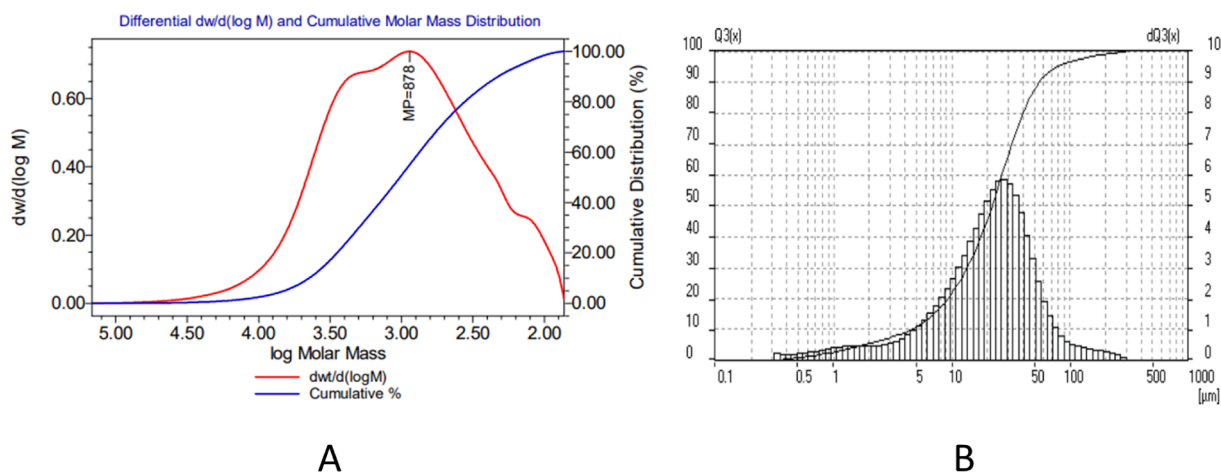


Fig. 1. Cumulative and molecular weight distribution curve graph (A); Plot of cumulative and distribution function of lignin particle size (B).

Table 1
Percentage representation of particle size.

Percentage representation	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %
Particles smaller than	5 μm	9 μm	14 μm	18 μm	22 μm	27 μm	32 μm	40 μm	50 μm

Table 2
Properties of Lignin-urea-formaldehyde resins.

Resin	Deflection at failure (mm)	Type of adhesive failure	T _g (°C)	Shear viscosity (Pa.s)
R-UF0	1,15	KA	81.7	1.56
R-UF10	0.66	KP	81.2	19.94
R-UF20	0.62	KP	76.0	31.86
R-UF30	0.28	KP	73.5	152.8
R-UF40	0.1	AP	71.9	250.3

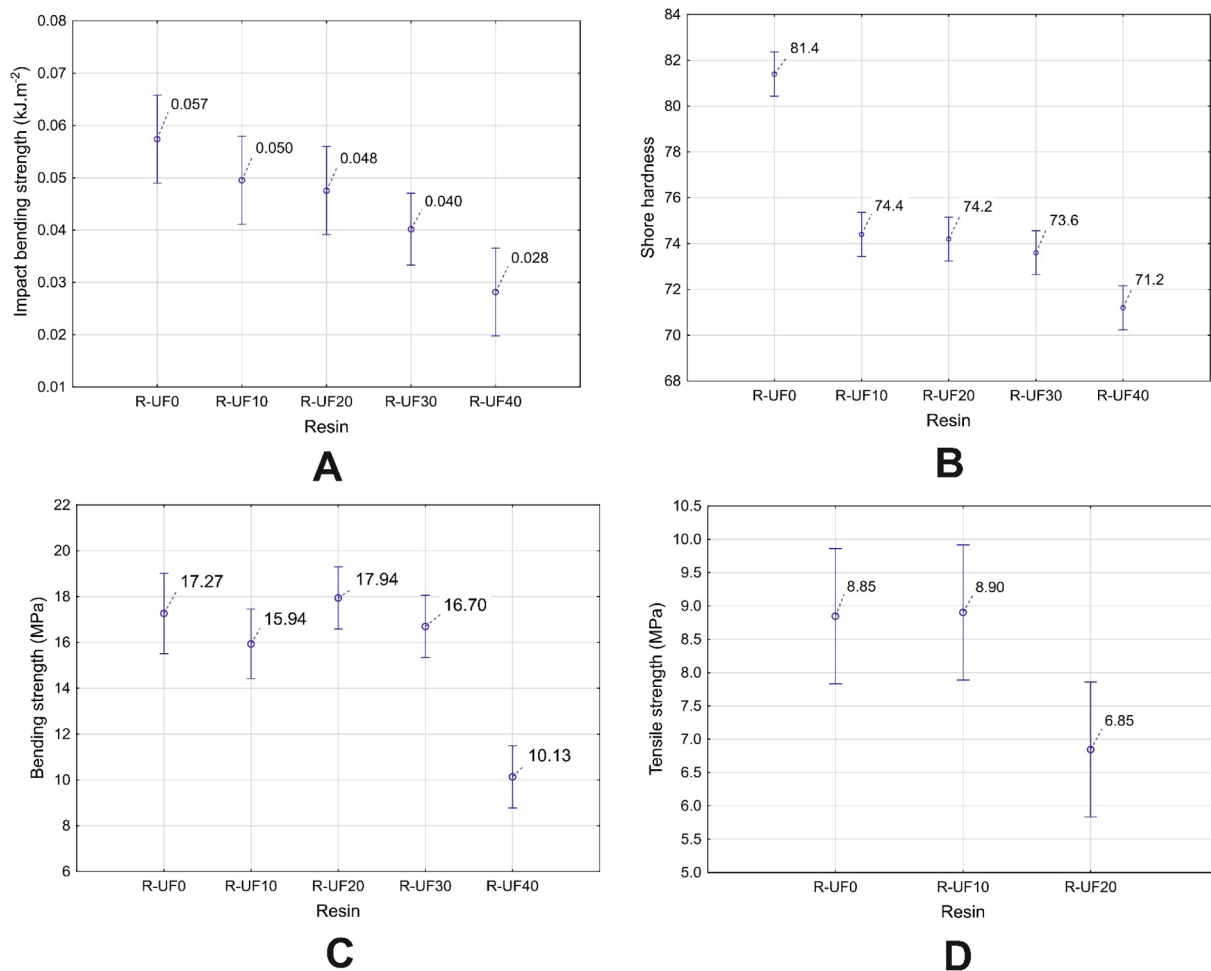


Fig. 2. Impact bending strength (A); Shore hardness (B); Bending strength (C); Tensile strength (D) of resins.

form bonds during the curing process, reflected in the low deformability of lignin-modified systems. These zones are weak points from which the material begins to break prematurely under stress. As a result, the maximum strength of the material is significantly reduced.

Tensile strength of resins

The tensile test can only be used for samples with a lignin concentration of up to 20 %, at higher concentrations the samples are too fragile and break already when attached to the tensile jaws. This confirms the results of the deflection during the bending tests, that as the addition of lignin increased, the brittleness of the resins also increased. The following graph (Fig. 2D) describes the dependence of the tensile

strength (MPa) depending on the concentration of lignin in the UF resin.

The graph of tensile strength shows that the tensile strength is the same up to a lignin content of 10 % (8.85 MPa and 8.9 MPa respectively), at a content of 20 % it decreases by approximately one quarter (6.85 MPa).

Tensile strength was also tested in a study from Cetin and Özmen, 2003 [45], where paper samples were impregnated with PF resin with a lignin content of 0–40 %. The results showed a significant increase in TS with the addition of 10 % lignin, then with a higher addition of lignin, TS had a decreasing tendency, however, up to 30 % lignin PF resin results exceeded the control PF resin. At the same time, an increased fragility of

the prepared samples was also observed.

Compression strength of resins

The following Fig. 3A shows the dependence of the maximum compressive strength (N) on the concentration of lignin in the UF resin measured on rollers with dimensions of 15x10 mm.

The graph shows that up to a concentration of 10 % lignin, the compression strength limit is not affected by the addition of lignin (36.11 MPa). A decrease of approximately one-fifth occurs only at a concentration of 20 % (28.82 MPa), and the most significant decrease of approximately 60 % occurs in the sample with a 40 % lignin content (14.17 MPa). The decreasing trend of compression strength is again caused by the increased brittleness of the resins at a higher lignin concentration.

Tejado [44] in their study on PF resins with lignin content, with the addition of 25 % kraft lignin, achieved a slight increase in compressive strength compared to the reference PF resin, but with the replacement 45 % of lignin has already experienced a significant decrease in properties. The author of the property improvement describes better deformability of the L-PF resin when lignin is integrated into the resin network.

Tensile shear strength of glued joints

From the point of view of the practical use of the given resins, this is a key test, because the binder used in the production of chipboards in the usual concentrations of 7–15 % fulfills the function of glue for wood chips. The following Table 2 shows the type of failure of the sample in the adherends bonded by UF resin with different lignin content. Cohesive failure of the adherend (KA), cohesive failure of the resin (KP), adhesive failure between the resin and the adherend (AP) may occur.

The following graph (Fig. 3B) shows the dependence of the ultimate shear strength on the lignin content of the UF resin on wood adherends.

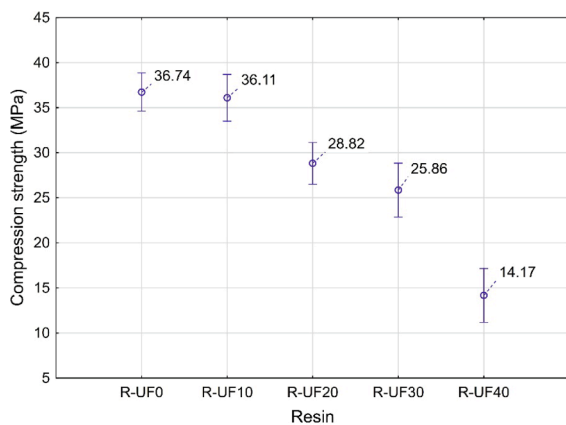
The graph shows a significant drop in the shear strength even with the addition of 10 % lignin, almost by half. However, the following values oscillate around the value of 1 MPa and are almost constant.

Hemmilä [46] also achieved a reduction in the shear strength of the glued joint in their study, where Ammonium liginosulfonate was added to the UF resin. The decrease in properties was attributed to the higher viscosity of the resin containing lignin, which subsequently worsened the penetration capabilities into the wood structure.

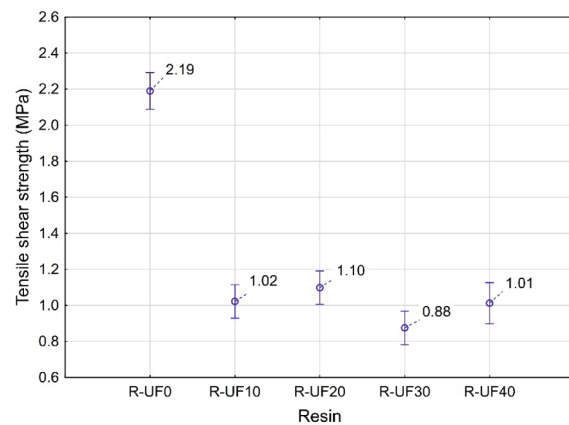
Another study [47] on the use of lignin for the preparation of phenol-formaldehyde resins showed that with the addition of lignin to the resin, the shear strength of the joint increases, but when 10 % of lignin is added, their strength decreases. Subsequent microscopic analysis by SEM revealed that samples with higher lignin content had significantly more failure zones between the resin and the wood fibers.

Moisture uptake of resins

Fig. 4 shows the dependence of weight change (%) on lignin



A



B

Fig. 3. Compression strength (A) and Tensile shear strength (B) of resins.

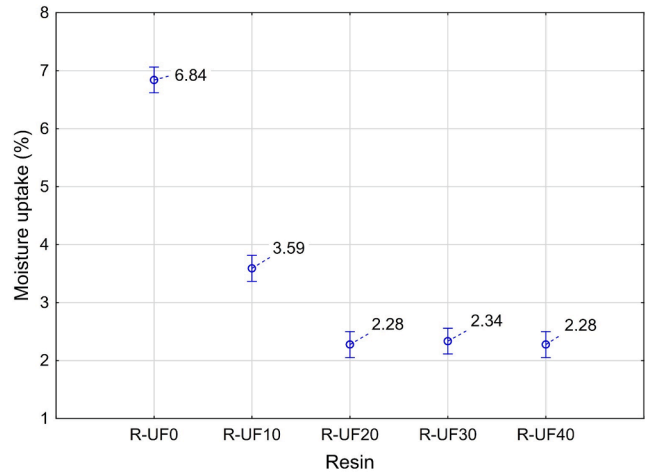


Fig. 4. Moisture uptake of resins.

concentration. As can be seen from the graph, even with the addition of 10 % lignin, the increase in weight is reduced by approximately 50 %, with a content of 20 % lignin there is a decrease of approximately 65 %. From an amount of lignin greater than 20 %, the weight change is already constant. By adding lignin, it is possible to achieve a lower absorbency of samples with UF resin and thus to improve this property. UF resins are not resistant to moisture compared to kraft lignin, which is characterized by a hydrophobic character.

Thermomechanical analysis of resins

The resulting glass transition temperatures determined by the TMA method for UF resin with different lignin content are shown in Table 2. From the obtained data, it follows that when lignin is added to the UF resin, the glass transition temperature gradually decreases, when at a content of 10 % lignin it is minimal (0.5 °C), the addition of 40 % lignin causes a decrease in T_g by about 10 °C.

3.3. Mechanical and physical properties of developed particleboards

Moisture uptake and thickness swelling

In the following graph the results of MU (Fig. 5A) and TS (Fig. 5B) of the tested PB samples can be observed. In both tests, the values of the commercial UF resin and LUF resin with 10 % lignin content were very similar. However, from the 20 % addition of lignin in UF resins, there was a significant deterioration in the resistance of PB against the effects of moisture.

The phenomenon in which the MU of the bonded PBs increases as the

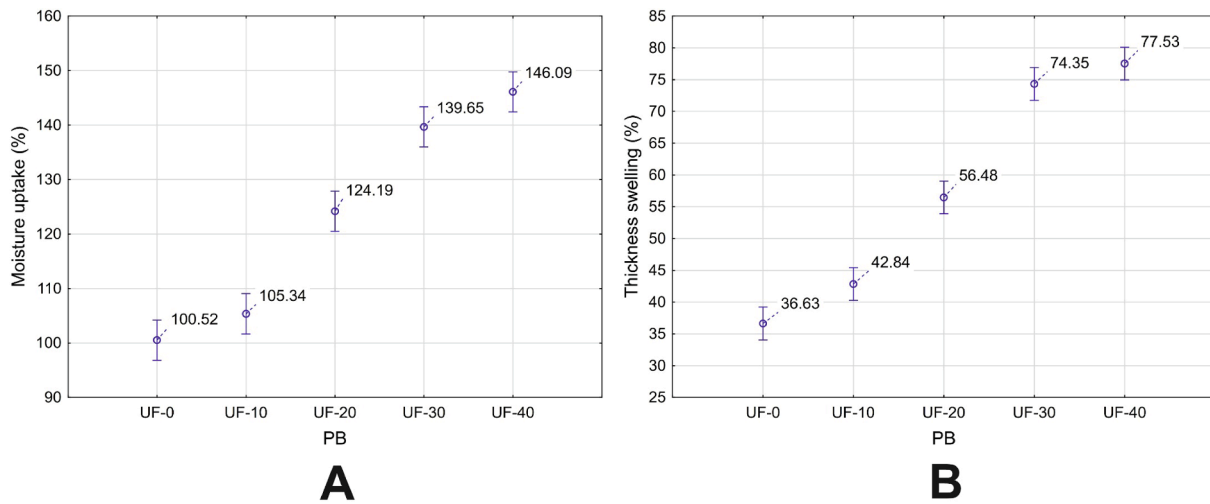


Fig. 5. Moisture uptake (A) and Thickness swelling (B) of particleboards.

lignin content in the UF resin increases is of the opposite nature to the tested individual resins, where the adhesive mixtures became more resistant to moisture as the lignin content increased. The unfavorable results of MU boards joined by UF with the addition of lignin are attributed to the fact that the lignin in the resin causes imperfectly connected places between the wood and the resin, as moisture can penetrate more easily into the PB structure. Our hypotheses are confirmed by images of the glued joint from the electron microscope (3.4 Microscopy analysis). However, the overall high MU values of boards containing alternative resources in generally known [48].

Our hypothesis is also supported by the results of Younesi-Kordkheili and Pizzi [49], when in their study particleboards with the addition of kraft lignin showed a lower rate of water absorption with increasing lignin content. This would also confirm the results of moisture uptake of resins (chapter 3.3 Moisture uptake of resins), where the hydrophobic character of resins containing lignin was observed.

Vertical density profile

The VDP curves of individual PB variants are shown in Fig. 6. It can be observed that all PB variants had a very similar VDP course, i.e. a

higher density in the surface parts of the plate and a lower density in the central part of the sample, which is caused by the type of surface pressing. Only the UF-40 variant showed a slightly slower increase in density on one of the surface sides. From the VDP results, it can be said that the addition of lignin to the UF resin did not have a significant effect on the resulting density distribution for individual PB variants.

Bending strength

The results of MOR are shown (Fig. 7A), where PB shows a downward tendency with increasing addition of lignin in UF resins, when from the addition of 30 % lignin there was a significant decrease in MOR for PB. According to the requirements of the ČSN EN 312 [50] standard, MOR of at least 11 MPa is required for PB class P2 with a thickness of 12 mm. Therefore, only samples UF-0 (13.15 MPa) and UF-10 (11.7 MPa) meet the requirements of the standard. The reason for the significant decrease with higher addition of lignin is again the worsened interaction between the resin and the wood mass.

Subsequently, the results of MOE (Fig. 7B) can be observed, where there is the same tendency of decreasing modulus with increasing addition of lignin in UF resins for the production of PB. Variants UF-0 to

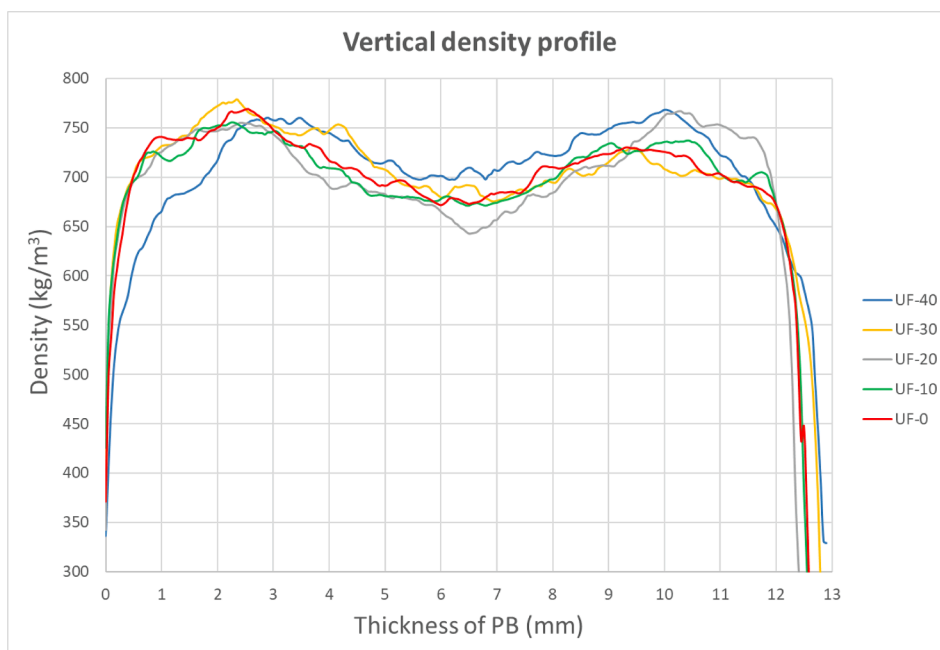


Fig. 6. Vertical density profile of particleboards.

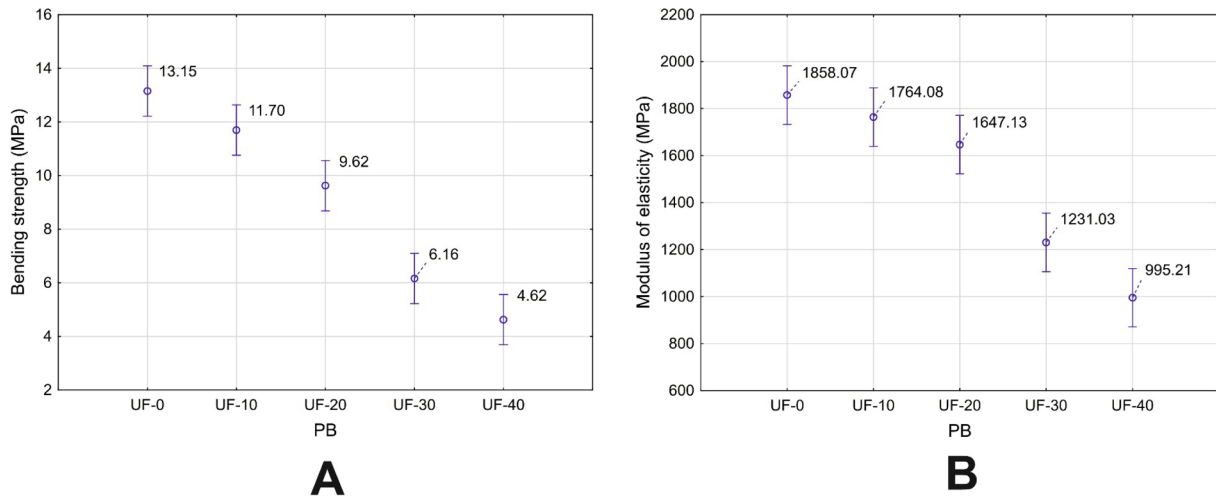


Fig. 7. Bending strength (A) and Modulus of elasticity (B) of particleboards.

UF-20 showed only a gradual decrease in values, while from UF-30 there was again a significant decrease in MOE. The ČSN EN 312 [50] standard for 12 mm thick P2 type plates require a minimum MOE value of 1800 MPa. Only the variant bonded with commercial UF resin UF-0 (1858.07 MPa) meets these requirements. The UF-10 variant ended up only just below the requirements of the standard (1764.08 MPa).

Similar MOR and MOE results were also obtained by Bekhta et al. [51] in their study using lignosulphonates in UF resins for PB. With lignin replacement in the resin above 20 %, there was a decrease in MOR (or a decrease in MOE with 30 % lignin replacement) compared to the reference UF resin for the tested PB. This was attributed to the increased fragility of the lignin containing boards. Evidence of a decrease in MOR and MOE with increasing lignin content in the resin is also provided by the study of Savov and Mihailov [52], where UF resin used for the production of medium density fibreboard (MDF) was modified with lignosulphonate and a decrease in properties was observed at 15 % lignin replacement in the resin.

Internal bonding

The results of internal bonding (Fig. 8A) show a continuing trend where the strength of the tested PB decreases with the addition of lignin. Between UF-0 and UF-20 the decrease is gradual, followed by a significant decrease in IB. However, the decrease is negligible between the UF-30 (0.21 MPa) and UF-40 (0.2 MPa) variants. The results of IB plate

variants UF-0 (0.79 MPa), UF-10 (0.64 MPa) and UF-20 (0.51 MPa) meet the requirements of the ČSN EN 312 [50] standard for type P2 (0.4 MPa) and are even greatly exceeded. From the point of view of the IB values, the UF-20 board variant would meet the requirements of the standard for category P5, and the UF-10 variant would even meet the requirements of category P6.

Fig. 8B shows photos of the PB samples after the IB test, specifically the UF-0 and UF-40 variants. It is with the UF-40 sample that you can observe black-brown spots inside the internal structure of the PB after the IB test. These spots are clumps of lignin that were not sufficiently homogeneously distributed in the resin during resin curing. This fact is the reason for the lower cohesion of the samples at IB with increasing lignin content in the resin.

The same trend of decreasing mechanical properties in bending strength and internal bonding with increasing lignin content was achieved by several studies [32,53], which attributed this effect to the lower reactivity of kraft lignin, which results in a lower degree of crosslinking between the resin components, leading to reduced cohesive properties of the cured resin.

3.4. Microscopy analysis

Results of scanning electron microscopy (Fig. 9A-E) correspond to

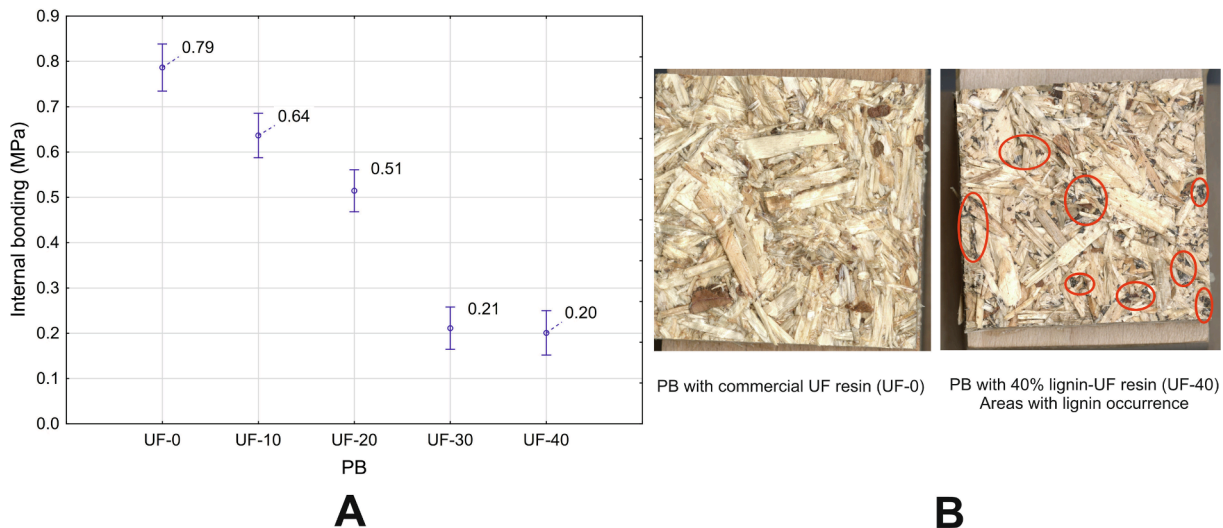


Fig. 8. Internal bonding (A) and Pictures of sample deformation (B) of particleboards.

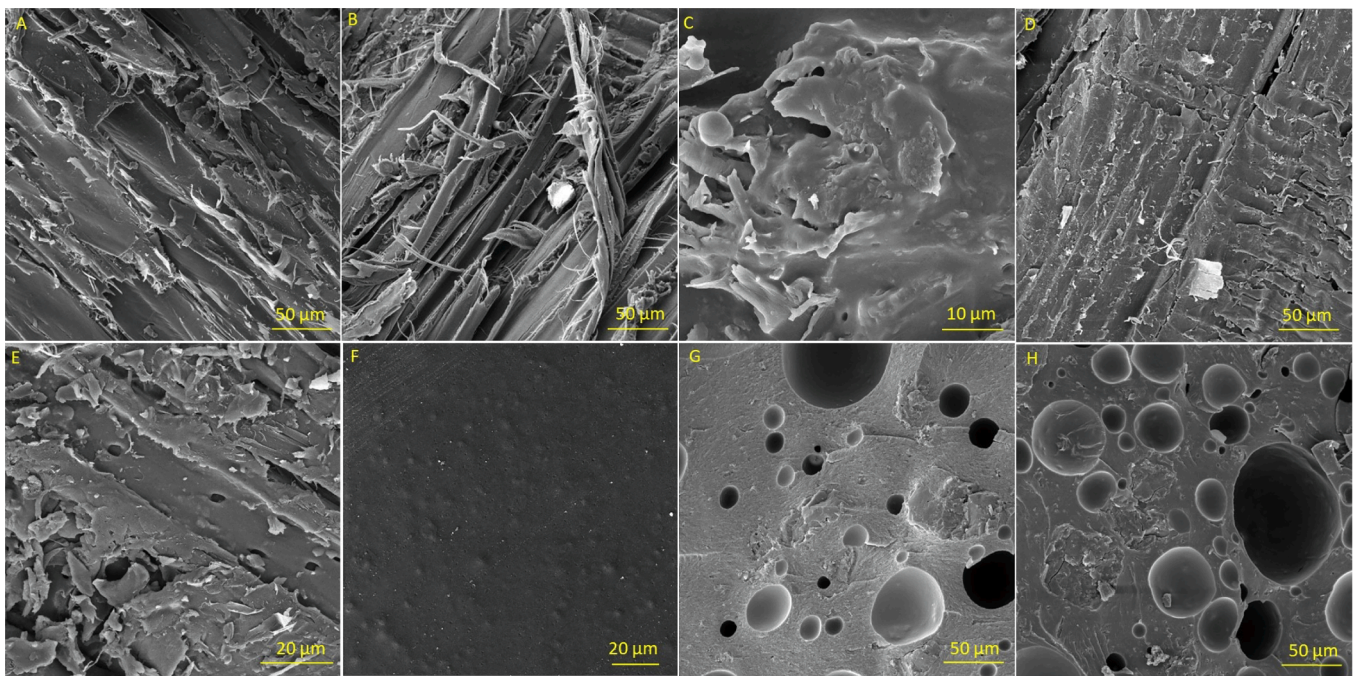


Fig. 9. SEM images of breached particleboard samples, UF-0 (A), UF-10 (B), UF-20 (C), UF-30 (D), UF-40 (E), surface of cured adhesive R-UF0 (F), cross section of cured adhesive R-UF20 (G), and cross section of cured adhesive R-UF40 (H).

those of mechanical properties of PB and confirm the assumption that with higher amount of lignin in the UF resin, its adhesive properties decrease. Namely, in the Fig. 9 A and B are obvious cohesive failures of the wood, which corresponds to the highest mechanical properties of variants UF-0 and UF-10. On the other hand, in Fig. 9 D and E, adhesive failures of the bonded joints are evident. In Fig. 9 C, at a higher magnification, lignin particles in the UF resin can be observed (marked by orange arrows).

The SEM of hardened adhesives (Fig. 9 F-H) provided an answer how the lignin particles interact with the UF resin. From the Fig. 9 G-H can be seen that lignin particles are mixed in the UF resin (marked by blue arrows), but no interface indicating partial solution of the particle in UF resin was found. Therefore, it can be stated that lignin acts only as filler in the presented application. The same findings are also confirmed by literature [34], where it is mentioned that lignin is not soluble in UF resin. Air bubbles can also be seen on the Fig. 9 G-H. These air bubbles originate from mixing lignin particles into the UF resin, since no air bubbles were found in the hardened reference UF resin (Fig. 9F). When using the produced adhesives for particleboard production, no air bubbles were found in the glued joints (Fig. 9B-E), since they vanished during particleboard pressing.

3.5. Formaldehyde content

The formaldehyde content results of PB samples show a decrease in formaldehyde with lignin replacement up to 20 % and 30 %, respectively, formaldehyde emission were lower than that of PB bonded with reference UF-0 resin (Table 3). However, with lignin substitution in the resin from 30 % onwards, formaldehyde content increased and with 40 % lignin substitution the emissions significantly exceed those of the reference UF resin.

Table 3
Formaldehyde content in PB samples.

Formaldehyde content	UF-0	UF-10	UF-20	UF-30	UF-40
mgFd/100ga.s.	9.25	9.00	8.93	9.17	10.27

Studies utilising lignin for modification of UF resins reported that with increasing lignin replacement in these resins, formaldehyde emissions are reduced and lignin behaves as a formaldehyde scavenger in the wood-based composites [14,32,54].

However, the effect of increasing formaldehyde content or free formaldehyde emissions with increasing lignin content has been observed in many studies on the development of phenol-formaldehyde resins [17,55,56]. The higher content/emissions of formaldehyde are attributed to the fact that although KL has a polyphenolic structure similar to phenol, its considerable molecular weight, limited activity and significant steric hindrance hinder the polycondensation reaction to some extent. This hindrance results from the potential occupation of the ortho-para position of lignin by a phenolic hydroxyl group, resulting in fewer active sites per unit mass in the benzene ring structure of lignin compared to phenol [57].

Since the phenolic content of lignin depends on the source of the raw material and the method of lignin isolation and modification, studies have reported a range of phenolic content of lignin from 1.55 to 8.65 mmol/g [58–61].

4. Conclusion

The measured data show a slight reduction in the properties of PB already when using 10 % lignin in UF resin (w/w). However, a further significant decrease occurs only at a lignin content of 40 %. This means that the lignin content between 10 % and 30 % can be effectively considered for replacing a larger amount of resin. Majority of the produced variants do not meet standardised criteria for PBs defined by EN 312. However, the PB variants with 10 % and 20 % lignin in UF resin meets requirements for P2 boards (boards to be used in interior) in terms of internal bonding and the PB variant with 10 % lignin in UF resin meets requirements for P2 boards in terms of bending strength.

The designed method of UF resin modification can be because of its simplicity easily implemented in industry and for this purpose, lignin content in the resins up to 30 % can be used. Although most variants fall short of the standardized requirements, we assume that by choosing the appropriate technology, it is possible to improve the standardized

properties even more.

CRedit authorship contribution statement

Miroslav Nėmec: Writing – original draft, Visualization, Project administration, Methodology, Investigation, Funding acquisition, Data curation. **Luboř Prokųpek:** Writing – original draft, Methodology, Data curation. **Vojtėch Obst:** Investigation, Data curation. **Tomáš Pipıřka:** Validation, Methodology, Data curation. **Pavel Král:** Writing – review & editing, Formal analysis, Conceptualization. **Stėpán Hýsek:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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